Quality Assurance Project Plan
For Exploration Drilling in Alaska
Outer Continental Shelf, Chukchi Sea, on the M/V *Noble Discoverer*

Final: April 2015

Version: 2015-1

This page intentionally left blank

Table of Contents

1.0 GENERAL REQUIREMENTS 1

1.1 ORGANIZATION 1
1.2 PURPOSE AND SCOPE 1
1.3 PROJECT DEFINITION/BACKGROUND 1
1.4 PROJECT TASK DESCRIPTION 2
1.5 PROJECT QUALITY OBJECTIVES 3
1.5.1 Data Quality Objectives 3
1.5.2 Data Quality Indicators 3
1.5.2.1 Precision 3
1.5.2.2 Accuracy 5
1.5.2.3 Representativeness 5
1.5.2.4 Comparability 5
1.5.2.5 Completeness 6
1.5.2.6 Sensitivity 6
1.6 SPECIAL TRAINING AND CERTIFICATIONS 6
1.6.1 Health, Safety, and Environment Program Training 6
1.6.2 General Permit Training Curriculum for M-I SWACO NPDES Compliance Specialists 7
1.6.3 M-I SWACO NPDES Compliance Specialist Demonstration of Capability 7
1.7 DOCUMENTS AND RECORDS 7
1.7.1 Document Revisions 8
1.7.2 Rig Compliance Laboratory Documentation 8
1.7.3 Archival, Maintenance, and Retention of Project Files 8
1.7.4 Confidentiality and Proprietary Rights 9
1.8 SAMPLE HANDLING, DOCUMENTATION, AND CHAIN-OF-CUSTODY PROCEDURES 9
1.8.1 Sample Containers and Preservation 10
1.8.2 Sample Storage 10
1.8.3 Sample Retention and Disposal 10
1.8.4 Sample Labeling 10
1.8.5 Chain-of-Custody Procedures 11
1.8.6 Packaging and Shipment of Samples 12
1.9 FIELD AND LABORATORY QC SAMPLES 13
1.9.1 Field QC Samples 13
1.9.1.1 Trip Blanks 13
1.9.1.2 Temperature Blanks 13
1.9.1.3 Field Duplicates 13
1.9.1.4 Matrix Spikes and Matrix Spike Duplicates (MS/MSDs) 14
1.9.2 Laboratory QC Samples 15
1.9.2.1 Method Blank 15
1.9.2.2 Laboratory Control Sample 15
1.9.2.3 Surrogates 15
1.9.2.4 Internal Standards 16
1.10 PROJECT ASSESSMENT AND OVERSIGHT 16
1.10.1 Project Audits/Assessments 16
1.10.2 Audit Reporting 16
1.10.3 Corrective Action 17
1.10.3.1 Audit Findings 17
1.10.3.2 Data Quality Issues 17
1.10.3.3 Staff Feedback 17

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.0 COMPLIANCE SAMPLING PROGRAM FOR OPERATIONAL DISCHARGES 19

2.1 INTRODUCTION AND OVERVIEW 19
2.2 OPERATIONAL DISCHARGE COMPLIANCE PROGRAM ROLES AND RESPONSIBILITIES 29
2.2.1 Wells Delivery Manager 29
2.2.2 Wells Health, Safety and Environmental Department 29
2.2.3 Shell Environmental Compliance Engineer 29
2.2.4 M-I SWACO NPDES Compliance Supervisor 30
2.2.5 M-I SWACO NPDES Compliance Specialist 30
2.3 DATA QUALITY OBJECTIVES 31
2.4 FIELD SAMPLING 31
2.4.1 Sampling, Measurement, and Observation Locations 31
2.4.2 Sampling, Measurement, and Observation Frequencies 34
2.4.2.1 Daily Tasks 34
2.4.2.2 Weekly Tasks 34
2.4.2.3 Monthly Tasks 34
2.4.3 Compliance Sampling Requirements for Each Operational Discharge 35
2.4.3.1 Effluent Toxicity Testing 35
2.4.3.2 Compliance Sampling for Water-Based Drilling Fluids and Drill Cuttings (Discharge 001) 38
2.4.3.3 Compliance Sampling for Deck Drainage (Discharge 002) 45
2.4.3.4 Compliance Sampling for Sanitary Wastes (Discharge 003) 49
2.4.3.5 Compliance Sampling for Domestic Wastes (Discharge 004) 51
2.4.3.6 Compliance Sampling for Desalination Unit Wastes (Discharge 005) 51
2.4.3.7 Compliance Sampling for Blowout Preventer Fluid (Discharge 006) 53
2.4.3.8 Compliance Sampling for Boiler Blowdown (Discharge 007) 53
2.4.3.9 Compliance Sampling for Fire Control System Test Water (Discharge 008) 55
2.4.3.10 Compliance Sampling for Non-contact Cooling Water (Discharge 009) 56
2.4.3.11 Compliance Sampling for Uncontaminated Ballast Water (Discharge 010) 58
2.4.3.12 Compliance Sampling for Bilge Water (Discharge 011) 58
2.4.3.13 Compliance Sampling for Excess Cement Slurry (Discharge 012) 60
2.4.3.14 Compliance Sampling for Muds, Cuttings, and Cement at the Seafloor (Discharge 013) 60
2.4.4 Field SOPs 61
2.4.4.1 M-I SWACO SOP and LWI Revisions 61
2.4.4.2 Sampling SOPs and LWIs 61
2.4.5 Analytical SOPs 62
2.4.6 Sample Handling and Custody 63
2.4.6.1 Responsibilities 63
2.4.6.2 Sample Containers, Preservation, and Storage 64
2.4.6.3 Sample Receipt 65
2.4.6.4 Holding Times 66
2.4.6.5 Sample Retention and Disposal 66
2.4.6.6 Decontamination 66
2.4.7 Field Instrument/Equipment Testing, Inspection, Calibration, and Maintenance 66
2.4.7.1 Responsibilities 67
2.4.7.2 Rig Compliance Laboratory Equipment 67
2.4.7.3 Field and Rig Compliance Laboratory Instrument Calibration 68
2.4.7.4 Standards and Reagents 69
2.4.7.5 Reference Materials and Standards 70
2.4.7.6 Refrigerator Testing 70
2.4.7.7 Field Compliance Instrument/Equipment Maintenance 71
2.4.8 Fixed Subcontract Laboratory Instrument/Equipment Testing, Inspection, Calibration, and Maintenance 71
2.4.8.1 Initial Toxicity Screening and Whole Effluent Toxicity Testing Laboratory Equipment Washing Procedures 71
2.4.8.2 Initial Toxicity Screening and Whole Effluent Toxicity Testing Laboratory Materials 71
2.5 FIXED LABORATORY ANALYSIS 72
2.5.1 Analytical Laboratory Methods 73

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.6 FIELD AND LABORATORY QUALITY CONTROL SAMPLES 76
2.6.1 Field Quality Control Samples and Frequencies 76
2.6.2 Laboratory Quality Control 78
2.6.2.1 Analytical Method Quality Control Criteria 78
2.6.2.2 Toxicity Testing Quality Control Criteria 79
2.7 DOCUMENTS AND RECORDS 81
2.7.1 Responsibilities 81
2.7.2 Field and Laboratory Records 82
2.7.2.1 Deviations 84
2.8 REPORTING 85
2.8.1 Notifications 85
2.8.2 Discharge Monitoring Reports 85
2.8.3 TAH/TAqH Reporting 85
2.9 DATA REPORTING 86
2.10 DATA REVIEW AND QUALIFICATION 87
2.10.1 Laboratory Data Evaluation 87
2.10.2 Data Review and Verification 87
3.0 ENVIRONMENTAL MONITORING PROGRAM 90
3.1 INTRODUCTION AND OVERVIEW 90
3.2 DATA QUALITY OBJECTIVES 91
3.3 EMP TECHNICAL APPROACH: (PHASE I THROUGH IV) 92
3.3.1 Phase I Assessments 93
3.3.2 Phase II Plume Monitoring and Observations 98
3.3.3 Phase III Assessment 100
3.3.4 Phase IV Assessment 102
3.4 FIELD SAMPLING 102
3.4.1 Sampling Methods 102
3.4.1.1 Navigation 102
3.4.1.2 Acoustic Doppler Current Profiler (ADCP) 103
3.4.1.3 Conductivity, Temperature, and Depth (CTD) 103
3.4.1.4 Water Samples 103
3.4.1.5 Muds and Cuttings 105
3.4.1.6 Sediment Samples 106
3.4.1.7 Sediment Samples - Benthic Ecology Samples 109
3.4.1.8 Tissue Samples for Chemistry 110
3.4.1.9 Sediment Profile Imaging 111
3.4.1.10 Contamination Prevention 113
3.4.2 Sample Handling and Custody 114
3.4.2.1 Sample Labeling 114
3.4.2.2 Sample Preservation and Packing for Shipment 115
3.4.2.3 Holding Times 116
3.4.2.4 Chain-of-Custody Records 116
3.4.2.5 Sample Archiving 117
3.4.3 Field Instrument/Equipment Calibration, Maintenance, and Operation 117
3.5 LABORATORY ANALYSIS 117
3.5.1 Analytical Methods 117
3.5.2 Samples for Metals Analysis 120
3.5.2.1 Metals in Water (Phase II) Samples 120
3.5.2.2 Metals in Sediment (Phases II, III, and IV) Samples 121
3.5.2.3 Metals in Tissue (Phases III and IV) Samples 124
3.5.3 Samples for Hydrocarbon Analysis (Phases II, III, and IV) 124
3.5.3.1 Hydrocarbons in Water Samples (Phase II) 124
3.5.3.2 Hydrocarbons in Sediment Samples (Phases III and IV) 130
3.5.3.3 Hydrocarbons in Tissue Samples (Phases III and IV) 134
3.5.4 Macrofaunal Analysis 134

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

3.5.5 Sediment Profile Imaging Analysis 135
3.5.6 Laboratory Instrument/Equipment Calibration, Maintenance, and Operation 137
3.6 QUALITY ASSURANCE/QUALITY CONTROL 142
3.6.1 Field Quality Control 144
3.6.1.1 Equipment (Rinsate) Blank (EB) 144
3.6.1.2 Field Blanks 144
3.6.1.3 Laboratory Duplicates (Laboratory Splits) 144
3.6.1.4 Benthic Samples 145
3.6.1.5 Accuracy and Precision of the ADCP and CTD Sensor Arrays 145
3.6.2 Laboratory Quality Control 147
3.6.3 Standard Reference Material 152
3.6.3.1 North Slope Crude Reference Oil 152
3.6.3.2 Samples for Biological Community Analysis 152
3.7 DATA MANAGEMENT 153
3.7.1 Document Control 153
3.7.1.1 Field Documentation 153
3.7.1.2 Laboratory Documentation 153
3.7.2 Data Storage Requirements 154
3.7.3 Documentation Standards 154
3.7.4 Hardware and Software Requirements 155
3.7.5 Changes and Deviations 155
3.7.6 Data Reporting 155
3.7.7 Data Reduction 156
3.7.7.1 Infaunal Analysis 156
3.7.7.2 Organics and Metals 156
3.7.7.3 Total Organic Carbon 157
3.7.7.4 Grain Size 157
3.7.7.5 Sediment Profile Imaging Analysis 157
3.8 DATA REVIEW/QUALIFICATION 157
4.0 REFERENCES 160

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Tables

Title **Page**

Chukchi Sea Permit No.: AKG-28-8100 QAPP Revision Summary Table I
Table 1-1 Geographical Drill Site Locations 2
Table 2-1 Effluent Limitations and Monitoring Requirements for Water-Based Drilling Fluids/Drill Cuttings (Discharge 001) 21
Table 2-2 Discharge Rate Limitations and Monitoring Frequency for Water-Based Drilling Fluids and Drill Cuttings (Discharge 001) 23
Table 2-3 Effluent Limitations and Monitoring Requirements for Deck Drainage (Discharge 002) 24
Table 2-4 Effluent Limitations and Monitoring Requirements for Sanitary and Domestic Wastes (Discharges 003 and 004) 25
Table 2-5 Effluent Limitations and Monitoring Requirements for Miscellaneous Discharges 26
Table 2-6 Discharge Sampling Locations 32
Table 2-7 Summary of Compliance Sampling, Measurement, and Observation Frequencies and Related SOPs 35
Table 2-8 Effluent Sample Holding Times for Toxicity Testing 37
Table 2-9 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 001 41
Table 2-10 Analytical Sampling for Water-Based Drilling Fluids and Drill Cuttings (Discharge 001)43
Table 2-11 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 002 46
Table 2-12 Analytical Sampling for Deck Drainage (Discharge 002) 47
Table 2-13 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 003 49
Table 2-14 Analytical Sampling for Sanitary Wastes (Discharge 003) 50
Table 2-15 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 004 51
Table 2-16 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 005 52
Table 2-17 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 006 53
Table 2-18 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 007 55
Table 2-19 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 008 56
Table 2-20 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 009 57
Table 2-21 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 010 58
Table 2-22 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 011 59

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 2-23 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 012 ... 60
Table 2-24 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 013 ... 61
Table 2-25 Operational Discharge Compliance Sampling Related SOPs ... 62
Table 2-26 Drilling Fluid and Effluent Toxicity Testing SOPs ... 63
Table 2-27 Sample Containers, Preservation, and Holding Times ... 64
Table 2-28 Rig Compliance Laboratory Equipment Calibration ... 69
Table 2-29 Analytical Subcontract Laboratories ... 72
Table 2-30 Drilling Fluid and Effluent Toxicity Testing Methods ... 74
Table 2-31 Analytical Laboratory Reporting Limits ... 74
Table 2-32 Field Quality Control Samples ... 77
Table 2-33 Analytical Method Quality Control Criteria ... 78
Table 2-34 Water Quality Criteria and Performance Standards ... 80
Table 2-35 Toxicity Test Acceptance Criteria and Performance Standards ... 80
Table 2-36 General Permit Compliance Records by Location ... 83
Table 2-37 Service Quality Non-Conformance Report ... 84
Table 3-1 Roles and Responsibilities of the EMP Implementation Team ... 90
Table 3-2 Summary of Field Sampling for the Four Monitoring Phases ... 92
Table 3-3 Summary of Analytical Parameters by Matrix ... 94
Table 3-4 Number of Samples Slated for Collection during Phase II ... 100
Table 3-5 Summary of Near-Field and Far Field[1] Phase III and IV Samples Slated for Collection 102
Table 3-6 Sample Containers, Sample Sizes, Preservative Requirements, and Holding Times for Sediments, Tissue, and Water ... 108
Table 3-7 Sample Identification Scheme ... 114
Table 3-8 Field Equipment Calibration, Maintenance, Testing, and Inspection ... 117
Table 3-9 Laboratory Analytical Methods ... 119
Table 3-10 Metals and Analytical Instruments for Each Phase of Environmental Monitoring with Laboratory Limits[1] ... 122
Table 3-11 List of Polycyclic Aromatic Hydrocarbon and Alkyl PAH Target Analytes with Reporting Limits and Method Detection Limits[1] ... 126
Table 3-12 List of Saturated Hydrocarbons Target Analytes with Reporting Limits and Method Detection Limits[1] ... 128
Table 3-13 List of VOC Target Analytes with Reporting Limits and MDLs[1] ... 130
Table 3-14 List of Petroleum Biomarker (St/Tr) Target Analytes with Reporting Limits and Method Detection Limits[1] ... 132
Table 3-15 Sediment Profile Imaging Parameters ... 135
Table 3-16 Calibration Procedures for Laboratory Instruments ... 138
Table 3-17 Standard Operating Procedures ... 142
Table 3-18 Typical Accuracy and Precision of Instrument Sensors (ADCP and OBS) ... 145

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 3-19 Typical Accuracy and Precision of Instrument Sensors (CTD) 146
Table 3-20 Measurement Quality Criteria[1] 147
Table 3-21 Analytical Data Qualifiers 158

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Figures

Title		Page
Figure 3-1	Phase II Water Sampling Stations	99
Figure 3-2	Phase III and IV Sampling Stations	101
Figure 3-3	Example Carousel Water Sampler with Go-Flow Bottles and CTD Sensors	105
Figure 3-4	Sediment Profile Imaging and Plan View Camera Systems	112
Figure 3-5	Example Sample Label	115

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Acronyms List

°C	degrees Celsius
°F	degrees Fahrenheit
ADCP	Acoustic Doppler Current Profilers
Ag	silver
Al	aluminum
ANIMIDA	Arctic Nearshore Impact Monitoring in Development Area
ANOVA	analysis of variance
As	arsenic
Ba	barium
bbl/h	barrel(s) per hour
Be	beryllium
BI	benthic infauna (sample identification code)
BOD_5	5-day biochemical oxygen demand
BOP	Blowout Preventer
CA	SPI computer analysis
CAB	Chemistry and Benthos
cANIMIDA	continuation Arctic Nearshore Impact Monitoring in Development Area
CC	Drilling cuttings chemistry (sample identification code)
CCA	canonical correspondence analysis
CCV	continuing calibration verification
Cd	cadmium
CFR	Code of Federal Regulations
cm	centimeter
CoC	chain-of-custody
COMIDA	Chukchi Sea Offshore Monitoring in Drilling Area
Cr	chromium
CRM	certified reference material
CSESP	Chukchi Sea Environmental Studies Program
CTD	conductivity, temperature, depth (profiler)
Cu	copper
CVAAS	cold vapor atomic absorption spectrometry
CVAF	cold vapor atomic fluorescence
DC	drilling fluid chemistry (sample identification code)
DCM	dichloromethane
DDW	distilled deionized water
DL	detection limit

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Acronyms List (Continued)

DMR	Discharge Monitoring Report
DOC	demonstration of capability
DOT	(U.S.) Department of Transportation
DQI	data quality indicator
DQO	data quality objective
DU	duplicate
EB	equipment blank
EDD	electronic data deliverable
EMP	environmental monitoring program
EPA	(U.S.) Environmental Protection Agency
FAAS	Flame Atomic Absorption Spectrophotometry
FB	field blank
FC	fecal coliform
Fe	iron
FIT	Florida Institute of Technology
FWS	Fairweather Science
g	grams
gal	gallons
GC	gas chromatograph
GC/FID	gas chromatography/flame-ionization detection
GC/MS	gas chromatography/mass spectrometry
GFAAS	graphite furnace atomic absorption spectrometry
GP	GP
GPS	global positioning system
H_2O_2	hydrogen peroxide
H_2SO_4	sulfuric acid
HCl	hydrochloric acid
$HClO_4$	perchloric acid
HF	hydrofluoric acid
Hg	mercury
HMIS	Hazardous Materials Identification System
HNO_3	nitric acid
HPLC	high performance liquid chromatography
HSE	Health, Safety, and Environment
IATA	International Air Transport Association

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Acronyms List (Continued)

ICAL	initial calibration
ICC	independent calibration check
ICP-MS	inductively coupled plasma/mass spectrometry
ID	identification
IS	internal standards
ISO	International Organization for Standardization
LC	water (liquid) chemistry (sample identification code)
LCL	lower control limit
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
LOD	limit of detection
LOQ	limit of quantitation
LWI	Local Work Instruction
m	meter(s)
MB	method blank
MDL	method detection limit
MeHg	methyl mercury
mg	milligram
mgd	million gallons per day
mg/kg	milligram(s) per kilogram
mg/L	milligram(s) per liter
µg/L	microgram(s) per liter
M-I SWACO	contractor to Shell
mL	milliliter(s)
MLLW	mean lower low water
MQO	measurement quality objectives
MRL	method reporting limit
MS	matrix spike
MSD	matrix spike duplicate
M/V	motor vessel
NA	not available
NAD	North American Datum
$Na_2S_2O_3$	sodium thiosulfate
ng/g	nanograms per gram
ng/L	nanograms per Liter
nMDS	non-metric multidimensional scaling

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Acronyms List (Continued)

NMFS	National Marine Fisheries Service
Ni	nickel
NIST	National Institute of Standards and Technology
Noble Discoverer	M/V *Noble Discoverer*
NPDES	National Pollutant Discharge Elimination System
NS	not spiked
NSC	North Slope Crude
OBS	optical backscatter turbidity sensor
OCS	Outer Continental Shelf
OPR	ongoing precision and recovery
OSI	organism sediment index
PAH	polycyclic aromatic hydrocarbons
PARCCS	precision, accuracy, comparability, completeness, sensitivity
Pb	lead
PCA	principal component analysis
PD	percent difference
PIV	pre-injection volume
PM	project manager
ppm	parts per million
POC	particulate organic carbon
PV	sediment profile imagery plan view photograph (sample identification code)
QA	quality assurance
QADU	laboratory duplicates
QAM	quality assurance manager
QAPP	quality assurance project plan
QC	quality control
RIS	recovery internal standard
RL	reporting limit
ROV	remotely operated vehicle
RPD	relative percent difference
RSD	relative standard deviation
SAV	submerged aquatic vegetation
Sb	antimony
SC	sediment chemistry (sample identification code)
SDG	sample delivery group
Se	selenium

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Acronyms List (Continued)

SHC	saturated hydrocarbons
Shell	Shell Gulf of Mexico, Inc.
SIM	selected ion-monitoring
SIS	surrogate internal standard
Sn	tin
SOP(s)	Standard Operating Procedure(s)
SP	Sediment Profile Imagery photograph (sample identification code)
SPI	sediment profile imaging
SPI RPD	redox potential discontinuity (for SPI analysis)
SPP	suspended particulate phase
SRM	standard reference material
St/Tr	sterane/triterpanes
s.u.	standard units
TAH	total aromatic hydrocarbons
TAqH	total aqueous hydrocarbons
TB	trip blank
TBD	to be determined
TEM	total extractable material
Ti	titanium
Tl	thallium
TOC	total organic carbon
TPH	total petroleum hydrocarbons
TSS	total suspended solids
TU_c	chronic toxic units
UCL	upper control limit
U.S.	United States
USCG	United States Coast Guard
USEPA	United States Environmental Protection Agency
V	SPI visual analysis
VOC	volatile organic compound
WBM	water based mud
WC	worm chemistry (sample identification code)
WET	whole effluent toxicity (testing)
ZGFAAS	Zeeman or Continuum background correction
Zn	zinc

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Chukchi Sea Permit No.: AKG-28-8100
QAPP Revision Summary Table

Revision Number	Revision Date	Revision Reason

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

This page intentionally left blank

1.0 General Requirements

1.1 Organization

This document serves as the Quality Assurance Project Plan (QAPP) for all requirements under the Permit No.: AKG-28-8100 National Pollutant Discharge Elimination System (NPDES) General Permit (New and Existing Sources and New Dischargers in the Offshore Subcategory of the Oil and Gas Extraction Category) (herein referred to as the GP) for wastewater discharges into Arctic Ocean Outer Continental Shelf (OCS) waters. Section 1 presents quality assurance and quality control information that is relevant to the larger permit requirements (i.e., including both operational, on-rig discharges and the environmental monitoring program (EMP). Section 2 presents quality assurance and quality control information that is specific to the operational, on-rig discharge monitoring permit requirements (e.g., Permit Section II.B). Section 3 presents quality assurance and quality control information that is specific to the EMP Plan of Study (e.g., Permit Section II.A.13a-n).

1.2 Purpose and Scope

This section identifies Shell Gulf of Mexico, Inc. (Shell) as the operator for the Chukchi Sea Exploration Program and holder of the GP for wastewater discharges into Arctic Ocean Outer Continental Shelf (OCS) waters.

This QAPP defines policies and systems governing the assessment and quality control of sampling, data collection, and laboratory analyses performed to document compliance with the GP. This QAPP will be used to assist in sampling and analysis required to support compliance with effluent limitations and monitoring requirements for operational discharges as well as planning for the collection and analysis of data required in the Environmental Monitoring Program Plan of Study (EMP) specified in the GP.

Development of the QAPP for work performed under the GP was based upon applicable guidelines and regulatory documents including:

- AKG-28-8100 NPDES GP;
- Title 40 of the Code of Federal Regulations, Part 435 (40 CFR Part 435);
- 40 CFR Part 136; and
- U.S. Environmental Protection Agency (USEPA) regulations and guidance, including Requirements for Quality Assurance Project Plans (EPA/QA/R-5) (USEPA 2001) and Guidance for Quality Assurance Project Plans (EPA/QA/G-5) (USEPA 2002).

1.3 Project Definition/Background

In order to fulfill the requirements of the GP, field measurements and environmental samples will be collected as part of investigations and characterizations as specified in the EMP and also to demonstrate compliance with effluent limitations and monitoring requirements specified for operational discharges.

This QAPP has been prepared to satisfy the requirements of Section IV.A. of the GP. This QAPP defines the quality assurance (QA) and quality control (QC) procedures that will be followed to ensure that the data obtained from field and laboratory analyses is of known and acceptable quality to achieve project data quality objectives. The QC procedures outlined herein are intended to support the activities requiring the collection of data as described in the EMP, the Best Management Practices (BMP) Plan, written procedures and this QAPP. This QAPP provides specific guidance regarding sample collection and handling procedures, referencing the Appendices to the BMP, as appropriate.

General information about the drillship, support vessels, and exploratory well locations can be found in Section 3 of the BMP. Additional information about the Chukchi Sea site description can be found in the EMP Plan of Study.

1.4 Project Task Description

Shell has contracted Noble Drilling Holding, LLC (Noble Drilling), the owner of the drillship, M/V (Motor Vessel) *Noble Discoverer* (*Noble Discoverer*), for operations of the vessel during transit and while exploration activities are being conducted. The *Noble Discoverer* is an offshore oil and gas drillship adapted for operation under Arctic conditions. The *Noble Discoverer* has all necessary drilling equipment and ancillary facilities to explore and complete exploratory wells in the Chukchi Sea.

Shell plans to drill six exploratory wells in the Burger Prospect of the Chukchi Sea. Each of the six possible drill sites will be permitted for drilling to allow for operational flexibility. The prospect location is depicted in Figure 3-1 of the BMP. Table 1-1 presents geographical drill site locations for each well in the drilling program.

Table 1-1 Geographical Drill Site Locations

Wells Covered by BMP Plan	Area	Lease Block (Surface)	Surface Locations (NAD 83)[1]		OCS-Y Number
			Latitude (N)	Longitude (W)	
Burger A	Posey	6764	N71°18’30.92”	W163°12’43.17”	OCS-Y-2280
Burger F	Posey	6714	N71°20’13.96”	W163°12’21.75”	OCS-Y-2267
Burger J	Posey	6912	N71°10’24.03”	W163°28’18.52”	OCS-Y-2321
Burger R	Posey	6812	N71°16’06.57”	W163°30’39.44”	OCS-Y-2294
Burger S	Posey	6762	N71°19’25.79”	W163°28’40.84”	OCS-Y-2278
Burger V	Posey	6915	N71°10’33.39”	W163°04’21.23”	OCS-Y-2324

Note:
[1] North American Datum 1983.

Shell has requested authorization for a number of discharges during drilling operations that are regulated by the EPA under the GP and by 40 CFR Part 435. Data collection to verify compliance with the effluent limitations and monitoring requirements of the GP will include, but is not limited to, visual assessment of receiving waters; discharge flow-rate and volume measurements; and collection of samples for rig compliance laboratory analysis and fixed subcontract laboratory analysis. Operational discharge compliance monitoring activities and QA/QC procedures are defined in Section 2 of this QAPP.

CAUTION: All hardcopies of “Controlling Document” are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

In addition to operational discharge compliance monitoring activities, environmental samples will be collected as part of assessments and characterizations required by the EMP. Data collection activities and QA/QC procedures related to the EMP are described in Section 3 of this QAPP.

1.5 Project Quality Objectives

The overarching project objectives for Shell's exploration drilling program in the Chukchi Sea are to monitor effluent discharges, implement the EMP, and ensure the collection of data that are of sufficient type, quantity, and quality to meet the regulatory requirements specified by the GP.

1.5.1 Data Quality Objectives

The DQOs, details regarding the sampling design, QA/QC procedures, and data collection can be found in Section 2 for operational discharge compliance sampling and in Section 3 and for the EMP.

1.5.2 Data Quality Indicators

The quality of the data to be collected for this project will be verified through appropriate criteria established for both sampling procedures and analytical methods. The criteria should relate to data quality indicators (DQIs) consisting of precision, accuracy, representativeness, comparability, completeness, and sensitivity (commonly referred to as PARCCS) parameters. The quality of the sampling procedures and laboratory results will be evaluated for compliance with project DQOs through a review of these parameters. Project DQOs will be considered met when the quality of the data meet precision, accuracy, representativeness, completeness, comparability, and sensitivity requirements specified in this QAPP.

Analytical DQOs will be evaluated by reviewing the QC parameters described in the following sections. Laboratory and field quality control samples are described in more detail in Section 1.10. DQIs that relate specifically to analyses required for the monitoring of operational discharges are included in Section 2. DQIs that relate specifically to analyses required for the EMP are included in Section 3.

1.5.2.1 Precision

Precision measures the reproducibility of measurements. Analytical precision is the measurement of the variability associated with duplicate (two) or replicate (more than two) analyses. Precision will be evaluated by comparing the following:

- Laboratory control sample (LCS) and LCS duplicate (LCSD) (if prepared and analyzed) to determine the accuracy and precision of the laboratory procedures and verify matrix interference by comparing to MS results;
- Matrix spike (MS) and matrix spike duplicate (MSD) samples to determine the effect of the sample matrix on the precision of the results generated using the selected analytical method;
- Primary and field duplicate sample results;
- Analysis of standard reference material (SRM); and/or
- Laboratory replicate analyses.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

The LCS determines the precision of the analytical method. If the recoveries of the analytes in the LCS are within established control limits, then precision is within acceptable limits. In this case, the comparison is not between a sample and a duplicate sample analyzed in the same batch; rather, the comparison is between a given sample and those samples analyzed in previous batches. If an LCSD is prepared for the batch, the precision of the analysis can be evaluated for the batch.

Precision of two similar values is evaluated by calculating relative percent difference (RPD) using the following equation:

$$RPD = \frac{2|(D_1 - D_2)|}{D_1 + D_2} x\ 100$$

Where: D_1 = first sample value
D_2 = second sample value (replicate)
RPD = relative percent difference

Percent difference (PD) is a measurement of precision as an indication of how a measured value is different from a "real" value. It is used when one value is known or certified, and the other is measured. The formula for calculated PD is as follows:

$$Percent\ \ Difference = \frac{X_2 - X_1}{X_1} x\ 100$$

Where: X_1 = known value (e.g., SRM certified value)
X_2 = determined value (e.g., SRM concentration determined by analyst)

If two or more aliquots of the same sample are prepared and analyzed by the laboratory, then these are referred to as laboratory replicates. Precision of replicate samples is evaluated by calculating the RSD using the following equation:

$$\%RSD = \frac{\sqrt{\frac{\sum_{i=1}^{i=n} \left| D_i - \overline{D} \right|^2}{n}}}{\overline{D}} x\ 100$$

Where: D_i = the individual sample concentrations
$\overline{D}$ = the mean of *n* values
n = the total number of values

Note: Report the absolute value of the result. The RSD is always positive.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

1.5.2.2 Accuracy

Accuracy is a statistical measurement of correctness and includes components of random error (variability due to imprecision) and systemic error (variability that can be assigned to a specific component of the measurement process). Random errors and systematic errors reflect the total error associated with a measurement. A measurement is accurate when the value reported does not differ from the true value or known concentration of the spike or standard.

Percent recovery is a measurement of accuracy, where one value is compared with a known/certified value. Analytical accuracy is measured by comparing the percent recovery of analytes spiked into an LCS or a MS sample to a control limit. Analysis of SRM may also be used to evaluate accuracy.

The formula for calculating percent recovery is as follows:

$$Percent\ \ Recovery = \frac{amount\ \ detected}{amount\ \ expected}\ x\ 100$$

1.5.2.3 Representativeness

Representativeness is a qualitative term that refers to the degree by which the data accurately and precisely depict the characteristics of a population, whether referring to the distribution of a contaminant within a sample, a sample within a matrix, or a contaminant at a site. Representativeness is the qualitative term evaluated to determine that measurements are made and physical samples collected at locations and in a manner that result in proper characterization of a matrix or media. Subsequently, representativeness ensures that a sampled population represents the target population and an aliquot represents a sampling unit.

Assessment of representativeness shall be achieved through use of the standard field, sampling, and analytical procedures. Representativeness will be evaluated by reviewing the following:

- Sample quantities and locations;
- Sampling procedures and equipment;
- Sample CoC forms, laboratory report forms, and laboratory records; and
- Holding times and preservation.

1.5.2.4 Comparability

Comparability addresses the degree to which different methods or data agree or can be represented as similar. The objective for this QA/QC program is to produce data with the greatest possible degree of comparability. Comparability is achieved by the following:

- Using standard methods for sampling and analysis;
- Reporting data in standard units;
- Normalizing results to standard conditions;

- Operating instruments within their calibrated range according to established procedures based on approved methodology; and
- Using standard and comprehensive reporting formats.

1.5.2.5 Completeness

Completeness is calculated for the aggregate data for each analyte measured during any particular sampling event. Completeness is calculated and reported for each method, matrix, and analyte combination. The number of valid results divided by the number of possible individual analyte results, expressed as a percentage, determines the completeness of the data set. For completeness requirements, valid results are defined as all results not rejected through data validation.

The following formula is used to calculate completeness:

$$\%\,\text{completeness} = \frac{\text{number of valid results for samples analyzed}}{\text{number of possible results for all samples}}$$

1.5.2.6 Sensitivity

Sensitivity is the ability of a method or instrument to detect the target analytes at the level of interest. Analytical methods are selected that will provide results with the sensitivity to meet the project DQOs. The laboratory detection limits and reporting limits will be evaluated against the permit limits in order to determine whether the analytical methods and/or laboratory meet the project DQOs.

1.6 Special Training and Certifications

Each contractor has specific corporate policies, training manuals/programs, and compliance tracking systems as it applies to all oil and gas exploration operations. The validity of collected data depends, in part, on the qualifications and training of the personnel involved with sampling and analysis. Trained, qualified personnel are required to perform field activities related to operational discharge and monitoring and the EMP. Specialized training or certifications required to complete project tasks related to sampling and analysis are included in the following sections.

1.6.1 Health, Safety, and Environment Program Training

Shell and its contractors have implemented health, safety, and environmental compliance programs that direct all aspects of the operation of the *Noble Discoverer* and employees who are assigned to the ship. All assigned employees are provided regular training on these measures and programs. Aboard the ship, management of all health, safety, and environmental compliance programs are implemented by Shell and its contractors. The detailed plans may be available for review aboard the *Noble Discoverer* if requested. Shell will have full time Health, Safety, and Environment (HSE) staff on board during operational periods.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

1.6.2 General Permit Training Curriculum for M-I SWACO NPDES Compliance Specialists

The M-I SWACO NPDES Compliance Specialists are responsible for maintaining copies of their training records. Specific training requirements related to operational discharges and monitoring activities are specified in the written procedures, which are incorporated by reference into the BMP and in Appendix A of this QAPP.

Each M-I SWACO NPDES Compliance Specialist shall participate in a regulatory training curriculum prior to providing GP compliance data. The curriculum includes presentations and written tests on the following elements:

- Regulatory requirements.
- QAPPs.
- Documentation procedures.
- Applicable written procedures.

Upon completion of the training curriculum, each trainee and trainer shall complete the appropriate M-I SWACO NPDES Compliance Specialist Training Documentation Form (M-I SWACO Form 2009-1, Appendix A). This form documents the employee's training on the QAPP, written procedures, specific equipment, analytical techniques, and QC requirements. NPDES Compliance Specialist training and the Compliance Specialist Training Documentation Form must be completed prior to performing any GP compliance duties. The M-I SWACO NPDES Compliance Supervisor will maintain the original forms in the employee training records and the employee maintains a copy within the M-I SWACO NPDES Compliance Specialist notebook.

1.6.3 M-I SWACO NPDES Compliance Specialist Demonstration of Capability

M-I SWACO NPDES Compliance Specialists who perform measurements, analyses, or evaluations, or who operate instruments or equipment shall have demonstrated proficiency for the specific procedures for which there is a mandatory demonstration of capability (DOC) requirement in the written procedures. Demonstration of capability shall be performed each time there is a change in instrument type, personnel, or test method. Procedures for performing and documenting the demonstration of capability are discussed in SOP 1008 Demonstration of Capability (Appendix A). The Demonstration of Capability Certification Statement included in this procedure shall be completed for each analyst, matrix, and method after successful completion of the proficiency testing. One certificate may be used for multi-analyte methods.

1.7 Documents and Records

The quantity of supporting documentation required to conduct environmental analyses necessitates the establishment of a formal system for generating, checking, inventorying, and archiving documents. This section describes document control and recordkeeping as it applies to field and laboratory data generated to demonstrate compliance with the QAPP.

During the Chukchi Sea exploration drilling program, both hard copy and electronic records will be generated by numerous organizations involved in various aspects of the program. Each contractor to Shell is responsible for ensuring that the records generated by their field staff and/or subcontractors are in compliance with the requirements of this QAPP. All organizations will maintain original records in the

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

specific locations required by their respective QA programs, and copies of their records will be provided as required during and following execution of the project. In general, documentation and recordkeeping will be conducted in accordance with this document (Sections 2.7 and 3.9).

Rig compliance laboratory records are discussed in following sections. The QA program of subcontract laboratories, including the Barrow mobile laboratory and fixed laboratory, governs their document control. Maintenance, revision, approval, distribution, archival, and retention of records will be in accordance with the subcontract laboratory QA program.

1.7.1 Document Revisions

The QAPP and associated written procedures are controlled documents. Each time a revision is made to this manual, it shall be reviewed, documented, and approved. Whenever revisions are made, or addenda added to the QAPP, a document control system shall be initiated to confirm that all parties holding a controlled copy of the QAPP receive the revisions/addenda, and that outdated material is removed from circulation.

The following procedures will be implemented to ensure that project personnel have the current versions of these documents:

- The document includes a version number and effective date;
- Each organization will maintain a master list of current written procedures, which are approved by management and assigned a revision number and effective date;
- A distribution list is maintained for the QAPP; and
- Written procedures are reviewed and revised in accordance with each organization's internal QA program.

The QAPP shall be reviewed at least annually and will be revised or amended as substantive changes are warranted. As the QAPP is revised, the revision number on the appropriate pages is incremented and the modified pages are released to the distribution list. A summary of the revisions with the date and a description of the revision is maintained on the signature page. The QAPP revision shall be submitted for approval by the same authorities that performed the original review.

1.7.2 Rig Compliance Laboratory Documentation

Field personnel from each organization shall retain copies of observations, calculations and derived data, calibration records, results, and/or reports in accordance with the BMP and each organization's QA program. Field observations will be documented in real time in bound field logbooks and will provide a record of field activities, observations, and measurements during sampling. Details regarding field and laboratory documentation are included in Sections 2 and 3.

1.7.3 Archival, Maintenance, and Retention of Project Files

Central project files are maintained in accordance with each organization's internal QA program. The central project files consist of completed rig compliance laboratory documentation, as well as fixed laboratory reports, computer program documentation, training records, and qualified subcontractor files.

Pursuant to permit regulations, project files will be retained for a period of at least five years from the date of the sample, measurement, report, or application, whichever is longer. Records are maintained electronically and/or in hard copy. Records will be maintained, archived, and retained in accordance with Section 11.5 of the BMP.

Record retention includes, but is not limited to, the following:

- Laboratory reports;
- Chain-of-custody (CoC) forms;
- Original monitoring data, including logbooks, field forms, electronic data capture, or other records in which monitoring data are first documented;
- Logs or other documents used to record field measurements, such as flow meter readings; and
- Calibration and maintenance logs for field instruments and rig compliance laboratory equipment, as they relate to measurement of volume or monitoring quality.

1.7.4 Confidentiality and Proprietary Rights

Personnel may have access to confidential information concerning permittees operations and company operations. This knowledge may include expertise, technical information, technical software, and records related to operations, finance, accounting, sales, personnel, and management, policies, or other matters. Personnel may also have access to permittee and company trade secrets, including secret formulations, techniques, methods, processes, data, discoveries, developments, designs, improvements, inventions, and the like. The protection of these trade secrets and confidential information against unauthorized disclosure or use is of critical importance. Consequently, employees and contractors may be required to execute nondisclosure and confidentiality agreements.

Any confidential business information, defined as trade secrets and commercial or financial information obtained from a person and privileged or confidential provided as part of voluntary and/or mandatory submittals to the EPA shall not be disclosed.

1.8 Sample Handling, Documentation, and Chain-of-Custody Procedures

This section includes sampling and data collection procedures and policies for ensuring compliance with requirements of the GP applicable to exploration drilling activities to be conducted by Shell in the Chukchi Sea.

An essential part of the sampling activities of any environmental project is assuring the integrity of the samples from collection through data reporting. Environmental analyses involve the collection and shipping of numerous samples from different sampling sites. Sample labels and CoC forms are used to document identification and handling of samples from the time of collection through the completion of chemical and/or physical analysis. Documentation of the history of a sample will be prepared and maintained to demonstrate that the data are a true representation of the environmental media. The CoC record is used to demonstrate that a sample was not tampered with or altered in any way that may bias the analytical accuracy of the laboratory results. It is extremely important that CoC records be complete, accurate, and consistent.

This QAPP governs field and analytical sample handling, documentation, and CoC procedures for samples analyzed in the field at the rig compliance and Barrow mobile laboratories and for samples transported to fixed subcontract laboratories. Additional details specific to the handling, documentation, and CoC procedures for the operational discharge compliance sampling program are included in Section 2; and for the EMP are included in Section 3.

The QA program of the fixed subcontract laboratory performing analyses governs laboratory sample control procedures.

1.8.1 Sample Containers and Preservation

Subcontract laboratories supply containers for fixed laboratory analyses. These containers are pre-cleaned and/or preserved in accordance with analytical method requirements. Details regarding the containers required for specific analyses can be found in Sections 2 and 3.

1.8.2 Sample Storage

Samples shall be stored in limited-access, temperature controlled areas while in the rig compliance laboratory or until packaged and shipped to the Barrow mobile laboratory or fixed subcontract laboratory for analysis. In general, the acceptance criterion for sample storage is <6°C. Thermal preservation requirements for specific analyses are outlined in Sections 2 and 3.

1.8.3 Sample Retention and Disposal

Samples will be retained under proper storage conditions in accordance with the written procedures and/or analytical methods. Analytical samples are retained and disposed of at the subcontract laboratories in accordance with the internal laboratory QA program.

1.8.4 Sample Labeling

As samples are collected and containerized, each sample is given an unique sample identification (ID) number. The sample ID is documented in the field logbook and on the CoC form. Sample IDs will be assigned in accordance with the specific procedures in Sections 2 and 3.

Each sample container must include the following information:

- Date - A six-digit number indicating the year, month, and day of collection, in this order;
- Time - A four-digit number indicating the military time of collection;
- Sample ID - A unique identification number which may contain the above information, but which distinguishes among samples collected from the same site;
- Preservative (if any);
- Sampler – Signature or initials of person collecting the sample; and
- Requested analyses.

Field QC samples (equipment blanks, field duplicates, etc.) are labeled as above, but are not identified as QC samples on the labels.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

1.8.5 Chain-of-Custody Procedures

After collection, preservation, and identification, the sample is maintained under CoC procedures discussed in this section.

Sample custody records are the administrative records associated with the physical possession and/or storage history of each individual sample from sample collection to the final analytical result and sample disposal. Sample custody will be initiated by the sample collection records that identify for each sample the unique sample ID, date, time, location, and collector.

CoC forms document sample collection and shipment to the laboratory. CoCs are legal documents that record the transfer and disposition of collected environmental samples. The CoC form will identify the contents of each shipment and provide objective physical evidence of the possession history and integrity of each sample from collection through analysis. Transfer of physical custody shall be recorded.

CoC procedures begin in the field with the collection and containerization of samples. A sample is considered under CoC if:

- The samples are in a person's possession, or
- The samples are in a person's view after being in that person's possession, or
- The samples were in a person's possession and then were locked or sealed to prevent tampering, or
- The samples are in a secure area.

As soon as each sample has been collected, containerized and labeled, it is entered on the CoC form. Each cooler should contain one CoC form representing all of the samples present in the cooler. The sampler shall complete the information on the form accurately and legibly. Any corrections to the CoC form must be made using a single line through the incorrect entry. Corrections must be initialed and dated by the person making the change.

The chain-of-custody form must include:

- Sample originator (client);
- Sample identification / location;
- Project identification;
- Date and time of collection;
- Collector's name (printed);
- Sample type (e.g., liquid or sediment);
- Analyses required;
- Preservation used; and
- Signatory of release/acceptance through transport.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Once they have been properly labeled and logged, samples are packaged for shipment and sent to the laboratory with a CoC record sealed into each cooler. Before the sample cooler is shipped, the sampler must sign and date the CoC form under "Relinquished by". The original CoC form accompanies the samples during shipment; a copy is maintained by the shipper. Coolers containing samples will be custody sealed prior to shipment to subcontract analytical laboratories.

When samples are received at the subcontract laboratory, the laboratory sample custodian signs the CoC form as "Received by," and enters the date and time. The sample custodian shall carefully inspect samples as described in the laboratory SOP, including:

- Intact air-tight seal,
- Intact CoC,
- Evidence of alteration or damage to samples or packaging, and
- Completeness of accompanying records.

The laboratory's sample receipt record shall explicitly state the condition, including the measurement of the temperature blank or cooler temperature, for each incoming sample. The Shell Environmental Compliance Engineer or his/her designee is notified of arrival and condition of each shipment, and of any discrepancies in accompanying paperwork, immediately after login inspection. After the sample log-in is complete, another copy of the CoC record, which includes laboratory sample numbers and notations of any discrepancies, is sent to the sampler identified on the CoC form and/or to the Shell Environmental Compliance Engineer, as instructed. The original CoC is filed in the laboratory, with the shipper's waybill or airway bill attached, and a copy of this record is provided to Shell.

Samples for rig compliance laboratory analyses shall be kept in a designated secure area. CoC forms are not required for rig compliance laboratory samples. Sample collection activities and identification of samples shall be recorded in field logbooks.

1.8.6 Packaging and Shipment of Samples

Samples shall be packaged and shipped in accordance with each organization's QA program and written procedure. Standard procedures for packaging and shipment of samples are necessary for the following reasons:

1) To protect persons handling, receiving and unpacking shipped samples;
2) To minimize loss of samples through breakage or delays in shipment;
3) To document sample integrity; and
4) To comply with applicable U.S. Department of Transportation (DOT) (49 CFR) and International Air Transport Association (IATA) regulations.

Details regarding specific procedures for packaging and shipping samples are included in Sections 2 and 3.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Environmental samples are samples of drilling fluids or other media where contamination is expected to be in relatively low concentrations. For the purpose of this QAPP, environmental samples are those samples whose toxic, flammable, corrosive or otherwise hazardous constituents represent less than one percent by volume.

1.9 Field and Laboratory QC Samples

The sampling designs for the operational discharge compliance sampling program and the EMP incorporate QC procedures and checks in both the field and laboratory to assess data quality. The following sections outline the most common types of field and laboratory QC samples that may be collected for the project. Sections 2 and 3 include specific types and frequencies of QC samples that will be collected and analyzed for operational discharge compliance sampling and the EMP. Section 3 also includes additional QC samples that will be collected for the EMP.

1.9.1 Field QC Samples

Field QC samples will be collected in the same type of sample containers and handled in the same manner as other field samples. The field QC samples will be assigned unique sample numbers and will be submitted to the analytical laboratory as routine samples. If nonconformances are detected in the results for field QC samples, the data associated with the QC samples will be evaluated to determine if the quality and/or usability of the data are affected.

1.9.1.1 Trip Blanks

Trip blanks are collected only for volatile organic compound (VOC) samples. A trip blank consists of a uncontaminated sample of similar matrix that is transported from the laboratory to the sampling site, handled like an environmental sample, and returned to the laboratory for analysis without having been exposed to sampling procedures (i.e., not opened in the field). The results are used to assess contamination introduced during shipping and field handling procedures. Trip blanks are prepared and analyzed at the frequency of one per shipping container of VOC samples.

1.9.1.2 Temperature Blanks

A temperature blank is a container of water that is packed and shipped to the laboratory with the field samples requiring preservation by cooling. Upon arrival of a cooler at the laboratory, the laboratory measures the temperature of the blank. This temperature reading is used to represent the conditions of the field samples during shipment to the laboratory. This information is used by both the laboratory and by the data reviewer. If the temperature blank exceeds the sample-specific thermal preservation criteria, the laboratory must notify Shell immediately for guidance.

1.9.1.3 Field Duplicates

A field duplicate is a generic term for two (or more) field samples collected at the same time in the same location. Field duplicate samples are submitted as blind samples to the laboratory and are taken through all steps of the analytical preparation and analysis process in an identical manner. These samples are used to assess precision of the entire data collection activity, including sampling, analysis, and site heterogeneity. Field duplicates shall be collected where measurable contamination is likely to be present. If contaminant levels in the duplicates are below detection limits, they cannot be used for data quality

assessment. Field duplicates are collected at a frequency of 5% of the field samples (one field duplicate sample for every 20 or fewer field samples).

There are two categories of field duplicate samples defined by the collection method: co-located field duplicates and subsample field duplicates. Co-located field duplicates are two or more independent samples collected from side-by-side locations at the same point in time and space so as to be considered identical. Co-locates are samples collected from adjacent locations, or water samples collected from the same sampling point at the same time that have not been homogenized. Subsample field duplicates samples are obtained from one sample collection at one sample location. The sample is homogenized and then subsampled in the field to form an original and duplicate sample.

Drilling fluid samples may contain gradients of chemical constituents. It is therefore necessary to thoroughly mix a quantity of drilling fluid and then split the resulting homogenized material into two separate sample containers to obtain identical field duplicate samples. The contamination risk is mitigated through the use of specially cleaned containers and properly decontaminated or disposable sampling equipment and implements for mixing and transferring the sample material.

1.9.1.4 Matrix Spikes and Matrix Spike Duplicates (MS/MSDs)

A matrix spike (MS) is performed by spiking one of a pair of duplicate samples with a known quantity of target analyte and extracting and analyzing both the spiked and the unspiked samples. In the absence of matrix interferences, the difference between the analytical results for these two duplicates will yield an acceptable recovery rate for the spike compound. If matrix interferences are present, their effect on the analytical results for the MS sample can indicate a similar effect on other samples of a similar matrix.

Matrix spikes may also be used to measure precision and accuracy of the sampling and analysis process by analyzing two spiked aliquots and one unspiked aliquot of a sample. This second spiked sample aliquot is called a MS duplicate (MSD). Accuracy is measured by calculating the difference between the measured spike concentration and the known concentration added to the MS and MSD. The closer the two measured concentrations are to the true concentration, the higher the level of accuracy in the analytical process. Precision is measured by calculating the difference between the two spike concentrations recovered in the MS and MSD. The greater the difference between the two recovered spike amounts, the lower the precision of the sampling and analysis process.

Because three separate aliquots, or portions, of sample have to be analyzed when performing an MS/MSD, it is often necessary to submit double or triple the volume of sample for an MS/MSD than that required for a normal sample. The MS/MSD samples are not separate samples, and the same sample number will be assigned to the primary (parent) sample and the extra volume supplied for the laboratory MS/MSD. CoC forms will indicate the sample designated for MS/MSD when additional material is provided. MS/MSD samples will be collected at a frequency of 5% of the field samples (one MS/MSD pair for every 20 field samples).

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

1.9.2 Laboratory QC Samples

Laboratory samples will be processed and analyzed in analytical batches or sample delivery groups (SDGs) of 20 or fewer field samples plus laboratory QC. A suite of QC samples that monitors the accuracy and precision of the methods will be incorporated into each batch; these samples are defined below. In addition to these QC samples, surrogate internal standards will be spiked into each sample analyzed for organic compounds. Laboratory QC and acceptance criteria for the specific analytical methods are included in Sections 2 and 3.

1.9.2.1 Method Blank

A method blank is an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. A method blank is prepared and analyzed with every analytical batch. The method blank is carried through the complete sample preparation and analytical procedure and is used to assess possible contamination resulting from the analytical process.

The presence of analyte in a method blank at a concentration exceeding the analytical data quality objective indicates the need for further assessment of the data. The source of contamination should be investigated, and measures must be taken to correct, minimize, or eliminate the problem. No analytical data shall be corrected for the presence of analytes in blanks.

1.9.2.2 Laboratory Control Sample

A laboratory control sample (LCS) is a sample of known composition that is spiked with all target analytes. The LCS is used with each analytical batch to determine whether the method is in control. Each analyte in the LCS shall be spiked at a level less than or equal to the midpoint of the calibration curve, which is defined as the median point of the curve instead of the middle of the range. The LCS shall be carried through the complete sample preparation and analysis procedure. The LCS cannot be used as the continuing calibration verification (CCV) sample.

At least one LCS shall be included in every analytical batch. If more than one LCS is analyzed in an analytical batch (e.g., LCS duplicate [LCSD]), results from all LCSs shall be reported. A failure of an analyte in any of the LCSs shall require appropriate corrective action, including qualification of the failed analyte in all of the samples, as required.

1.9.2.3 Surrogates

Surrogates are compounds used in organic compound analysis that are similar to the target analytes in chemical composition and behavior, but not normally found in environmental samples. Surrogates are used to evaluate accuracy, method performance, and extraction efficiency. Surrogates shall be added to environmental samples, controls, and blanks in accordance with the method requirements.

If a surrogate recovery is outside the acceptance limit, corrective action must be performed. After the system problems have been resolved and system control has been reestablished, the sample should be re-prepared and reanalyzed. If corrective actions are not performed or are ineffective, an appropriate flag shall be applied to the sample results.

1.9.2.4 Internal Standards

Internal standards (ISs) are known amounts of standards that are added to a portion of a sample or sample extract and carried through the entire procedure. ISs are used as a reference for calibration and for controlling the precision and bias of the analytical method. ISs shall be added to environmental samples, controls, and blanks, in accordance with the method requirements.

If the IS results are outside of the acceptance limits, corrective actions shall be performed. After the system problems have been resolved and system control has been reestablished, all samples analyzed while the system was malfunctioning shall be reanalyzed. If corrective actions are not performed or are ineffective, an appropriate flag shall be applied to the sample results.

1.10 Project Assessment and Oversight

The QA programs are designed to measure performance and to monitor adherence to corporate QA policies, method, and project-specific requirements and regulatory requirements. Quality assessment is the responsibility of QA staff or designees, and is performed in cooperation with the affected operating group personnel. The purpose of this section is to establish standard procedures for quality assessment and the formulation of assessment criteria. Systems for corrective action are discussed in Section 1.9.3.

1.10.1 Project Audits/Assessments

The following project audits and assessments are planned:

- *Pre-mobilization audit (readiness review).* Prior to project mobilization, a systematic evaluation of readiness for field activities will be performed.
- *Well records review.* Once per well, a review of the documents and records associated with drilling activities will be reviewed. Verify accuracy and completeness. Verify that all planned activities were documented and that all associated documentation has been completed.
- *Subcontract laboratory sample receipt information.* Verify accuracy and completeness. Verify that discrepancies were documented and resolution of any potential data quality issues. Verify that all planned samples were collected and documented. Compare planned samples with the CoC forms and laboratory login information for samples actually submitted to the laboratory. Verify that corrective action is documented, if required and appropriate, for any data quality issues identified.

1.10.2 Audit Reporting

The response to audit or assessment findings may require written documentation, verbal communication, or formal corrective action. The timeframe and format of the response depends on the audit or assessment findings. Findings should include a discussion of the audit, explaining each finding, its significance, and whenever possible, its root cause. Deviations from plans, policies, or written procedures, if any, shall be discussed in terms of whether they were warranted by the circumstances of the project, and why. Finally, recommended corrective actions should be provided, if required and appropriate, as determined by the manager and technical personnel involved in the audit.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

1.10.3 Corrective Action

Feedback and corrective action are required when deviations from documented policies, procedures or QC, if any, occur. These deviations may be identified through audits, data review and assessment, or staff feedback. The following sections describe the general procedures to be followed when departures from documented policies, procedures, or QC have occurred.

1.10.3.1 Audit Findings

The Shell Environmental Compliance Engineer and/or QA Auditor (member of the Shell Environmental / Science Department) shall be responsible for initiating and recommending corrective action, if any, in response to audit findings. Items requiring corrective action may require written documentation addressed to the Wells Superintendent. Corrective action steps shall be fully documented to assist in determining future corrective action procedures. When satisfactory progress has been achieved on each requested action, the Wells Superintendent or designee enters descriptions of actions and results on the form, retains a copy and returns the original to the Shell Environmental Compliance Engineer to close out the corrective action. The Shell Environmental Compliance Engineer maintains a file of Service Quality Non-Conformance Reports and keeps track of their progress. Unresolved corrective action requests, if any, are listed in a QA report to Management.

1.10.3.2 Data Quality Issues

Staff reviewing permit compliance data shall be responsible for requesting corrective actions in response to deficiencies that affect data quality and usability. To identify any potential impacts on the analytical results, a data usability summary shall include an evaluation of the data as applicable to the analytical method and GP requirements. Repetitive QC problems may result in staff retraining or subcontractor disqualification.

1.10.3.3 Staff Feedback

Each person involved in the data accumulation process shall be responsible for recognizing and reporting deviations, if any, from documented policies, procedures, and/or QC. If required and appropriate, deviations shall be documented and addressed to Shell. Analysts, Compliance Specialists, supervisors, and QC personnel shall use this system to document problems, deviations, and discrepancies encountered during sample collection, sample analysis, or data reporting, if any.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

This page intentionally left blank

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.0 Compliance Sampling Program for Operational Discharges

This section presents the applicable compliance requirements for operational discharges in the Authorization to Discharge under the NPDES GP for Oil and Gas Exploration Facilities on the OCS in the Chukchi Sea, Permit Number AKG-28-8100 issued by the USEPA, in compliance with the provisions of the Clean Water Act, 33 U.S.C. §1251 et seq., effective November 28, 2012.

2.1 Introduction and Overview

In the management of its activities, Shell has contracted with M-I SWACO (M-I SWACO) for its compliance assurance for the exploration program in the Chukchi Sea on the drillship M/V *Noble Discoverer*. This section addresses those GP compliance tasks that will be performed by M-I SWACO under contract to the permittee during offshore drilling exploration. GP discharge limitations and monitoring requirements applicable to the offshore drilling exploration program in the Chukchi Sea are presented in Tables 2-1 through 2-5. The following sections detail the compliance monitoring requirements for each discharge.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

This page intentionally left blank

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 2-1 Effluent Limitations and Monitoring Requirements for Water-Based Drilling Fluids/Drill Cuttings (Discharge 001)

Discharge	Effluent Parameter	Effluent Limitations		Monitoring Requirements	Seasonal Restrictions
		Average Monthly Limit	Maximum Daily Limit		
Discharge 001 Water-Based Drilling Fluids and Drill Cuttings	SPP toxicity [note 1,10]	Minimum 96-hour LC_{50} of 30,000 ppm		Weekly Grab & End of Well [note 2]	Not Applicable
	Drilling fluids and cuttings	Static Sheen Test [note 3,10]		Daily Grab	
	Free oil	No Discharge [note 4,10]		Daily Grab	
	Diesel oil	No Discharge [note 5,10]		Daily Grab	
	Mercury	1 mg/kg [note 6]		Grab Once/well	
	Cadmium	3 mg/kg [note 6]		Grab Once/well	
	pH	Report (s.u.)		Grab Once/ well	
	Total Aqueous Hydrocarbons (TaqH)	Report (µg/L)		Grab Once /well [note 7]	
	Total Aromatic Hydrocarbon (TAH)	Report (µg/L)		Grab Once /well [note 8]	
	Total volume	Report (gal)		Daily Estimate [note 9]	

Notes:

LC_{50} = lethal concentration, 50% (in water, that kills 50% of the inhabitants in a given time)
mg/kg = milligram per kilogram
MLLW = Mean lower low water
µg/L = microgram per liter
ppm = parts per million
s.u. = standard units
SPP = suspended particulate phase

1. As determined by the 96-hour suspended particulate phase (SPP) toxicity test in accordance with Appendix 2 to Subpart A of 40 CFR Part 435, Drilling Fluids Toxicity Test. The discharge of water-based drilling fluids or drill cuttings generated using drilling fluids with a daily minimum or monthly average minimum 96-hour LC_{50} of less than 30,000 ppm is prohibited. If inclement weather conditions affect timely deliveries of samples, the permittee must notify EPA within 24 hours and document the conditions and rationale in the following monthly DMR.
2. See requirement of Section II.B.5.b. (Mineral Oil Pill). At the end-of-well, a sample must be collected for SPP toxicity testing where no mineral oil pill is used. The end-of-well sample can also serve as the monthly monitoring sample.
3. No discharge allowed upon failure of the static sheen test as determined in accordance with Appendix 1 to Subpart A of 40 CFR Part 435, Static Sheen Test.
4. As determined by the static sheen test in accordance with Appendix 1 to Subpart A of 40 CFR Part 435, Static Sheen Test.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

5. The discharge of drilling fluids or drill cuttings generated using drilling fluids which contain diesel oil is prohibited. Compliance will be demonstrated by gas chromatograph (GC) analysis of drilling fluid collected from the drilling fluid used at the greatest well depth ("end-of-well" sample) and of any drilling fluids or cuttings which fail the static sheen test compared to GC analysis of diesel oil in storage at the facility. Whenever drilling fluids or drill cuttings fail the static sheen test, the permittee is required to analyze an undiluted sample of the material which failed the test to determine the presence or absence of diesel oil in accordance with EPA SW846 Method 8015C (2007). Gas chromatography/mass spectrometry (GC/MS) may be used if an instance should arise where the permittee and the Director or DEC determine that greater resolution of the drilling fluid "fingerprint" is needed for a particular drilling fluid sample.
6. Dry weight in the stock barite. Results must be expressed as mg/kg (dry weight) of barite. The permittee must analyze a representative sample of stock barite once prior to drilling each well and submit the results with the DMR for the month in which drilling operations commence for the respective well. If any analytical result exceeds the mercury or cadmium effluent limitations in Table 1, the permittee must report the results to the Director in accordance with Section III.G., including the twenty-four hour notice of noncompliance requirement, of this GP. If the permittee uses the same supply of stock barite to drill subsequent wells, the permittee may submit the same analysis for those subsequent wells if no new supplies of barite have been received since the prior analysis. In this case, the DMR should state that no new barite was received since the last reported analysis.
7. As determined by summing the results of EPA Method 602 (plus Xylenes) or EPA Method 624 to quantify monoaromatic hydrocarbons and to measure TAH and EPA Method 610 or EPA Method 625 to quantify polynuclear aromatic hydrocarbons listed in EPA Method 610. Sample must be collected at the same time as the SPP toxicity test, to the extent practicable, and at the end of well.
8. As determined by EPA Method 602 (plus Xylenes) or EPA Method 624. Sample must be collected at the same time as the SPP toxicity test, to the extent practicable, and at the end of well.
9. Record separate total daily volumes of drilling fluids and drill cuttings and report the separate daily volumes in the End of Well Report. Report combined total volume of drilling fluids and drill cuttings discharged on a calendar day in the DMR.
10. The permittee must report the following discharge occurrences of noncompliance to the Director in accordance with Section III.G.l., including the twenty-four hour notice of noncompliance requirement, of this GP: (a) exceedance of the SPP toxicity limitation; (b) failure of the static sheen test; or (c) presence of diesel oil.

Table 2-2 Discharge Rate Limitations and Monitoring Frequency for Water-Based Drilling Fluids and Drill Cuttings (Discharge 001)

Water Depth [note 1]	Rate of Discharge [note 2]	Measurement Frequency	Sample Type
0 to 5 meters	No discharge	Hourly during discharge [note 3]	Estimate [note 4]
>5 to 20 meters	500 bbl/hr		
>20 to 40 meters	750 bbl/hr		
>40 meters	**1000 bbl/hr**		

Notes:

bbl/hr = barrels per hour

1. As measured from the MLLW.
2. Rate of discharge limitations do not include entrained seawater.
3. The maximum daily discharge limitation is calculated by multiplying the maximum hourly rate of discharge by 24 hours. For purposes of reporting, each hourly measurement must be recorded for each calendar day of discharge within the month. The monthly average limit is the average of the maximum daily hourly rate for each calendar day.
4. One-TRAX software based on operational data input and Pit Volume Totalizer.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 2-3 Effluent Limitations and Monitoring Requirements for Deck Drainage (Discharge 002)

Discharge	Effluent Parameter	Effluent Limitations	Monitoring Requirements
Discharge 002 Deck Drainage	pH	s.u.	Monthly sample
	Free oil	No discharge [note 1]	Grab sample and visual per discharge event
	Total Volume (gal)	-	Monthly estimate
	TAqH	µg/L	Grab sample per discharge event [note 2,4]
	TAH	µg/L	Grab sample per discharge event [note 3,4]
	WET	TU_c	Use rapid toxicity test 4X/well as initial screen.

Notes:

µg/L = microgram per liter
gal = gallons
s.u. = standard units
WET = whole effluent toxicity

1. Once per discharge event, the permittee must sample deck drainage discharges that are processed through an oil-water separator and test for sheen using the static sheen test in accordance with Appendix 1 to Subpart A of 40 CFR Part 435, Static Sheen Test. For discharges during unstable or broken ice conditions, a water temperature that approximates surface water temperatures after breakup must be used. During periods of discharge, the permittee must also conduct a visual observation for visual sheen as determined by the presence of a film or sheen upon or a discoloration of the surface of the receiving water.
2. As determined by summing the results of EPA Method 602 (plus Xylenes) or 624 to quantify monoaromatic hydrocarbons to measure TAH and EPA Method 610 or EPA Method 625 to quantify polynuclear aromatic hydrocarbons.
3. As determined by EPA Method 602 (plus Xylenes) or EPA Method 624.
4. Sample must be collected from the oil-water separator effluent.
5. Only applicable if initial toxicity screening exceeds threshold criteria outlined in Section 2.4.3.1. Also required once per well if discharge exceeds 10,000 gallons during any 24-hour period and if chemicals are added to the system.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 2-4 Effluent Limitations and Monitoring Requirements for Sanitary and Domestic Wastes (Discharges 003 and 004)

Discharge	Effluent Parameter	Effluent Limitations		Monitoring Requirements	
		Average Monthly Limit	Maximum Daily Limit	Sample Frequency	Sample Type
Discharge 003 Sanitary Waste	Flow (mgd)	----	----	Daily	Measured/Recorded
	BOD_5	30 mg/L	60 mg/L	Weekly	Grab or composite [note 1]
	TSS	30 mg/L	60 mg/L	Weekly	Grab or composite [note 1]
	Floating solids	No discharge		Daily	Visual [note 2]
	Foam	No discharge		Daily	Visual [note 2]
	Oily Sheen	No discharge		Daily	Visual [note 2]
	pH	6.5-8.5 s.u.		Weekly	Grab
	Fecal Coliform Bacteria	100 colonies/100 mL [note 3]	200 colonies/100 mL	Weekly	Grab
	Total Residual Chlorine [note 5]	----	1.0 mg/L	Weekly	Grab
	Flow	Report		Monthly	Meter
Discharge 004 Domestic Waste	pH	Report s.u.		Monthly	Grab
	Floating solids, garbage, foam	No discharge		Daily [note 2]	Visual
	Flow (mgd)	Report		Monthly	Estimated

Notes:

mgd = million gallons per day
mg/L = milligram per liter
mL = milliliters
s.u. = standard unit

1. Composite samples may be collected in lieu of grab samples and must consist of at least four equal volume grab samples, two of which must be taken during periods of peak flow.
2. The permittee must monitor by observing the surface of the receiving water in the vicinity of the outfall(s) during daylight at the time of maximum estimated discharge and during conditions when observations on the surface of the receiving water are possible in the vicinity of the discharge. The observations and time of day must be recorded. The numbers of days floating solids, garbage, foam or oily sheen are observed must be recorded and reported in the DMR.
3. Must be reported as the geometric mean.
4. If inclement weather conditions affect timely deliveries of samples, the permittee must notify EPA within 24 hours document the conditions and rationale in the following monthly DMR.
5. Must be maintained as close to this concentration as possible. Sample must be collected immediately after chlorination and prior to any commingling of the waste streams. The analytical detection limit for this parameter is 0.1 mg/L. Residual chlorine may be monitored according to test procedures approved under 40 CFR Part 136 or using a Hach Test Kit capable of measuring free chlorine in the range of 0-3.5 mg/L with a sensitivity of 0.1 mg/L or better. Monitoring is not required if chlorine is not used as a disinfectant or for facilities serving fewer than 10 persons. One composite sample must consist of at least four equal volume grab samples, two of which must be taken during periods of peak flow.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 2-5 Effluent Limitations and Monitoring Requirements for Miscellaneous Discharges

Discharge	Effluent Parameter	Effluent Limitations		Monitoring Requirements	
		Average Monthly Limit	Maximum Daily Limit	Sample Frequency	Sample Type
Discharge 005 Desalination Unit Wastes	pH	Report (s.u.)		Monthly	Grab
	Free oil	No discharge [note 1,2]		Once/discharge	Visual /Grab
	Total Volume	Report (gal)		Monthly	Flow Meter
	WET	Report (TU_c)		Use rapid toxicity test 4X/well as initial screen.	Collect grab sample for analysis if results show potential toxicity or 1X/well if discharge >10,000 gal during 24 hr and if chemicals are added to the system.
Discharge 006 Blowout Preventer Fluid	pH	Report (s.u.)		Monthly	Grab
	Free oil	No discharge [note 1,2]		Once/discharge	Visual /Grab
	Total Volume	Report (gal)		Monthly	Estimate
Discharge 007 Boiler Blowdown	pH	Report (s.u.)		Monthly	Grab
	Free oil	No discharge [note 1,2]		Once/discharge	Visual /Grab
	Total Volume	Report (gal)		Monthly	Estimate
	WET	Report (TU_c)		Use rapid toxicity test 4X/well as initial screen.	Collect grab sample for analysis if results show potential toxicity or 1X/well if discharge >10,000 gal during 24 hr and if chemicals are added to the system.
Discharge 008 Fire Control System Test Water	pH	Report (s.u.)		Monthly	Grab
	Free oil	No discharge [note 1,2]		Once/discharge	Visual /Grab
	Total Volume	Report (gal)		Monthly	Estimate
	WET	Report (TU_c)		Use rapid toxicity test 4X/well as initial screen.	Collect grab sample for analysis if results show potential toxicity or 1X/well if discharge >10,000 gal during 24 hr and if chemicals are added to the system.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Discharge	Effluent Parameter	Effluent Limitations		Monitoring Requirements	
		Average Monthly Limit	Maximum Daily Limit	Sample Frequency	Sample Type
Discharge 009 Non-Contact Cooling Water	pH [note 3]	Report (s.u.)		Monthly	Grab
	Free oil	No discharge [note 1]		Daily	Visual
	Total Volume	Report (gal)		Daily [note 4]	Meter
	Temperature	Report (°F)		Continuous [note 4]	Measure
	WET	Report (TU_c)		Use rapid toxicity test 4X/well as initial screen.	Collect grab sample for analysis if results show potential toxicity or 1X/well if discharge >10,000 gal during 24 hr and if chemicals are added to the system.
Discharge 010 Uncontaminated Ballast Water	pH	Report (s.u.)		Monthly	Grab
	Free oil	No discharge [note 1,2]		Once/discharge	Visual /Grab
	Total Volume	Report (gal)		Monthly	Estimate
Discharge 011 Bilge Water	pH	Report (s.u.)		Monthly	Grab
	Free oil	No discharge [note 5]		Once/discharge & Daily	Grab/Visual
	Total Volume	Report (gal)		Monthly	Meter
	WET	Report (TU_c)		Use rapid toxicity test 4X/well as initial screen.	Collect grab sample for analysis if results show potential toxicity or 1X/well if discharge >10,000 gal during 24 hr and if chemicals are added to the system.
Discharge 012 Excess Cement Slurry	pH	Report (s.u.)		Monthly	Grab
	Free oil	No discharge [note 1]		Once/discharge	Visual
	Total Volume	Report (gal)		Monthly	Estimate
Discharge 013 Mud, Cuttings & Cement at Sea Floor	Free oil	No discharge [note 1]		Daily	Visual
	Total Volume	Report (gal)		Monthly	Estimate

Notes:

°F = degrees Fahrenheit
gal = gallons
s.u. = standard units
TU_c = chronic toxic units
WET = whole effluent toxicity

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

1. Once per discharge event, the permittee must conduct a visual observation for visual sheen as determined by the presence of a film or sheen upon or a discoloration of the surface of the receiving water. The permittee must monitor by observing the surface of the receiving water in the vicinity of the outfall(s) during daylight at the time of maximum estimated discharge and during conditions when observations on the surface of the receiving water are possible in the vicinity of the discharge. The observations and time of day must be recorded. The number of days sheen is observed must be recorded and reported in the DMR. For discharges during unstable or broken ice conditions, a water temperature that approximates surface water temperatures after breakup must be used.
2. If visual observations of the discharge are not possible, the permittee must sample (grab sample) the discharge and test for sheen using the static sheen test in accordance with Appendix 1 to Subpart A of 40 CFR Part 435.
3. pH montoring and reporting is required. pH limit of 6.5-8.5 applies if chemicals are added to the system.
4. Estimated daily discharge volume and maximum and minimum recorded daily temperature must be reported for each outfall.
5. Once per discharge event, the permittee must sample bilge water discharges that are processed through an oil-water separator and test for sheen using the static sheen test in accordance with Appendix I to Subpart A of 40 CFR Part 435. For discharge during unstable or broken ice conditions, a water temperature that approximates surface water temperatures after breakup must be used. On a daily basis during discharge, the permittee must also conduct a visual observation for visual sheen as determined by the presence of a film or sheen upon or discoloration of the surface of the receiving water. The permittee must monitor by observing the surface of the receiving water in the vicinity of the outfall(s) during daylight at the time of maximum estimated discharge and during conditions when observations on the surface of the receiving water are possible in the vicinity of the discharge. The obesrvations and time of day must be recorded. The number of days sheen is observed must be recorded and reported in the DMR.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.2 Operational Discharge Compliance Program Roles and Responsibilities

Communication and coordination between compliance monitoring personnel, drilling operations management officials, and drillship operations officials will be critical to ensuring compliance with GP requirements. M-I SWACO NPDES Compliance Specialists must have a general understanding of oil and gas drilling procedures and drillship operations. They will be aware of the schedule for drilling operations and planned discharges of drilling fluids as well as discharges of materials related to drillship operations that are regulated under the GP.

The primary roles and responsibilities for individuals and teams responsible for implementing the operational discharge compliance program are defined in the following sections.

2.2.1 Wells Delivery Manager

The Wells Delivery Manager is the single individual responsible for the entire exploration program. In turn, the Wells Delivery Manager delegates authority to the Wells Superintendent, Engineering Team Lead, and the Environmental Manager who are responsible for recognizing the requirements of this manual in their planning and budgeting and for implementing the QA program as assigned in this chapter. The Wells Delivery Manager has overall responsibility for the technical operation of the permit compliance program. Additional personnel will be assigned to assist in implementation of the quality program. The Wells Delivery Manager is specifically responsible for:

- Ensuring that personnel are free from any commercial, financial, or other undue pressures that may affect the quality of their work;
- Ensuring the implementation of the QA program as it pertains to operational discharge compliance under the GP;
- Ensuring that responsible, trained, and qualified personnel are assigned to manage, perform, or verify work affecting the quality of data; and
- Supervising personnel familiar with the procedures, the objective of the procedures, and the assessment of the results.

2.2.2 Wells Health, Safety and Environmental Department

The Wells Health, Safety and Environmental (HSE) Department has overall responsibility for the health and safety of employees as well as implementation of environmental regulatory programs. The HSE Department is specifically responsible for providing health and safety oversight in compliance with the requirements of the Shell HSE Program.

2.2.3 Shell Environmental Compliance Engineer

The Shell Environmental Compliance Engineer has independent reporting authority from the Wells Superintendent, Engineering Team Lead, and the Environmental Manager. The Environmental Compliance Engineer may assign personnel to assist in implementation of the quality program. The responsibilities of the Environmental Compliance Engineer are to:

- Conduct regularly scheduled audits of quality programs; and
- Advise operational managers of deficiencies (if any) in quality programs or performance.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.2.4 M-I SWACO NPDES Compliance Supervisor

The M-I SWACO NPDES Compliance Supervisor reports to the Wells Delivery Manager and is responsible for implementing the technical operation of the permit compliance program. The M-I SWACO NPDES Compliance Supervisor may assign personnel to assist with specific duties. Specific responsibilities of the M-I SWACO NPDES Compliance Supervisor include:

- Training M-I SWACO NPDES Compliance Specialists;
- Coordinating rig compliance laboratory assignments;
- Coordination with the Barrow mobile laboratory;
- Coordination with the fixed analytical laboratories;
- Providing overall direction to, and coordination of, quality programs as related to documenting compliance with the GP;
- Providing, and replacing as necessary, the equipment required for compliance tests;
- Approving and publishing written procedures;
- Reviewing Daily Activity Reports and associated records; and
- Archiving records at the end of drill season.

2.2.5 M-I SWACO NPDES Compliance Specialist

Personnel are responsible for complying with QA/QC requirements that pertain to their technical function. Each M-I SWACO NPDES Compliance Specialist shall have a combination of experience and education to adequately demonstrate a specific knowledge of their function and a general knowledge of operations, test methods, QA/QC procedures, and records management. M-I SWACO NPDES Compliance Specialists shall be responsible for recognizing and reporting deviations from documented policies, procedures, and/or QC to the M-I SWACO NPDES Compliance Supervisor and the Shell Environmental Compliance Engineer.

The responsibility for implementing the QA program ultimately rests with the M-I SWACO NPDES Compliance Specialist. The M-I SWACO NPDES Compliance Specialist is specifically responsible for:

- Maintaining technical proficiency in the compliance procedures;
- Maintaining records for field equipment;
- Maintaining and calibrating equipment for compliance tests;
- Collecting and/or analyzing effluent samples;
- Transferring documents to the records custodian at the end of the drilling season;
- Providing copies of analytical reports to the permittee; and
- Reporting deviations from procedures to supervisory personnel.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.3 Data Quality Objectives

The DQOs for the monitoring of operational discharges are to address the following GP requirements:

- Ensure that samples and measurements taken for the purpose of monitoring are representative of the monitored activity;
- Collect and analyze effluent samples in accordance with the methods specified in 40 CFR Part 435 and 40 CFR Part 136; and
- Collect and analyze samples of the type, frequency, quantity, and quality to meet the effluent limitations and monitoring requirements outlined in Section II of the GP.

2.4 Field Sampling

The following sections outline the operational discharge compliance sampling program design, which is intended to meet project DQOs and the effluent limitations and monitoring required by the GP.

2.4.1 Sampling, Measurement, and Observation Locations

This section presents discharge sampling, flow/volume measurement, and observation locations. Samples of treated discharge media will be collected after the final treatment system component and prior to the applicable discharge point or caisson. Discharge flow rates will either be estimated (total volume discharged) or recorded by using a dedicated inline flow meter in accordance with M-I SWACO SOP. Discharges that include a chemical additive and exceed 10,000 gallons during any 24-hour period, will be sampled once per well for whole effluent toxicity testing in accordance with M-I SWACO SOP. Visual discharge observations for sheen, floating solids, or other residues will be conducted from vantage points aboard the surface of the drill ship that allow for unobstructed observation of the receiving waters in accordance with M-I SWACO SOP 3005.

Table 2-6 presents the discharge sampling locations, flow/volume measurement locations, and visual observation locations as well as station identifiers and ship sample location designators. Ship sample locations correlate to points identified on the *Noble Discoverer* in Figure 1 (Appendix B to the BMP).

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 2-6 Discharge Sampling Locations

Discharge	Ship Location/ Station ID[1]	Sample Location(s)	Type of Measurement	Effluent Parameter
Discharge 001 Drilling Fluids and Drill Cuttings	Figure 2	Drilling fluids and cuttings from shale shakers (prior to discharge into caisson trough); Mud Tank	Analytical sample	SPP toxicity
				TAH
				TAqH
				Diesel oil
			Field sample	pH, Static sheen
			Estimate	Flow Volume (mgd)
			Visual observation	Free Oil (visual sheen)
Discharge 002 Deck Drainage	Figures 1, 2, & 3	OWS Effluent line; Flow meter on OWS	Analytical sample	TAH
				TAqH
				Tox screen/WET
			Field sample	pH
			Calculation/Measurement	Total Volume (gal)
			Visual observation	Free Oil (visual sheen)
Discharge 003 Sanitary Waste	Figure 2 & 3	MSD Effluent Line	Analytical sample	BOD_5
				TSS
				Fecal Coliform Bacteria
			Field sample	pH, Total residual chlorine
			Flow meter reading	Flow Volume (mgd)
			Visual observation	Oily Sheen, Floating solids & garbage, Foam
Discharge 004 Domestic Waste	Figure 1 & 3	MSD Effluent Line	Field Sample	pH
			Flow Meter	Flow Volume (mgd)
			Visual observation	Floating solids & garbage, Foam
Discharge 005 Desalination Unit Wastes	Figures 1, 2, & 3	Desalination Unit Effluent Line	Analytical sample	Tox screen/WET
			Field sample	pH
			Flow Meter	Total Volume (gal)
			Visual observation	Free Oil (visual sheen)
Discharge 006 Blowout Preventer Fluid	Not depicted	Holding tank	Field sample	pH
			Calculation/Measurement	Total Volume (gal)
			Visual observation	Free Oil (visual sheen)

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Discharge	Ship Location/ Station ID[1]	Sample Location(s)	Type of Measurement	Effluent Parameter
Discharge 007 Boiler Blowdown	Figures 1, 2 & 3	Holding Tank	Analytical sample	Tox screen/WET
			Field sample	pH
			Calculation/Measurement	Total Volume (gal)
			Visual observation	Free Oil (visual sheen)
Discharge 008 Fire Control System Test Water	Figures 1, 2 & 3	Common manifold	Analytical sample	Tox screen/WET
			Field sample	pH
			Calculation/Measurement	Total Volume (gal)
			Visual observation	Free Oil (visual sheen)
Discharge 009 Non-contact Cooling Water	Figures 1, 2, & 3	Common manifold	Analytical sample	Tox screen/WET
			Field sample	pH
			Flow Meter	Total Volume (gal)
			Visual observation	Free Oil (visual sheen)
			Data logger	Temperature (continuous)
Discharge 010 Uncontaminated Ballast Water	Figures 1, 2, & 3	Ballast Water Discharge Line	Field sample	pH
			Calculation/Measurement	Total Volume (gal)
			Visual observation	Free Oil (visual sheen)
Discharge 011 Bilge Water	Figures 2 & 3	OWS Effluent Line	Analytical sample	Tox screen/WET
			Field sample	pH, Static sheen
			Flow meter reading	Total Volume (gal)
			Visual observation	Free Oil (visual sheen)
Discharge 012 Excess Cement Slurry	Figures 1 & 3	Cement Unit Mix Tanks	Field sample	pH
			Calculation/Measurement	Total Volume (gal)
			Visual observation	Free Oil (visual sheen)
Discharge 013 Muds, Cuttings, and Cement at the Seafloor	Not depicted	Receiving water	Calculation/Measurement	Total Volume (gal)
			Visual observation	Free Oil (visual sheen)

Notes:

[1] Locations are identified in Appendix B of the BMP.
bbl/hr = barrels per hour
BOD_5 = 5-day biochemical oxygen demand
BOP = blowout preventer
gal = gallons
mgd = millions of gallons per day
MSD = marine sanitation device
OWS = oil/water separator
SPP = suspended particulate phase
TSS = total suspended solids
WET = whole effluent toxicity

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.4.2 Sampling, Measurement, and Observation Frequencies

This section summarizes the procedures for ensuring compliance with the required sampling, measurement, and observation frequencies specified in the GP. Frequencies of general tasks related to the operational discharge compliance sampling program are summarized in Table 2-7.

Compliance monitoring requirements and sampling tasks for each discharge are presented in the following sections. All sampling related activities shall be conducted in accordance with this QAPP and the applicable written procedure.

2.4.2.1 Daily Tasks

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a daily basis:

- Attend project health and safety meetings and project planning meetings and provide input and communication as it relates to sampling requirements;
- Maintain and document the condition of the sample storage refrigerator in accordance with the procedures outlined in this QAPP and M-I SWACO SOPs 1005 and 1006; and
- Provide Daily Activities Report to the M-I SWACO NPDES Compliance Supervisor.
- Document flow/volume estimates and sampling/testing performed to ensure compliance with M-I SWACO SOPs and permit stipulations.
- Monitor to ensure if a chemical additive is used and if discharges from 002 (deck drainage), 005 (desalination unit wastes), 007 (boiler blowdown), 008 (fire control system test water), 009 (non-contract cooling water) and 011 (bilge water) exceed 10,000 gallons during any 24-hour period.
- Collect samples and submit to a contract laboratory (Environ or equivalent laboratory). Perform initial toxicity screening four times per well in accordance with the M-I SWACO SOP and the analytical protocols established by Environ for conducting the required toxicity testing. WET testing required if any initial toxicity screening does not meet criteria listed in Section 2.4.3.1.

2.4.2.2 Weekly Tasks

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a weekly basis:

- Inspect and document the current inventory of sampling equipment, supplies, and containers in accordance procedures outlined in this QAPP and M-I SWACO SOP 1006; and
- Request additional materials as necessary.
- Document weekly measurements and sampling /testing performed to ensure compliance with M-I SWACO written procedures and permit stipulations.

2.4.2.3 Monthly Tasks

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a monthly basis:

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

- Document or estimate monthly discharge flow volumes from daily measurements in accordance with procedures outlined in this QAPP and M-I SWACO SOP 1006 for all discharges; and
- Provide a monthly discharge flow volume report to the Shell Environmental Compliance Engineer and M-I SWACO NPDES Compliance Supervisor detailing all discharges performed during the month, including daily discharge volume measurements.

Table 2-7 Summary of Compliance Sampling, Measurement, and Observation Frequencies and Related SOPs

Frequency	Task	M-I SWACO SOP
Daily	Attend HSE and project planning meetings	N/A
	Maintain sample refrigerator	1005, 1006
	Daily activity report	N/A
	Monitor if chemicals are added to the system and if discharges exceed 10,000 gals/24-hr period	1006, 2001, Section 2.4.3
Weekly	Sampling supply inventory	1006
Monthly	Document or estimate monthly discharge flow volumes	1006
	Monthly discharge flow volume report	N/A

Notes:
HSE = Health, Safety, and Environment
SOP = standard operating procedure

2.4.3 Compliance Sampling Requirements for Each Operational Discharge

Compliance activities include the collection of samples for analysis at the rig compliance laboratory, and collection of samples for shipment to the Barrow mobile laboratory and fixed subcontract laboratory. Environmental samples will be collected using methods selected to ensure that project DQOs are met. Written procedures that outline the procedures to be followed for the collection and analysis of environmental samples are included as an attachment to this QAPP. These written procedures ensure that project personnel collect representative samples in a consistent manner for all required sampling matrices and locations, that contamination is not introduced during collection, and that the sample volumes are properly preserved in order to meet project objectives and analytical method requirements.

The following sections describe the samples to be collected for each discharge to support compliance with this QAPP and the GP. For each discharge, the following information is presented: sampling tasks and frequency; the type and matrix of samples to be collected; analytical methods; required volume of sample; QC samples and frequency; and sample containers, preservation, and holding times.

2.4.3.1 Effluent Toxicity Testing

As part of the Phase II Assessment of the EMP, initial toxicity testing will be conducted four times per well during exploration drilling activities for the following discharges: 002 (deck drainage), 005 (desalination unit wastes), 007 (boiler blowdown), 008 (fire control system test water), 009 (non-contact cooling water), and 011 (bilge water).

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

The effluent samples will be collected from the discharge stream after the last treatment on the drilling rig and before the discharge stream enters the receiving waters. If samples are collected for both toxicity testing and operational discharge compliance analyses at the same time, a split sample will be collected. Split samples are two or more representative portions taken from one sample collected at the appropriate sampling location. To ensure that split samples are representative, the volume of sample collected must equal the total volume required for all of the laboratory analyses. For example, if the WET tests were triggered by a failure of the initial rapid screening test for a particular discharge, then the maximum volume of effluent to be collected at any given time would be 49 L of effluent: WET testing (45 L), TAH (0.12 L), TAqH (2 L), static sheen (0.5 L), and pH (0.1 L) analyses.

Effluent toxicity testing as required under the GP will consist of an initial toxicity screening (100% effluent may not be attainable if sample must be salinity corrected to accommodate the optimal salinity range for echinoderms) at four different time periods selected to reflect discharge practices and operational processes. If the initial toxicity screen indicates the effluent sample may cause adverse biological impacts as defined by the toxicity testing threshold limits established for this program, then whole effluent toxicity (WET) testing is required and the WET testing sample will be collected as soon as practical. In addition, if other discharge thresholds are exceeded as specified by greater than 10,000 gallons in a 24 hour period and if chemicals are added such that they will end up in the discharge, then WET testing will also be initiated.

The threshold limits established for this program are based on the initial toxicity screening test using echinoderm fertilization success. This test has been demonstrated to have a detectable significant criteria ranging (i.e., ability to detect an effect) from 15.5% to 25% for various laboratories (Carr et al. 1996, USGS 1998, and Porebski et al. 1999). For this program, the initial toxicity screening thresholds include the following three criteria, which must all be met to indicate a positive toxicity result:

1) Test validation requires >70% fertilization.
2) A sample that has sufficient reduction in fertilization to be identified as an adverse effect requires a statistically significant difference between the validated control fertilization test and the 100% effluent.
3) The decline in fertilization compared to the validated control response must be at least 25%.

For example, if the control percent fertilization was 80%, then the effluent response *must* be statistically significantly different from the control and have exhibited a greater than 25% difference in percent fertilization (≤55% fertilization).

The remote location of the drilling sites in the Chukchi Sea creates logistical challenges for transporting samples to the laboratory within the method-required holding times. Due to these challenges, the volume of effluent initially collected to conduct the WET testing will include sufficient volume to carry all testing through completion (if WET testing is triggered). An adequate volume for each effluent sample will be collected to conduct the rapid screening test (2 L), or the chronic WET testing, if triggered (45 L), for a particular discharge. The practice of collecting all volume required for the WET testing requirements up front has been used to assess the chronic toxicity of discrete discharge events such as storm water runoff or de-icing activities, where renewal samples are not able to be collected beyond the time period of the event in question. Adequate volume of the initial WET testing sample (45L) will be sufficient to accomplish all test initiation activities, including daily test solution renewals of the 7 day chronic assays.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Renewal samples will attempt to be collected and transported on an every-other day basis following collection of the initial WET sample per EPA guidance. The volume of the second and third sample will be 30 L and 20 L, respectively. Effluent samples will be collected for toxicity testing in accordance with the Environ *Collection of Effluent Samples for Biological Testing SOP ENV001* (Appendix A).

Testing should be initiated on samples within 36 hours of sample collection, but must not exceed 72 hours as prescribed in the GP and method guidance. Effluent samples used for test solution renewals on the WET 7-day chronic tests (days 1-6) may be used up to 48-hours after the initial use (test initiation) (USEPA 2002). This guidance indicates that samples may be used for test solution renewals at up to 120 hours from the time of collection. Table 2-8 summarizes these holding times.

Table 2-8 Effluent Sample Holding Times for Toxicity Testing

Holding Time for Test Initiation	Sample Aging for Use as Test Solution Renewal (During Test)
0 – 36 hours (recommended) 0 – 72 hours (allowed maximum)	0 – 84 hours (recommended) 0 – 120 hours (allowed maximum)

Note:
Holding times are from time of sample collection.

All toxicity testing will be conducted at the Environ Port Gamble Environmental Laboratory located in Port Gamble, Washington. In order to meet holding times for testing, effluent sample collection for an applicable discharge event will be coordinated with helicopter transport and priority air freight shipping from Barrow, Alaska.

An example scenario and timeline for effluent sample collection and shipment is provided below. The timeline allows for minor delays in transport. Alaska Airlines has ~20 flights each day from Anchorage to Seattle. Departure of samples from Anchorage can occur aboard an earlier or slightly later flight to meet the 36 hour holding time (initiate test by 2000 on second day).

0800-1200 Effluent samples are collected during the morning of the applicable discharge event.

1200-1300 All samples are packed with ice packs in coolers and CoC procedures are initiated as described in this QAPP.

1300-1400 Samples are transported in the afternoon by helicopter to Alaska Air Cargo GoldStreak® in Barrow, Alaska.

1843-2035 Samples are transported by cargo only or a cargo/passenger aircraft (cargo and passengers) in the early evening to Anchorage, Alaska.

0150-0615 Samples are transported by cargo only, combination of cargo and passenger, or passenger aircraft in the early morning to Seattle, Washington. Alaska Air Cargo GoldStreak® known shipper status allows transport on passenger aircraft for packages less than 100 pounds.

0900-1200 Samples are transported by courier from the Seattle Airport to Environ Port Gamble Environmental Laboratory in the morning for sample log-in and test initiation by the afternoon.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

If WET testing is required, 45 L will be collected at the time of initial sample collection. This initial volume of sample for WET testing, which includes renewal water volume, will be assigned Priority 1 (Type I Samples) in the helicopter support priority matrix due to the short holding time for test initiation (Table 2-8). Subsequent volumes of renewal water (Sample 2: 30 L; Sample 3: 20 L) will be collected as required for compliance with the analytical method, and an attempt to transport this renewal water will be made. Transportation of renewal water samples will be assigned transport Priority 3 (Crew Change) priority.

If transport of the renewal water sample is delayed, the laboratory will use the initial aliquot that was received; M-I SWACO NPDES Compliance Specialists will continue to attempt to collect the required volume of renewal water during the next feasible time.

The laboratory will document the condition of the sample volume used for WET testing, including any variance in receipt of the sample (such as weather delays, or delays due to competing helicopter priorities); the nature of the waste stream and effect on toxicity degradation (if any); and the action taken by the laboratory (e.g., utilization of the initial sample). Shell will notify EPA of any variance in samples collected for WET testing.

2.4.3.2 Compliance Sampling for Water-Based Drilling Fluids and Drill Cuttings (Discharge 001)

Prior to drilling each well, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following sampling tasks:

- Stock barite is analyzed and assigned a lot number by the vendor and a Certificate of Analysis accompanies each shipment. The M-I SWACO NPDES Compliance Specialist will retain a copy of the Certificate of Analysis in the field notebook for the lot of stock barite prior to its use. Each time a new lot batch of barite is utilized within the drilling season, the M-I SWACO NPDES Compliance Specialist will retain the Certificate of Analysis and record the lot number in the field notebook prior to its use.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following sampling tasks while discharging water-based drilling fluids and cuttings:

- Document the flow volume from discharge flow meters or estimate the volume of fluids and cuttings discharged hourly by calculating the hourly discharge rate in bbl/hr, and ensure that the depth-dependent discharge rate in Table 2-2 is not exceeded. The Shell Environmental Compliance Engineer and M-I SWACO NPDES Compliance Supervisor will be notified when the discharge rate exceeds 75% of the maximum allowable hourly discharge rate and there is potential for that rate to be exceeded.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following sampling tasks on a daily basis:

- Document the flow volumes from all discharge flow meters and waste volumes in bulk discharge holding tanks aboard the drillship in accordance with procedures outlined in this QAPP and M-I SWACO SOP 1006. The total daily volumes of drilling fluids and drill cuttings will be recorded and reported in the End of Well Report, and total volume discharge per calendar day will be recorded daily and reported monthly in the Discharge Monitoring Report (DMR).

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

- Perform and document visible sheen tests in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 3005.
- Collect samples and document results for static sheen tests in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 3004. As soon as practicable, perform static sheen analysis.
- Document the quantity of any chemical additive used.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following sampling tasks on a weekly basis:

- Collect and document a water-based drilling fluids and cuttings sample SPP toxicity in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006, 2001, and 2002. Immediately transfer the SPP toxicity sample to the sample refrigerator for storage awaiting packaging for transportation to the fixed analytical laboratory. Package samples for transport to the fixed analytical laboratory in accordance with procedures outlined in this QAPP and M-I SWACO SOP 2003. Retain one SPP toxicity sample container in the sample refrigerator until acceptable results are received for the sample transported to the fixed analytical laboratory. If problems occur with the original SPP toxicity sample transported to the fixed analytical laboratory that will invalidate the results, package and transport the remaining sample to the fixed analytical laboratory for analysis.

Once per well, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following sampling tasks:

- Collect and document samples for pH analysis in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 2012. Immediately deliver pH samples to the rig compliance laboratory for analysis.
- Collect and document a water-based drilling fluid sample for TAH and TAqH in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006, 2001, and 2008. Immediately transfer the samples to the sample refrigerator for storage awaiting packaging for transportation to the fixed analytical laboratory. Package samples for transport to the fixed analytical laboratory in accordance with procedures outlined in this QAPP and M-I SWACO SOP 2003. Samples must be collected at the same time as the SPP toxicity sample, to the extent practical (see end of well tasks below).
- When total depth of the well (end of well) has been reached or static sheen test fails, the M-I SWACO NPDES Compliance Specialist will collect and document a water-based drilling fluid sample for diesel oil (fingerprint) analysis in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006, 2001, and 2008. Immediately transfer the samples to the sample refrigerator for storage awaiting packaging for transportation to the fixed analytical laboratory. Package samples for transport to the fixed analytical laboratory in accordance with procedures outlined in this QAPP and M-I SWACO SOP 2003.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

- When total depth of the well (end of well) has been reached, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks: Collect and document a water-based drilling fluids and cuttings sample for SPP toxicity in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006, 2001, and 2002. Immediately transfer the sample to the sample refrigerator for storage awaiting packaging for transportation to the fixed analytical laboratory. Package samples for transport to the fixed analytical laboratory in accordance with procedures outlined in this QAPP and M-I SWACO SOP 2003. Retain one SPP toxicity sample container in the sample refrigerator until acceptable results are received for the sample transported to the fixed analytical laboratory. If problems occur with the original SPP toxicity sample transported to the fixed analytical laboratory that will invalidate the results, package and transport the remaining sample to the fixed analytical laboratory for analysis.
- In support of the EMP, two samples of water-based drilling fluids and two samples of drill cuttings will be collected during drilling of the largest casing interval (after the blowout preventer (BOP) is set), and two samples of used water-based drilling fluids will be collected during bulk-mud discharge (if applicable), in Phase II of the monitoring program for a total of six samples (Table 3-4). Drilling-mud compositions and monitoring records will be obtained from Transocean to the degree possible. The drilling phases targeted for this sampling include 1.) drilling the largest casing interval after the BOP is set; and 2.) bulk-mud discharges (if this occurs). The water-based drilling fluids and drill cuttings will be collected in clean glass jars, and sample handling and analysis will be performed in accordance with Section 3.0. Samples will be analyzed for the metals identified in Table A of the GP and for hydrocarbons (specific suite of analytes and individual analytes reported in Section 3.0).
- As required by Section II.A.13.j.1 of the GP, samples will be collected for the analysis of each drilling fluids system for the metals identified in Table A of the GP. A sample will be collected from each drilling fluids system at the three casing intervals of the lower hole section as described in the Drilling Fluid Plan and in accordance with Section 3.4.1.5. Samples of the drilling fluids system must be collected when the metals concentrations are projected to be at their maximum value for each applicable system. Samples of water-based drilling fluids will be collected in clean glass jars, and sample handling and analysis will be performed in accordance with Section 3.0.

Table 2-9 summarizes the drilling fluid and effluent monitoring tasks and frequencies, and Table 2-10 summarizes the analytical samples that will be collected for Discharge 001, Water-Based Drilling Fluids and Drill Cuttings.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 2-9 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 001

Frequency	Task	M-I SWACO SOP
Daily	Document discharge flows and waste volumes	1006
	Visual sheen tests	1006, 3005
	Static sheen tests	1006, 2001, 3004
Prior to drilling	Stock barite metals certificate of analysis	1006
Weekly	SPP toxicity sample	1006, 2001, 2002, 2003, Section 2.4.3
Once per well	pH samples of drilling fluid	1006, 2001, 2012
	TAH/TAqH samples of drilling fluid	1006, 2001, 2003, 2008
End of well	SPP toxicity sample	1006, 2001, 2002, 2003, Section 2.4.3
	Diesel fingerprint sample of aqueous drilling fluid	1006, 2001, 2003, 2008
During discharge	Daily volume measurements and flow rate estimates for discharge of water-based drilling fluids/drill cuttings	1006

Notes:

HSE = Health, Safety, and Environment
SOP = standard operating procedure
SPP = suspended particulate phase
TAH = total aromatic hydrocarbons
TAqH = total aqueous hydrocarbons

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

This page intentionally left blank

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 2-10 Analytical Sampling for Water-Based Drilling Fluids and Drill Cuttings (Discharge 001)

Type of sample	Matrix	Parameter	Analytical Method	Permit Limit/ Water Quality Standard	Required Volume	Sample Container	Preservative	Holding Time	Sampling Frequency
Mud & cuttings from shale shakers	Aqueous	Suspended particulate phase (SPP) toxicity	40 CFR 435, App. 2 to Subpart A (E1619)	96-hr LC_{50} > 30,000 ppm	1 L	(1) 1-gal (4L) LDPE jar	0 to 4°C	90 days	Weekly and End of well
		TAH/TAqH[1]	E624	Report (µg/L)	40 mL	(3) 40-mL VOA vials w/TLS	Cool <6°C, HCl to pH<2	14 days	Once per well
			E625 SIM	Report (µg/L)	1 L	(2) 1-L amber glass jars w/TLC	Cool <6°C	7 days to extraction, 40 days to analysis	
	Aqueous	Diesel fingerprint	SW8015C	No discharge	10 mL	(2) 40-mL VOA vials w/TLS	Cool <6°C	7 days to extraction, 40 days to analysis	End of well, or if static sheen test fails
	Oil				10 mL	(2) 40-mL VOA vials w/TLS			

Notes:

All samples will be collected as grab samples.
[1] Sample must be collected at the same time as the SPP toxicity test, to the extent practicable, and at the end of well.
µg/L = micrograms per liter
mg/kg = milligrams per kilogram
mL = milliliter
L = liter
HCl = hydrochloric acid
LDPE = low-density polyethylene
VOA = volatile organic analysis
OWS = oil/water separator
SPP = suspended particulate phase
TAH = total aromatic hydrocarbons
TAqH = total aqueous hydrocarbons
TLC = Teflon-lined cap
TLS = Teflon-lined septa

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

This page intentionally left blank

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.4.3.3 Compliance Sampling for Deck Drainage (Discharge 002)

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a monthly basis:

- Collect samples and document samples for pH analysis in accordance with QAPP procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 2012. As soon as practicable, transport pH samples to the rig compliance laboratory for analysis.

The M-I SWACO NPDES Compliance Specialist is responsible for performing the following sampling tasks four times per well:

- Four times per well, at intervals designated to be representative of the discharge's toxicity, a sample will be collected for initial toxicity screening. Each sample will be collected at a time period selected to reflect discharge processes and operational processes. Collect and document initial toxicity screening samples in accordance with the procedures outlined in Section 2.4.3.1 of this QAPP.
- WET testing will be required if either of the following occurs: 1) Initial rapid toxicity screening threshold criteria are exceeded OR 2) discharge exceeds 10,000 gallons during any 24-hr period and chemicals are added to the system. If WET testing is required, collect and document three samples from the OWS effluent on an every-other-day basis in accordance with the procedures outlined in Section 2.4.3.1 of this QAPP. Immediately transfer the samples to the sample refrigerator for storage awaiting packaging for transportation to the fixed analytical laboratory. Package samples for transport to the fixed analytical laboratory in accordance with procedures outlined in this QAPP and M-I SWACO SOP 2003.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks once per discharge event (if conducted continuously):

- Collect and document samples from the OWS effluent for TAH and TAqH in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006, 2001, and 2008. Immediately transfer the samples to the sample refrigerator for storage awaiting packaging for transportation to the fixed analytical laboratory. Package samples for transport to the fixed analytical laboratory in accordance with procedures outlined in this QAPP and M-I SWACO SOP 2003.
- Document the quantity of any chemical additive used.
- Perform and document visible sheen test in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 3005.
- Document the flow volumes from the OWS effluent flow meter in accordance with procedures outlined in this QAPP and M-I SWACO SOP 1006. Additionally, the volume discharged directly overboard will be estimated and recorded. The total volume in gallons will be reported monthly.
- Collect samples for static sheen tests from OWS effluent and document results in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 3004. Immediately deliver samples to the rig compliance laboratory for analysis.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 2-11 summarizes the effluent monitoring tasks and frequencies, and Table 2-12 summarizes the analytical samples that will be collected for Discharge 002, Deck Drainage.

Table 2-11 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 002

Frequency	Task	M-I SWACO (or Misc.) SOP
Once per discharge event (if conducted continuously)	Document discharge flow volumes	1006
	TAH/TAqH samples of deck drainage	1006, 2001, 2003, 2008
	Visual sheen test	1006, 3005
	Static sheen test	1006, 2001, 3004
Monthly	pH sample	1006, 2001, 2012
Four times per well	Initial effluent toxicity screening	1006, 2001, ENV001, TOX045
	WET testing (if any initial toxicity screening exceeds threshold criteria)	1006, 2001, Section 2.4.3, TOX002, TOX012, TOX014B, TOX043
Once per well	WET testing (if discharge exceeds 10,000 gallons during any 24-hour period and if chemicals are added to the system)	1006, 2001, Section 2.4.3, TOX002, TOX012, TOX014B, TOX043

Notes:

SOP = standard operating procedure
TAH = total aromatic hydrocarbons
TAqH = total aqueous hydrocarbons
WET = whole effluent toxicity

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 2-12 Analytical Sampling for Deck Drainage (Discharge 002)

Type of sample	Matrix	Parameter	Analytical Method	Effluent Limit/ Water Quality Standard	Required Volume	Sample Container	Preservative	Holding Time	Sampling Frequency
OWS Effluent	Aqueous	TAH/TAqH	E624	Report (µg/L)	40 mL	(3) 40-mL VOA vials w/TLS	Cool <6°C, HCl to pH<2	14 days	Once per discharge event (if conducted continuously)
			E625 SIM	Report (µg/L)	1 L	(2) 1-L amber glass jars w/TLC	Cool <6°C	7 days to extraction, 40 days to analysis	
		Initial toxicity screening	EPA/600/R-95-136 (TOX045)	Report – Test is statistically significantly different from control AND there is >25% decline in fertilization relative to control	2-L	(1) 2-L HDPE bottle	0 to 4°C	90 days	Four times per well
		WET[2]	EPA/600/R-95-136 (Topsmelt Chronic 7d Survival and Growth Test)[1] or EPA/821-R-02-014 (Menidia Chronic 7d Survival and Growth Test)[1]	Report	45-L + renewal samples (see Section 2.4.3.1)	(2) 20-L and (1) 10-L LDPE cubitainers	Cool <6°C	36 hours (Max 72 hrs) and requiring justification for holding time if >36 hours	Upon failure of toxicity screening criteria, OR Once per well if discharge exceeds 10,000 gal and chemicals are added to the system
			EPA/821-R-02-014 (Mysid Chronic 7d Survival, Growth, and Fecundity Test)[1]						
			EPA/600/R-95-136 (Echinoderm Larval Development Test)						

Notes:

All samples collected as grab samples.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Notes (continued):
[1] Samples for these tests should be provided as one, 10-L sample on an every-other-day basis. If this sample strategy is not feasible, a single sample of 30 L may be provided at one time.
[2] Samples for WET testing may be collected in larger containers (up to 20-L LDPE cubitainers or different combination thereof) to facilitate sufficient volume to conduct all three tests.
µg/L = micrograms per liter
mL = milliliter
L = liter
WET = whole effluent toxicity
EPA = U.S. Environmental Protection Agency
HCl = hydrochloric acid
LDPE = low-density polyethylene
OWS = oil/water separator
TAH = total aromatic hydrocarbons
TAqH = total aqueous hydrocarbons
TLC = Teflon-lined cap
TLS = Teflon-lined septa
VOA = volatile organic analysis

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.4.3.4 Compliance Sampling for Sanitary Wastes (Discharge 003)

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a daily basis:

- Document the sanitary waste flow volume from the effluent flow meter in accordance with procedures outlined in this QAPP and M-I SWACO SOP 1006.
- Document the quantity of any chemical additive used.
- Perform and document visual assessments for floating solids, sheen, debris, sludge, foam, deposits, scum, or other residues from discharges of sanitary wastes in accordance with this QAPP and M-I SWACO SOP 1006.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a weekly basis:

- Collect and document treated sanitary waste samples for pH, BOD_5, TSS, fecal coliform (FC) bacteria, and total residual chlorine (if used as disinfectant) in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006, 2001, 2010, 2011, 2012, 2013, and 2014. Immediately deliver pH and total residual chlorine samples to the rig compliance laboratory for analysis. Immediately transfer BOD_5, TSS, and FC samples to the sample refrigerator for storage awaiting packaging for transportation to the Barrow mobile laboratory. Package samples for transport to the Barrow mobile laboratory in accordance with procedures outlined in this QAPP and M-I SWACO SOP 2003.

Table 2-13 summarizes the effluent monitoring tasks and frequencies, and Table 2-14 summarizes the analytical samples that will be collected for Discharge 003, Sanitary Wastes.

Table 2-13 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 003

Frequency	Task	M-I SWACO SOP
Daily	Document discharge flows and waste volumes	1006
	Visual assessments of receiving waters	1006, 3005
	Visual sheen tests	1006, 3005
Weekly	pH sample	1006, 2001, 2012
	BOD_5, TSS, Total residual chlorine samples	1006, 2001, 2003, 2010, 2013, 2014
	Fecal coliform bacteria sample	1006, 2001, 2003, 2011

Notes:

BOD_5 = 5-day biochemical oxygen demand
SOP = standard operating procedure
TSS = total suspended solids
WET = whole effluent toxicity

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 2-14 Analytical Sampling for Sanitary Wastes (Discharge 003)

Type of sample	Matrix	Parameter	Preparation and Analysis Method	Effluent Limit/ Water Quality Standard	Required Volume	Sample Container	Preservative	Holding Time	Sampling Frequency
Treatment System Effluent	Aqueous	BOD_5	SM5210-B	30 mg/L (Monthly average); 60 mg/L (Daily limit)	1 L	(1) 1-L poly bottle	Cool <6°C	48 hours	Weekly
		TSS	SM2540-D	30 mg/L (Monthly average); 60 mg/L (Daily limit)	1 L	(1) 1-L poly bottle	Cool <6°C	7 days	
		Fecal coliform bacteria	SM9222-D	100 colonies/100 mL (Monthly average); 200 colonies/100 mL (Daily Limit)	100 mL	(1) 125-mL sterile poly container w/ $Na_2S_2O_3$	Cool <6°C, Na_2SO_3	8 hours	

Notes:

All samples will be collected as grab samples.
L = liter
mg/L = milligrams per liter
mL = milliliter
BOD_5 = 5-day biochemical oxygen demand
$Na_2S_2O_3$ = sodium thiosulfate
TSS = total suspended solids

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.4.3.5 Compliance Sampling for Domestic Wastes (Discharge 004)

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a daily basis:

- Document the domestic waste flow volume in accordance with procedures outlined in this QAPP and M-I SWACO SOP 1006.
- Document the quantity of any chemical additive used.
- Perform and document visual assessments for floating solids, garbage, or foam from discharges of domestic wastes in accordance with QAPP Section 3.0 and M-I SWACO SOP 1006.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a monthly basis:

- Collect and document samples for pH analysis in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 2012. Immediately deliver pH samples to the rig compliance laboratory for analysis.

Table 2-15 summarizes the effluent monitoring tasks and frequencies for Discharge 004, Domestic Wastes.

Table 2-15 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 004

Frequency	Task	M-I SWACO SOP
Daily	Document discharge flows and waste volumes	1006
	Visual assessments of receiving waters	1006, 3005
Weekly	pH sample	1006, 2001, 2012

Notes:
SOP = standard operating procedure

2.4.3.6 Compliance Sampling for Desalination Unit Wastes (Discharge 005)

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a daily basis:

- Document the estimated flow volume in accordance with procedures outlined in this QAPP and M-I SWACO SOP 1006.
- Document the quantity of any chemical additive used.

The M-I SWACO NPDES Compliance Specialist is responsible for performing the following sampling tasks four times per well:

- Four times per well, at intervals designated to be representative of the discharge's toxicity, a sample will be collected for initial toxicity screening. Each sample will be collected at a time period selected to reflect discharge processes and operational processes. Collect and document initial toxicity screening samples in accordance with the procedures outlined in Section 2.4.3.1 of this QAPP.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

- WET testing will be required if either of the following occurs: 1) Initial rapid toxicity screening threshold criteria are exceeded OR 2) discharge exceeds 10,000 gallons during any 24-hr period and chemicals are added to the system. If WET testing is required, collect and document samples in accordance with the procedures outlined in Section 2.4.3.1 of this QAPP. Immediately transfer the samples to the sample refrigerator for storage awaiting packaging for transportation to the fixed analytical laboratory. Package samples for transport to the fixed analytical laboratory in accordance with procedures outlined in this QAPP and M-I SWACO SOP 2003.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks per discharge event (if conducted continuously):

- Perform and document visual sheen tests in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 3005.
- If visual sheen tests cannot be performed, collect and document samples for static sheen tests in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 3004.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a monthly basis:

- Collect and document samples for pH analysis in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 2012. As soon as practicable, deliver pH samples to the rig compliance laboratory for analysis.

Table 2-16 summarizes the effluent monitoring tasks and frequencies for Discharge 005, Desalination Unit Wastes.

Table 2-16 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 005

Frequency	Task	M-I SWACO (or Misc.) SOP
Daily	Document discharge flows and waste volumes	1006
Four times per well	Initial effluent toxicity screening	1006, 2001, ENV001, TOX045
	WET testing (if any initial toxicity screening exceeds threshold criteria)	1006, 2001, Section 2.4.3, TOX002, TOX012, TOX014B, TOX043
Once per well	WET testing (if discharge exceeds 10,000 gallons during any 24-hour period and if chemicals are added to the system)	1006, 2001, TOX002, TOX012, TOX014B, TOX043
Monthly	pH sample	1006, 2001, 2012
Discharge event	Visual sheen test	1006, 2001, 2003, 2008
	Static sheen test (if required)	1006, 2001, 3004

Notes:

SOP = standard operating procedure
WET = whole effluent toxicity

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.4.3.7 Compliance Sampling for Blowout Preventer Fluid (Discharge 006)

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a daily basis:

- Document the estimated flow volume in accordance with procedures outlined in this QAPP and M-I SWACO SOP 1006.
- Document the quantity of any chemical additive used.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks per discharge event (if conducted continuously):

- Perform and document visual sheen tests in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 3005.
- If visual sheen tests cannot be performed, collect and document samples for static sheen tests in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 3004.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a monthly basis:

- Collect and document samples for pH analysis in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 2012. As soon as practicable, deliver pH samples to the rig compliance laboratory for analysis.

Table 2-17 summarizes the effluent monitoring tasks and frequencies for Discharge 006, Blowout Preventer Fluid.

Table 2-17 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 006

Frequency	Task	M-I SWACO SOP
Daily	Document discharge flows and waste volumes	1006
Monthly	pH sample	1006, 2001, 2012
Discharge event	Visual sheen test	1006, 2001, 2003, 2008
	Static sheen test (if required)	1006, 2001, 3004

Notes:
SOP = standard operating procedure

2.4.3.8 Compliance Sampling for Boiler Blowdown (Discharge 007)

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a daily basis:

- Document the estimated flow volume in accordance with procedures outlined in this QAPP and M-I SWACO SOP 1006.
- Document the quantity of any chemical additive used.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

The M-I SWACO NPDES Compliance Specialist is responsible for performing the following sampling tasks four times per well:

- If possible four times per well, at intervals designated to be representative of the discharge's toxicity, a sample will be collected for initial toxicity screening. Each sample will be collected at a time period selected to reflect discharge processes and operational processes. Collect and document initial toxicity screening samples in accordance with the procedures outlined in Section 2.4.3.1 of this QAPP. Due to the infrequency of discharge and limited volume of water produced, it is unlikely that this screening will be able to be performed four times per well.
- WET testing will be required if either of the following occurs: 1) Initial rapid toxicity screening threshold criteria are exceeded OR 2) discharge exceeds 10,000 gallons during any 24-hr period and chemicals are added to the system. If WET testing is required, collect and document samples in accordance with the procedures outlined in Section 2.4.3.1 of this QAPP. Immediately transfer the samples to the sample refrigerator for storage awaiting packaging for transportation to the fixed analytical laboratory. Package samples for transport to the fixed analytical laboratory in accordance with procedures outlined in this QAPP and M-I SWACO SOP 2003.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks per discharge event (if conducted continuously):

- Perform and document visual sheen tests in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 3005.
- If visual sheen tests cannot be performed, collect and document samples for static sheen tests in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 3004.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a monthly basis:

- Collect and document samples for pH analysis in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 2012. As soon as practicable, deliver pH samples to the rig compliance laboratory for analysis.

Table 2-18 summarizes the effluent monitoring tasks and frequencies for Discharge 007, Boiler Blowdown.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 2-18 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 007

Frequency	Task	M-I SWACO (or Misc.) SOP
Daily	Document discharge flows and waste volumes	1006
Four times per well	Initial effluent toxicity screening	1006, 2001, ENV001, TOX045
	WET testing (if any initial toxicity screening exceeds threshold criteria)	1006, 2001, Section 2.4.3, TOX002, TOX012, TOX014B, TOX043
Once per well	WET testing (if discharge exceeds 10,000 gallons during any 24-hour period and if chemicals are added to the system)	1006, 2001, TOX002, TOX012, TOX014B, TOX043
Monthly	pH sample	1006, 2001, 2012
Discharge event	Visual sheen test	1006, 2001, 2003, 2008
	Static sheen test (if required)	1006, 2001, 3004

Notes:
SOP = standard operating procedure
WET = whole effluent toxicity

2.4.3.9 Compliance Sampling for Fire Control System Test Water (Discharge 008)

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a daily basis:

- Estimate flow volume in accordance with procedures outlined in this QAPP and M-I SWACO SOP 1006.
- Document the quantity of any chemical additive.

The M-I SWACO NPDES Compliance Specialist is responsible for performing the following sampling tasks four times per well:

- Four times per well, at intervals designated to be representative of the discharge's toxicity, a sample will be collected for initial toxicity screening. Each sample will be collected at a time period selected to reflect discharge processes and operational processes. Collect and document initial toxicity screening samples in accordance with the procedures outlined in Section 2.4.3.1 of this QAPP.
- WET testing will be required if either of the following occurs: 1) Initial rapid toxicity screening threshold criteria are exceeded OR 2) discharge exceeds 10,000 gallons during any 24-hr period and chemicals are added to the system. If WET testing is required, collect and document samples in accordance with the procedures outlined in Section 2.4.3.1 of this QAPP. Immediately transfer the samples to the sample refrigerator for storage awaiting packaging for transportation to the fixed analytical laboratory. Package samples for transport to the fixed analytical laboratory in accordance with procedures outlined in this QAPP and M-I SWACO SOP 2003.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks per discharge event (if conducted continuously):

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

- Perform and document visual sheen tests in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 3005.
- If visual sheen tests cannot be performed, collect and document samples for static sheen tests in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 3004.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a monthly basis:

- Collect and document samples for pH analysis in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 2012. Immediately deliver pH samples to the rig compliance laboratory for analysis.

Table 2-19 summarizes the effluent monitoring tasks and frequencies for Discharge 008, Fire Control System Test Water.

Table 2-19 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 008

Frequency	Task	M-I SWACO (or Misc.) SOP
Daily	Document discharge flows and waste volumes	1006
Four times per well	Initial effluent toxicity screening	1006, 2001, ENV001, TOX045
	WET testing (if any initial toxicity screening exceeds threshold criteria)	1006, 2001, Section 2.4.3, TOX002, TOX012, TOX014B, TOX043
Once per well	WET testing (if discharge exceeds 10,000 gallons during any 24-hour period and if chemicals are added to the system)	1006, 2001, TOX002, TOX012, TOX014B, TOX043
Monthly	pH sample	1006, 2001, 2012
Discharge event	Visual sheen test	1006, 2001, 2003, 2008
	Static sheen test (if required)	1006, 2001, 3004

Notes:
SOP = standard operating procedure
WET = whole effluent toxicity

2.4.3.10 Compliance Sampling for Non-contact Cooling Water (Discharge 009)

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a daily basis for each of the non-contact cooling water discharges:

- Document the flow volume from the effluent flow meters in accordance with procedures outlined in this QAPP and M-I SWACO SOP 1006.
- Perform and document visual sheen tests for each outfall in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 3005.
- Temperature will be monitored continuously and documented for non-contact cooling water (009) in accordance with procedures outlined in this QAPP and M-I SWACO LWI-001.
- Document the quantity of any chemical additive used.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

The M-I SWACO NPDES Compliance Specialist is responsible for performing the following sampling tasks four times per well:

- Four times per well, at intervals designated to be representative of the discharge's toxicity, a sample will be collected for initial toxicity screening. Each sample will be collected at a time period selected to reflect discharge processes and operational processes. Collect and document initial toxicity screening samples in accordance with the procedures outlined in Section 2.4.3.1 of this QAPP.
- WET testing will be required if either of the following occurs: 1) Initial rapid toxicity screening threshold criteria are exceeded OR 2) discharge exceeds 10,000 gallons during any 24-hr period and chemicals are added to the system. If WET testing is required, collect and document three samples from the OWS effluent on an every-other-day basis in accordance with the procedures outlined in Section 2.4.3.1 of this QAPP. Immediately transfer the samples to the sample refrigerator for storage awaiting packaging for transportation to the fixed analytical laboratory. Package samples for transport to the fixed analytical laboratory in accordance with procedures outlined in this QAPP and M-I SWACO SOP 2003.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a monthly basis:

- Collect and document samples for pH analysis in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 2012. As soon as practicable, deliver pH samples to the rig compliance laboratory for analysis.

Table 2-20 summarizes the effluent monitoring tasks and frequencies for Discharge 009, Non-contact Cooling Water.

Table 2-20 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 009

Frequency	Task	M-I SWACO (or Misc.) SOP
Daily	Document discharge flows and waste volumes	1006
	Visual sheen tests	1006, 3005
	Temperature monitoring of non-contact cooling water	1006, LWI-001
Four times per well	Initial effluent toxicity screening	1006, 2001, ENV001, TOX045
	WET testing (if any initial toxicity screening exceeds threshold criteria)	1006, 2001, Section 2.4.3, TOX002, TOX012, TOX014B, TOX043
Once per well	WET testing (if discharge exceeds 10,000 gallons during any 24-hour period and if chemicals are added to the system)	1006, 2001, TOX002, TOX012, TOX014B, TOX043
Monthly	pH sample	1006, 2001, 2012

Notes:

SOP = standard operating procedure
WET = whole effluent toxicity

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.4.3.11 Compliance Sampling for Uncontaminated Ballast Water (Discharge 010)

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a daily basis:

- Document the estimated flow volume in accordance with procedures outlined in this QAPP and M-I SWACO SOP 1006.
- Document the quantity of any chemical additive used.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks per discharge event (if conducted continuously):

- Perform and document visual sheen tests in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 3005.
- If visual sheen tests cannot be performed, collect and document samples for static sheen tests in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 3004.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a monthly basis:

- Collect and document samples for pH analysis in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 2012. As soon as practicable, deliver pH samples to the rig compliance laboratory for analysis.

Table 2-21 summarizes the effluent monitoring tasks and frequencies for Discharge 010, Uncontaminated Ballast Water.

Table 2-21 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 010

Frequency	Task	M-I SWACO SOP
Daily	Document discharge flows and waste volumes	1006
Monthly	pH sample	1006, 2001, 2012
Discharge event	Visual sheen test	1006, 2001, 2003, 2008
	Static sheen test (if required)	1006, 2001, 3004

Notes:

SOP = standard operating procedure
WET = whole effluent toxicity

2.4.3.12 Compliance Sampling for Bilge Water (Discharge 011)

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a daily basis:

- Document the flow volume for discharges from the effluent flow meters in accordance with procedures outlined in this QAPP and M-I SWACO SOP 1006.
- Document the quantity of any chemical additive used.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

The M-I SWACO NPDES Compliance Specialist is responsible for performing the following sampling tasks four times per well:

- Four times per well, at intervals designated to be representative of the discharge's toxicity, a sample will be collected for initial toxicity screening. Each sample will be collected at a time period selected to reflect discharge processes and operational processes. Collect and document initial toxicity screening samples in accordance with the procedures outlined in Section 2.4.3.1 of this QAPP.
- WET testing will be required if either of the following occurs: 1) Initial rapid toxicity screening threshold criteria are exceeded OR 2) discharge exceeds 10,000 gallons during any 24-hr period and chemicals are added to the system. If WET testing is required, collect and document samples in accordance with the procedures outlined in Section 2.4.3.1 of this QAPP. Immediately transfer the samples to the sample refrigerator for storage awaiting packaging for transportation to the analytical laboratory. Package samples for transport to the analytical laboratory in accordance with procedures outlined in this QAPP and M-I SWACO SOP 2003.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks per discharge event (if conducted continuously):

- Collect and document a sample for static sheen test for discharge of bilge water (011) that has been processed through the OWS in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 3004.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a monthly basis:

- Collect and document samples for pH analysis in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 2012. As soon as practicable, deliver pH samples to the rig compliance laboratory for analysis.

Table 2-22 summarizes the effluent monitoring tasks and frequencies for Discharge 011, Bilge Water.

Table 2-22 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 011

Frequency	Task	M-I SWACO (or Misc.) SOP
Daily	Document discharge flows and waste volumes	1006
	Visual sheen tests	1006, 3005
Four times per well	Initial effluent toxicity screening	1006, 2001, ENV001, TOX045
	WET testing (if any initial toxicity screening exceeds threshold criteria)	1006, 2001, Section 2.4.3, TOX002, TOX012, TOX014B, TOX043
Once per well	WET testing (if discharge exceeds 10,000 gallons during any 24-hour period and if chemicals are added to the system)	1006, 2001, TOX002, TOX012, TOX014B, TOX043
Monthly	pH sample	1006, 2001, 2012
Discharge event	Static sheen test	1006, 2001, 3004

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Notes:
SOP = standard operating procedure
WET = whole effluent toxicity

2.4.3.13 Compliance Sampling for Excess Cement Slurry (Discharge 012)

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a daily basis:

- Document the estimated flow volume in accordance with procedures outlined in this QAPP and M-I SWACO SOP 1006.
- Document the quantity of any chemical additive.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks per discharge event (if conducted continuously):

- Perform and document visual sheen tests in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 3005.

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a monthly basis:

- Collect and document samples for pH analysis in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 2012. As soon as practicable, deliver pH samples to the rig compliance laboratory for analysis.

Table 2-23 summarizes the effluent monitoring tasks and frequencies for Discharge 012, Excess Cement Slurry.

Table 2-23 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 012

Frequency	Task	M-I SWACO SOP
Daily	Document discharge flows and waste volumes	1006
Monthly	pH sample	1006, 2001, 2012
Discharge event	Visual sheen test	1006, 2001, 3004

Notes:
SOP = standard operating procedure

2.4.3.14 Compliance Sampling for Muds, Cuttings, and Cement at the Seafloor (Discharge 013)

During active drilling operations, the M-I SWACO NPDES Compliance Specialist is responsible for performing the following tasks on a daily basis:

- Document the estimated flow volume in accordance with procedures outlined in this QAPP and M-I SWACO SOP 1006.
- Perform and document visual sheen tests for each outfall in accordance with procedures outlined in this QAPP and M-I SWACO SOPs 1006 and 3005.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 2-24 summarizes the effluent monitoring tasks and frequencies for Discharge 013, Muds, Cuttings, and Cement at the Seafloor.

Table 2-24 Summary of Compliance Sampling, Measurement, and Observation Frequencies for Discharge 013

Frequency	Task	M-I SWACO SOP
Daily	Document discharge flows and waste volumes	1006
	Visual sheen tests	1006, 3005

Notes:
SOP = standard operating procedure

2.4.4 Field SOPs

The SOPs and LWIs are formal, revision-controlled documents that:

- Define the methods used in the performance of tasks having an effect on the quality of data, findings, or conclusions;
- Provide standard methods for execution and documentation of work, so as to maximize uniformity and reliability of products; and
- Facilitate coordination among individuals performing separate but interdependent tasks. SOPs and/or LWIs are generated through a cooperative effort among operations and QA personnel.

QA personnel coordinate their development, which involves an iterative process of review and revision until they are satisfactory to both QA and the technical reviewers.

2.4.4.1 M-I SWACO SOP and LWI Revisions

As a SOP or LWI is revised, the revision number is incremented and the revised SOP released to the distribution list. SOP and LWI revisions shall be processed through the M-I SWACO NPDES Compliance Supervisor or appropriate QA staff. SOP revisions may be necessitated by regulatory requirements, technological advancements, or other causes.

Dated acceptance signatures signify approval of the revisions. One technical reviewer and the M-I SWACO NPDES Compliance Supervisor or designee shall approve revisions of SOPs and LWIs. Once formally accepted, the revised document replaces the previous version and is distributed to SOP holders with instructions as to which document(s) it replaces.

The M-I SWACO NPDES Compliance Supervisor distributes SOPs and LWIs to technical staff and maintains distribution lists to confirm revisions. New SOPs and LWIs are distributed to responsible individuals.

2.4.4.2 Sampling SOPs and LWIs

Sampling SOPs and LWIs shall be developed, approved, and distributed to M-I SWACO NPDES Compliance Specialists. The SOP and/or LWI shall address, as applicable, the following elements:

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

- The objectives of the GP;
- A description of the overall sampling scheme (see below);
- The number and location of sampling points;
- The number and location of control samples;
- Requirements for QC samples such as blanks, duplicates/replicates, matrix spikes, etc;
- The analyses to be performed (physical, chemical, toxicological, biological);
- The number and size (weight or volume) of samples to be collected for each type of analysis;
- Sample collection methods, specifying sampling equipment or SOPs, where applicable;
- Field screening procedures and criteria; and
- Sample containerization, preservation, and transportation procedures.

The M-I SWACO NPDES Compliance Specialists and subcontract laboratories shall be notified of sampling program schedules in advance, so that personnel and physical resources can be scheduled to meet sample holding time limitations and other GP requirements.

M-I SWACO operational discharge sampling-related SOPs and LWIs are listed in Table 2-25. The SOPs and LWIs listed in these tables are also included in Appendix A to this QAPP.

2.4.5 Analytical SOPs

Environ effluent toxicity testing SOPs are listed in Table 2-26 and included in Appendix A to this QAPP. Analytical SOPs for additional methods performed by subcontract laboratories are available upon request.

Table 2-25 Operational Discharge Compliance Sampling Related SOPs

M-I SWACO SOP Number	M-I SWACO SOP Title
1001	Qualification and Documentation of Computer Programs
1002	Traceability of Reagents, Standards, and Reference Materials
1003	Equipment Tracking
1004	Balance Calibration
1005	Laboratory Refrigerators
1006	Field Logs
1008	Demonstration of Capability
2001	Chain-of-Custody (C-O-C) Procedures
2002	Sample Collection for Suspended Particulate Phase (SPP) Toxicity Test
2003	Packaging and Shipment of Samples
2004	Decontamination of Equipment
2008	Sample Collection for TAH and TAqH Analyses
2010	Sample Collection for Biochemical Oxygen Demand (BOD_5) Analysis

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2011	Sample Collection for Fecal Coliform Analysis
2012	Field Measurement of pH
2013	Field Measurement of Total Residual Chlorine
2014	Sample Collection for Total Suspended Solids (TSS) Analysis
3004	Free Oil by Static Sheen Method
3005	Visual Sheen Test Method
LWI-001	Continuous Temperature Monitoring
LWI-002	Chemical Inventory Management

Notes:

BOD_5 = biochemical oxygen demand
SOP = standard operating procedure
SPP = suspended particulate phase
TAH = total aromatic hydrocarbons
TAqH = total aqueous hydrocarbons
TSS = total suspended solid

Table 2-26 Drilling Fluid and Effluent Toxicity Testing SOPs

Environ SOP Number	Environ SOP Title
TOX002	7-Day Chronic Toxicity Study with *Atherinops affinis*
TOX012	7-Day Chronic Toxicity Study with *Menidia beryllina*
TOX014B	7-Day Chronic Toxicity Study with *Americamysis bahia* – Survival, Growth, and Fecundity
TOX043	Chronic Toxicity Test Using Echinoderm Larvae *(Strongylocentrotus purpuratus or Dendraster excentricus)*
TOX045	Chronic Toxicity Fertilization Test Using Echinoderms *(Strongylocentrotus purpuratus or Dendraster excentricus)*
ENV001	Chukchi Sea BES – Collection of Effluent Samples for Biological Testing

Notes:

SOP = standard operating procedure
SPP = suspended particulate phase

2.4.6 Sample Handling and Custody

2.4.6.1 Responsibilities

The M-I SWACO NPDES Compliance Supervisor, or designee, is responsible for verifying that a sampling SOP is prepared that conforms to the provisions of this chapter, while fulfilling GP objectives. The M-I SWACO NPDES Compliance Supervisor is responsible for assembling or ordering rig compliance laboratory sampling kits. Fixed subcontract laboratories are responsible for supplying sample containers for fixed laboratory analyses and Barrow mobile laboratory analyses. M-I SWACO NPDES Compliance Specialists are responsible for collecting the field and QC samples as described in this chapter and as required by the GP; and for adhering to the sample packaging, labeling, and documentation requirements of this chapter and associated SOPs. The M-I SWACO NPDES Compliance Specialist is responsible for collecting grab samples at a point representative of the discharge. The subcontract laboratory sample custodian is responsible for the proper inspection, login, and storage of incoming samples, as defined in the laboratory's SOPs.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.4.6.2 Sample Containers, Preservation, and Storage

In general, samples will be collected for rig compliance laboratory analysis, Barrow mobile laboratory analysis, and fixed subcontract laboratory analysis in containers as required by the analytical methods. Sample containers are provided by the laboratory and may be pre-cleaned and/or pre-preserved (if required by the analytical method).

The M-I SWACO NPDES Compliance Specialist will clean containers for static sheen and retort cuttings samples in the rig compliance laboratory following the procedures in SOP 2004 Decontamination of Equipment (Appendix A).

After collection, the samples are maintained at the required temperature (for most samples, 0 - 6°C) under CoC procedures until analysis or until they are shipped to a subcontract laboratory for analysis. For operational discharge compliance program samples, the samples should not be frozen. Procedures for packaging and shipping samples are outlined in M-I SWACO SOP 2003 Packaging and Shipment of Samples.

A summary of the analytical methods, sample containers, preservation, and holding times for samples that will be submitted to subcontract laboratories for analysis is included in Table 2-27.

Table 2-27 Sample Containers, Preservation, and Holding Times

Analyte/ Analyte Group	Method/SOP	Container(s) (number, size, & type per sample)	Preservation	Holding Time
OIL MATRIX				
Diesel fingerprint	SW8015C	(2) 40-mL VOA vials w/TLS	Cool <6°C	7 days to extraction, 40 days to analysis
AQUEOUS MATRIX				
TAH/TAqH[1]	E624	(3) 40-mL VOA vials w/TLS	Cool <6°C, HCl to pH<2	14 days
	E625 SIM	(2) 1-L amber glass jars w/TLC	Cool <6°C	7 days to extraction, 40 days to analysis
Diesel fingerprint	SW8015C	(2) 40-mL VOA vials w/TLS	Cool <6°C	7 days to extraction, 40 days to analysis
SPP toxicity	40 CFR 435, App. 2 to Subpart A (E1619)	(1) 1-gal (4L) LDPE jar	0 to 4°C	90 days
Initial toxicity screening	EPA/600/R-95-136 (Echinoderm Fertilization Test)	(1) 2-L HDPE bottle	Cool 0-6°C; not frozen	36 hours (72 hours maximum)
WET[2]	EPA/600/R-95-136 (Topsmelt Chronic 7d Survival and Growth Test)[1] or EPA/821-R-02-014 (Menidia Chronic 7d Survival and Growth Test)[1]	2) 20-L and (1) 10-L HDPE cubitainers	Cool 0-6°C; not frozen	36 hours (72 hours maximum)

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Analyte/ Analyte Group	Method/SOP	Container(s) (number, size, & type per sample)	Preservation	Holding Time
	EPA/821-R-02-014 (Mysid Chronic 7d Survival, Growth, and Fecundity Test)[1]			
	EPA/600/R-95-136 (Echinoderm Larval Development Test)			
BOD_5	SM5210-B	(1) 1-L poly bottle	Cool <6°C	48 hours
TSS	SM2540-D	(1) 1-L poly bottle	Cool <6°C	7 days
Fecal coliform bacteria	SM9222-D	(1) 125-mL sterile poly container w/ $Na_2S_2O_3$	Cool <6°C, Na_2SO_3	8 hours

Notes:

[1] Samples for these tests may be provided as one, 10-L sample on an every-other-day basis. If this sample strategy is not feasible, a single sample of 30 L may be provided at one time.

[2] Samples for WET testing may be collected in larger containers (up to 20-L LDPE cubitainers or different combination thereof) to facilitate sufficient volume to conduct all three tests.

BOD_5 = biochemical oxygen demand
HCl = hydrochloric acid
mL = milliliter
L = liter
$Na_2S_2O_3$ = sodium thiosulfate
SOP = standard operating procedure
SPP = suspended particulate phase
TAH = total aromatic hydrocarbons
TAqH = total aqueous hydrocarbons
TLC = Teflon-lined cap
TLS = Teflon-lined septa
TSS = total suspended solids
VOA = volatile organic analysis
WET = whole effluent toxicity

2.4.6.3 Sample Receipt

Sample receipt and CoC will be maintained at the fixed subcontract laboratories in accordance with the procedures outlined in Section 1.8 of this QAPP. Drilling and effluent samples for toxicity testing require additional procedures to verify acceptability upon receipt at the fixed laboratory.

Receipt of Drilling Fluid Samples for SPP Toxicity Analysis

Drilling fluid samples provided for biological testing must also meet the temperature requirements described above. The pH of the drilling fluid samples will be tested upon receipt at the laboratory. If the pH is less than 9, if black spots have appeared on the walls of the sample container, or if the mud sample has a foul odor, then the sample does not meet the method specific acceptability criteria for drilling fluids as specified in Appendix 2, Subpart A of 40 CFR Part 435. If the drilling fluid does not meet the acceptability criteria for testing, the client will be notified and the decision to proceed will be evaluated. The drilling fluid should be used for testing within three months from the time of collection. Elutriate samples prepared at the laboratory from the drilling fluids should be used for testing within the same day.

Receipt of Effluent Samples for Initial Toxicity Screening and WET Testing Samples

Upon receipt at the subcontract laboratory, water quality parameters are measured for effluent samples. These parameters include dissolved oxygen, temperature, pH, and salinity/conductivity. Acceptability criteria for water quality parameters are included in Section 2.6.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.4.6.4 Holding Times

Sample holding time begins with the collection of the sample and continues until the analysis is complete. Analytical method holding times are included in Table 2-27.

Testing for toxicity samples should be initiated on effluent samples within 36 hours of sample collection, but must not exceed 72 hours as prescribed in the GP and method guidance (does not apply to drilling fluid SPP toxicity testing). Effluent samples used for test solution renewals on the WET 7-day chronic tests (days 1-6) may be used up to 48-hours after the initial use (test initiation) and may be used for test solution renewals at up to 120 hours from the time of collection.

2.4.6.5 Sample Retention and Disposal

Procedures ensuring internal laboratory chain-of-custody shall also be implemented and documented by the subcontract laboratory. Samples shall be stored in limited-access, temperature-controlled areas. Samples will be retained and disposed of in accordance with laboratory procedures.

Samples will be retained under proper storage conditions in the rig compliance laboratory. Static sheen samples will be retained until the end of the holding time or until the M-I SWACO NPDES Compliance Specialist verifies the acceptability of the sample results. In the event the analytical sample result shows a permit exceedance, the sample will be retained until the permittee requests additional testing or provides permission for disposal. After expiration of the sample retention period, mud samples are returned to the active mud system and cuttings samples are placed in the cuttings disposal system.

2.4.6.6 Decontamination

Decontamination is essential for the avoidance of cross-contamination among samples. Reusable, non-dedicated sampling implement are decontaminated before use and after each sample is collected, in accordance with M-I SWACO SOP 2004 Decontamination of Equipment. Generally, sample equipment used to collect samples for GP compliance is dedicated equipment and requires minimal decontamination.

2.4.7 Field Instrument/Equipment Testing, Inspection, Calibration, and Maintenance

Effluent limitations in the GP involve measurements that shall be made directly in the field –for example, the Free Oil by Static Sheen Method (M-I SWACO SOP 3004). In addition, effluent limitations in the GP involve measurements that are made in an analytical laboratory – for example, TAH/TAqH and toxicity testing. These measurements involve the use of instrumentation that shall be calibrated and in good working condition in order to fulfill the quality objectives of the GP.

This section discusses M-I SWACO's program for calibration and verification of measuring and test equipment used to provide compliance data for the GP. Specific procedures for operation, maintenance, and calibration of rig compliance laboratory instrumentation can be found in the associated M-I SWACO SOP and/or manufacturer's instructions for each instrument.

The fixed subcontract laboratory QA Manual documents the quality system under which the laboratory operates. The testing, inspection, calibration, and maintenance activities for analytical laboratory instrumentation are documented in the subcontract laboratory's QA Manual and SOPs.

2.4.7.1 Responsibilities

The M-I SWACO NPDES Compliance Specialist or designee will be responsible for maintaining, issuing, and tracking field equipment in accordance with this chapter and relevant M-I SWACO SOPs. The Shell Environmental Compliance Engineer is responsible for designing QC programs for field measurements. M-I SWACO NPDES Compliance Specialists are responsible for performing field measurements, and maintaining and calibrating field equipment in accordance with M-I SWACO SOPs, this QAPP, and the GP, and for accurately completing the attendant documentation.

The storage, preventive maintenance, issuing, and tracking of equipment are the responsibility of the M-I SWACO NPDES Compliance Supervisor. The M-I SWACO NPDES Compliance Supervisor or designee performs the following tasks:

- Storage of Equipment - Field equipment is kept in a designated, limited-access storage area.
- Controlling access to the storage area.
- Issuing Equipment - Field equipment is issued by the M–I SWACO NPDES Compliance Supervisor.
- Preventive Maintenance and Repair – The M-I SWACO NPDES Compliance Specialist performs preventive maintenance of field equipment in accordance with the manufacturers recommended schedule and procedures.
- Record keeping and tracking – The M-I SWACO NPDES Compliance Supervisor maintains one Equipment Manual for each model of equipment in the Area Office. The M-I SWACO NPDES Compliance Supervisor also keeps records of routine preventive maintenance, repairs and utilization of field equipment in an Equipment Log. Each time a piece of equipment is repaired, or routine maintenance is performed, an entry is made in the logbook, giving the date, nature of repair or maintenance, identification (description and serial number) of the equipment and the initials of the person performing the repairs or maintenance work.

Subcontract laboratories are responsible for performing analytical measurements and maintaining and calibrating equipment in accordance with laboratory SOPs, the laboratory QA Manual, applicable analytical methods, and the GP; and for accurately completing the attendant documentation. Subcontract laboratory documentation shall be available upon request for audit or inspection, and equipment and reference material records shall be maintained in accordance with laboratory record retention policy.

2.4.7.2 Rig Compliance Laboratory Equipment

Sampling and analytical procedures are performed at the permittee's drilling rig using M-I SWACO rig compliance laboratory. The M-I NPDES SWACO Compliance Specialist shall provide sampling equipment to safely collect representative samples of drilling fluids and drill cuttings and other effluents. The M-I SWACO NPDES Compliance Specialist shall also provide analytical equipment and supplies necessary to perform the Free Oil by Static Sheen Method (M-I SWACO SOP 3004).

M-I SWACO shall maintain duplicate equipment for the Free Oil by Static Sheen Method (M-I SWACO SOP 3004) test at the rig compliance laboratory.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

The permittee shall provide M-I SWACO with access to a sample refrigerator that is capable of maintaining the drilling fluid and drill cutting samples at < 6 degrees Celsius (°C). The permittee shall provide a well-ventilated work area with sufficient counter space and adequate fluorescent lighting to perform procedures. Electricity shall be of sufficient voltage and amperage to operate retorts, balances, computers, and ultraviolet light. The permittee shall also provide storage space for the flammable solvent, isopropanol.

2.4.7.3 Field and Rig Compliance Laboratory Instrument Calibration

Instrument calibration comprises initial calibration that is used directly for quantification and continuing calibration verification that is used to confirm the validity of the initial calibration. Analytical procedures for the rig compliance laboratory, such as pH analysis, may require initial calibration and/or calibration verification. Analytical procedures for the fixed laboratory analyses may require initial and continuing calibration. Calibration procedures will be described in the applicable laboratory SOPs.

Calibration of thermometers and balance weights shall be verified every two years using National Institute of Standards and Technology (NIST) standards. Each working day, balances and refrigerators, shall be checked in the expected use range with NIST traceable standards. Checks shall be recorded on the equipment logs provided in the applicable SOPs. The equipment logs shall indicate the acceptable range for the check. Corrective actions for calibration results outside the acceptance range shall also be recorded on the equipment logs. If a corrective action is not successful, then the equipment shall be removed from service.

<u>Calibration Procedures</u>

Equipment shall be calibrated at the frequency specified in the applicable SOPs. Equipment shall be calibrated using the procedures specified in the applicable SOPs. The appropriate form for recording the calibration of each device is provided in the applicable SOP. The status of equipment with regard to calibration needs to be readily available and clearly indicated on equipment and field logs. Applicable acceptance criteria for equipment inspection and calibration shall be met before any sample collection or sample analyses are performed. Specific procedures for equipment calibration shall be documented in the relevant SOP. The results of the inspection and calibration shall be documented on Equipment Inspection and/or Calibration Forms.

<u>Calibration Verification</u>

Equipment calibration shall be verified by the analysis of appropriate reference materials before samples are collected /analyzed and at the required frequency throughout collection and/or analysis. The results shall be within the acceptance limits for the applicable SOP in order to proceed with sample collection and/or analysis.

Calibrations shall be documented on the Equipment Log (in the M-I SWACO Area Office) or Equipment Calibration Form (on the Drilling Rig). Records pertaining to calibration shall be safely stored for the period described in M-I SWACO's record retention policy. The following information shall be recorded:

- Date;
- Time;

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

- Instrument type and serial number;
- Identification of calibration standard;
- True value (numerical result, positive, negative) of calibration standard;
- Response of instrument before repair or adjustment;
- Response of instrument after repair or adjustment; and
- Signature of person performing the calibration.

Rig Compliance Laboratory Equipment Calibration

Portable analytical instruments (e.g. retorts, balances, and ultraviolet lights) require preventive and corrective maintenance, as well as calibration. Calibrations shall be performed in accordance with the appropriate M-I SWACO SOP and/or manufacturer's instructions. Portable equipment shall be calibrated and inspected prior to and upon return from the field. Rig compliance laboratory equipment calibration is summarized in Table 2-28.

Table 2-28 Rig Compliance Laboratory Equipment Calibration

Equipment	Calibration Procedure	Calibration Verification		SOP
		Method	Frequency	
Balance	Manufacturer's specifications	Calibration check – 100 g, 500 g, 1000 g, and 2000 g F Class Calibration Weights	Daily	1004
pH Meter	Manufacturer's Specification	Calibration check by buffer solution(s)	Daily	2012
Refrigerator	Manufacturer's specifications	Verification of operating temperature by certified thermometer	Daily	1005

Notes:

g = grams

SOP = standard operating procedure

Complete calibration verification forms as indicated in applicable SOPs. Forms will be maintained on drilling rig until completion of drilling season. After completion of drilling season, forms will be archived in the M-I SWACO Area Office.

2.4.7.4 Standards and Reagents

The M-I SWACO NPDES Compliance Specialists shall retain records for standards and reagents, including the manufacturer/vendor, the Certificate of Analysis or purity, the date of receipt, recommended storage conditions, and an expiration date. Original containers shall be labeled with an expiration date and a unique standard or reagent identifier. The standard or reagent identifier shall also be recorded on the Certificate of Analysis or vendor documentation.

Standards and reagents records shall include the purchased stock or neat compound identifier number, a reference to the method of preparation (such as a SOP number) or a description of the preparation (including weights and/or volumes), the date of preparation, the expiration date and the preparer's initials. Each prepared standard and reagent will be assigned a unique identifier that is linked to the documentation described in this paragraph. The container for each standard and reagent will be labeled with the unique identifier and the material expiration date. In order to protect the health and safety of

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

personnel, containers will be labeled with the Hazardous Materials Identification System (HMIS) information.

2.4.7.5 Reference Materials and Standards

Equipment and standards shall be verified before use and on a continuing basis. Traceability and calibration of fixed laboratory equipment will be discussed in the subcontracted laboratory QA Manual. Documentation will be maintained at the fixed laboratory as discussed in Section 1.

Reference Materials

Reference materials are materials or substances for which one or more properties are sufficiently well established to be used for the calibration of an apparatus, for assessment of methods or for assigning values to materials. Generally reference materials are purchased from third parties such as NIST and are characterized for content, independent of an analytical method. Reference materials used to support data generated for permit compliance include:

- Class F weights
- NIST thermometers

Original certificates are maintained at the M-I SWACO Area Office and certificate copies are maintained with equipment in the rig compliance laboratory. Reference materials are removed from service upon expiration of the certificate and may only be placed back into service once the material is recertified.

Reference Standards

Reference standards shall be used for calibration only. Reference standards are removed from service upon expiration of the certificate or if calibration indicates the standard is outside of specifications. If the material is outside of specifications and correction factors can be established, the reference standard may continue in service. The M-I SWACO Area Office shall maintain original records of the correction factors with the applicable dates. Copies of relevant correction factors shall accompany the material in the field.

Traceability

Calibration certificates shall be provided by the manufacturer and shall indicate traceability to national standards. Class F weights, crude oil standards, and NIST thermometers are examples of materials for which calibration certificates shall be maintained. Certificates that describe purity or composition of standard materials shall also be maintained. Certificates shall be cross-referenced to a material identification, such as equipment number, standard, or reagent number.

2.4.7.6 Refrigerator Testing

Refrigerators will be monitored using thermometers that have been calibrated using a NIST-traceable thermometer. Refrigerator temperatures will be monitored daily and the temperature recorded on Form 1005-2 Refrigerator Calibration Log. Thermometer calibration procedures and refrigerator monitoring procedures are included in SOP 1005 Laboratory Refrigerators.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.4.7.7 Field Compliance Instrument/Equipment Maintenance

Field equipment is maintained under a tracking and preventive maintenance program. When a piece of permit-related equipment is sent to a vendor for repairs or maintenance, a log entry is made giving the date, name of vendor, identification of the equipment, description of services required, and initials of the person sending the equipment. When the equipment is returned, a similar entry is made to document the return and a copy of the repair slip is placed in the Equipment Log.

When equipment is issued, an entry is made in the Equipment Log giving the date, identification of the equipment, initials of the person issuing the equipment and the identity of the person to whom the equipment is issued. When the equipment is returned, a similar entry is made, noting date of return, and condition of the returned equipment. Through the use of the log, the M-I NPDES Compliance Supervisor maintains a continuous written record of the status and the location of each piece of field equipment.

Equipment that is overdue for scheduled maintenance or is in need of repair is placed "Out of Service". This equipment shall be clearly identified as "Out of Service" until the repair work has been completed and the equipment is operating satisfactorily. Equipment that is not marked shall be considered in proper working order.

2.4.8 Fixed Subcontract Laboratory Instrument/Equipment Testing, Inspection, Calibration, and Maintenance

Testing, inspection, calibration, and maintenance for fixed laboratory equipment is performed in accordance with laboratory QA Manuals and analytical method requirements. Calibration requirements for fixed laboratory equipment are documented in subcontract laboratory SOPs. Subcontract laboratories shall maintain equipment and have in place either a service contract, or sufficient spare parts, such that method holding times or analytical report due dates are not exceeded.

The following sections outline specific equipment, materials, and procedures used by the toxicity testing subcontract laboratory.

2.4.8.1 Initial Toxicity Screening and Whole Effluent Toxicity Testing Laboratory Equipment Washing Procedures

All laboratory equipment, glassware, and plasticware used for the toxicity testing program will be cleaned to eliminate potential toxicity associated with labware. Plastic and glassware are scrubbed with a solution of non-phosphate detergent and hot tap water, and then rinsed three times with deionized water. A rinse of 10% solution reagent grade hydrochloric acid is followed by three rinses with deionized water. A rinse of reagent grade acetone is followed by air drying under a fume hood. Acetone is not used on hard plastics. A final three rinses with deionized water is followed by air drying.

2.4.8.2 Initial Toxicity Screening and Whole Effluent Toxicity Testing Laboratory Materials

<u>Test Organisms Suppliers</u>

Test organisms used in the toxicity tests will be from either in-house cultures or collected in areas known to be generally free of pollutants, or purchased from reputable culturists. Organisms are purchased from

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

suppliers who are selected based on their reputation, depth of knowledge concerning the test organisms, and their ability to consistently deliver healthy test organisms.

Upon receipt in the laboratory, test organisms will be slowly acclimated to test conditions in environmentally controlled holding areas in accordance with the test protocol for each test organism. Test organisms will be evaluated on a performance basis for every test conducted in the laboratory. Negative controls will be tested concurrent to each study to evaluate the health of the test organisms and the acceptability of the test conditions. Positive controls (reference toxicant tests) will also be conducted to assess the relative sensitivity of test organisms compared to historical laboratory performance.

Source of Seawater

Seawater diluent that will be used in this study will come from the northern Hood Canal at Port Gamble, Washington. This water source (used as the laboratory control and sample diluent) has been used successfully on a wide range of bioassay testing programs. Artificial seawater may also be prepared from deionized water and bioassay-grade sea salts (Crystal Sea Marinemix™) if necessary. Extensive testing with a variety of test species has shown that there is no significant potential for toxicity or bioaccumulation from these water supplies. Chemical analyses are performed annually on these water sources and have shown no significant contaminants of concern or bioaccumulation potential.

2.5 Fixed Laboratory Analysis

The fixed subcontract laboratories that are proposed for use for the analysis of compliance monitoring samples are listed for the corresponding preparation and analytical methods in Table 2-29.

Table 2-29 Analytical Subcontract Laboratories

Analytical Parameter	Matrix	Preparation/ Analytical Method	Laboratory/Organization
TAH/TAqH	Aqueous	SW5030B/E624 SW3520C/E625 SIM	Primary Laboratory: SGS North America, Inc. 200 W. Potter Drive Anchorage, AK 99518 (907) 562-2343 Main (907) 561-5301 Fax Backup laboratory: TestAmerica Anchorage 2000 W. International Airport Rd. Suite A10 Anchorage, AK 99502 (907) 563-9200 Main (907) 563-9210 Fax
Diesel fingerprinting	Aqueous Oil	SW3520C/SW8015C SW3550C/SW8015C	
BOD_5	Aqueous	SM5210-B	
TSS	Aqueous	SM2540-D	
Fecal coliform	Aqueous	SM9222-D	Primary Laboratory: SGS Mobile Laboratory Barrow, AK 99723 Backup Laboratories: SGS North America, Inc. 200 W. Potter Drive Anchorage, AK 99518 (907) 562-2343 Main (907) 561-5301 Fax TestAmerica Anchorage

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Analytical Parameter	Matrix	Preparation/ Analytical Method	Laboratory/Organization
			2000 W. International Airport Rd. Suite A10 Anchorage, AK 99502 (907) 563-9200 Main (907) 563-9210 Fax Arctic Fox Environmental, Inc. Pouch 340043 Prudhoe Bay, AK 99734 (907) 659-2145 Main (907) 659-2146 Fax
SPP Toxicity	Aqueous	40 CFR Part 435, App. 2 to Subpart A (E1619)	Environmental Enterprises USA, Inc. 58485 Pearl Acres Road, Suite D Slidell, LA 70461 (800) 966-2788 Main (985) 646-2810 Fax

Analytical Parameter	Matrix	Preparation/ Analytical Method	Laboratory/Organization
Initial toxicity screening	Aqueous	EPA/600/R-95-136 (Echinoderm Fertilization Test)	Primary Laboratory: Environ 477 NE View Drive Port Gamble, WA 98364 (360) 297-6040 Main Backup Laboratories: Environmental Enterprises USA, Inc. 58485 Pearl Acres Road, Suite D Slidell, LA 70461 (800) 966-2788 Main (985) 646-2810 Fax Element Materials Technology 2417 West Pinhook Road Lafayette, LA 70508 (337) 235-0483 Main (337) 233-6540 Fax
WET testing	Aqueous	EPA/600/R-95-136 (Topsmelt Chronic 7d Survival and Growth Test) or EPA/821-R-02-014 (Menidia Chronic 7d Survival and Growth Test)	
		EPA/821-R-02-014 (Mysid Chronic 7d Survival, Growth, and Fecundity	
		EPA/600/R-95-136 (Echinoderm Larval Development Test)	

Notes:

BOD_5 = biochemical oxygen demand
SPP = suspended particulate phase
TAH = total aromatic hydrocarbons
TAqH = total aqueous hydrocarbons
TSS = total suspended solids
WET = whole effluent toxicity

2.5.1 Analytical Laboratory Methods

Evaluation of the effluent limits and laboratory quantitation limits is required to ensure that project data quality objectives are met. Laboratory-specific detection limits and reporting limits will be evaluated against the permit effluent limitations to determine whether the sensitivity of the data will be sufficient for its intended use.

Proposed drilling fluid and effluent toxicity testing methods are summarized in Table 2-30. The initial toxicity screening of effluent discharges will utilize the Chronic Toxicity Fertilization Test using echinoderms (*Strongylocentrotus purpuratus* or *Dendraster excentricus*) as outlined in the "Short Term

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to West Coast Marine and Estuarine Organisms" (EPA/600/R-95-136).

The methods for WET testing are provided in established EPA procedures outlined in "Short Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Marine and Estuarine Organisms" (EPA-600-4-91-003-Third Ed.) and the "Short Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to *West Coast* Marine and Estuarine Organisms" (EPA/600/R-95-136). The WET testing program will use three different species of organisms including the topsmelt, *Atherinops affinis (or M. beryllina*-depending on availability*)*, the mysid shrimp, *Americamysis bahia*, and the purple sea urchin, *Strongylocentrotus purpuratus*.

Table 2-31 presents subcontract laboratory analytical methods, detection limits, and reporting limits for effluent monitoring.

Table 2-30 Drilling Fluid and Effluent Toxicity Testing Methods

Toxicity Test	Test Description	Species	Method
Drilling fluid SPP toxicity	Mysid 96-Hour Survival Test	*Americamysis bahia* (Formerly *Mysidopsis bahia*)	40 CFR Part 435 EPA-821-R-11-004 EPA-821-R-02-012
Initial (Rapid) toxicity screening test	Chronic Toxicity Echinoderm Fertilization Test	Purple Sea Urchin *(Strongylocentrotus purpuratus)* or Green Sea Urchin *Strongylocentrotus droebachensis* or Sand Dollar *(Dendraster excentricus)*	EPA/600/R-95/136
Marine Chronic Toxicity Test (WET testing)	Larval Fish 7-Day Larval Survival and Growth Test	Topsmelt (Atherinops affinis) or Inland Silverside[1] (Menidia beryllina)	EPA/600/R-95/136 or EPA-821-R-02-014
	Mysid Shrimp 7-Day Larval Survival, Growth, and Fecundity Test	*Americamysis bahia* (Formerly *Mysidopsis bahia*)	EPA-821-R-02-014
	Echinoderm Larval Survival and Development Test	Purple Sea Urchin (*Strongylocentrotus purpuratus*) or Sand Dollar (*Dendraster excentricus*)	EPA/600/R-95/136

Notes:

[1] *Menidia beryllina* may be used as a substitute for topsmelt.
EPA = U.S. Environmental Protection Agency
SPP = suspended particulate phase
WET = whole effluent toxicity

Table 2-31 Analytical Laboratory Reporting Limits

Analytical Method	Analyte	Matrix	Permit Limit	Units	DL	RL
SM5210-B	BOD_5	Aqueous	30	mg/L	2	2
SM2540-D	TSS	Aqueous	30	mg/L	0.15	0.5

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Analytical Method	Analyte	Matrix	Permit Limit	Units	DL	RL
SM9222-D	Fecal coliform	Aqueous	100	col/100 mL	1	1
E624	Benzene	Aqueous	NA	µg/L	0.12	0.4
E624	Toluene	Aqueous	NA	µg/L	0.31	1
E624	Chlorobenzene	Aqueous	NA	µg/L	0.15	0.5
E624	Ethylbenzene	Aqueous	NA	µg/L	0.31	1
E624	P & M -Xylene	Aqueous	NA	µg/L	0.62	2
E624	o-Xylene	Aqueous	NA	µg/L	0.31	1
E624	1,3-Dichlorobenzene	Aqueous	NA	µg/L	0.31	1
E624	1,4-Dichlorobenzene	Aqueous	NA	µg/L	0.15	0.5
E624	1,2-Dichlorobenzene	Aqueous	NA	µg/L	0.31	1
E625 SIM	Acenaphthene	Aqueous	NA	µg/L	0.015	0.05
E625 SIM	Acenaphthylene	Aqueous	NA	µg/L	0.015	0.05
E625 SIM	Anthracene	Aqueous	NA	µg/L	0.015	0.05
E625 SIM	Benzo[a]anthracene	Aqueous	NA	µg/L	0.015	0.05
E625 SIM	Benzo[a]pyrene	Aqueous	NA	µg/L	0.015	0.05
E625 SIM	Benzo[b]Fluoranthene	Aqueous	NA	µg/L	0.015	0.05
E625 SIM	Benzo[g,h,i]perylene	Aqueous	NA	µg/L	0.015	0.05
E625 SIM	Benzo[k]fluoranthene	Aqueous	NA	µg/L	0.015	0.05
E625 SIM	Chrysene	Aqueous	NA	µg/L	0.015	0.05
E625 SIM	Dibenzo[a,h]anthracene	Aqueous	NA	µg/L	0.015	0.05
E625 SIM	Indeno[1,2,3-c,d] pyrene	Aqueous	NA	µg/L	0.015	0.05
E625 SIM	Fluoranthene	Aqueous	NA	µg/L	0.015	0.05
E625 SIM	Fluorene	Aqueous	NA	µg/L	0.015	0.05
E625 SIM	Naphthalene	Aqueous	NA	µg/L	0.031	0.1
E625 SIM	Phenanthrene	Aqueous	NA	µg/L	0.015	0.05
E625 SIM	Pyrene	Aqueous	NA	µg/L	0.015	0.05
SW8015C	Diesel Range Organics	Aqueous	NA	mg/L	0.15	0.4
SW8015C	Diesel Range Organics	Oil	NA	mg/kg	620	2000

Notes:

SGS North America, Inc. DLs and RLs.
BOD_5 = biochemical oxygen demand
DL = detection limit
mg/kg = milligrams per kilogram
mg/L = milligrams per liter
µg/L = micrograms per liter
RL = reporting limit
SPP = suspended particulate phase
TSS = total suspended solids
TU_c = chronic toxic units

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.6 Field and Laboratory Quality Control Samples

2.6.1 Field Quality Control Samples and Frequencies

Field QC samples that will be collected and/or submitted include field duplicates, MS/MSDs, trip blanks, and temperature blanks. Field QC samples will be collected and/or submitted at the following frequencies:

- Field duplicates will be collected at a frequency of one per 20 or fewer primary samples for each analyte and matrix as described in Table 2-32.
- MS and MSD samples will be collected for every 20 or fewer samples as described in Table 2-32.
- Trip blanks will be submitted with every cooler for every shipment containing volatile samples.
- Temperature blanks will be submitted with every cooler containing analytical samples.

Table 2-32 summarizes the type and quantity of QC samples required for compliance monitoring.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 2-32 Field Quality Control Samples

Discharge	Matrix	Monitoring Parameter	Method	Sampling Frequency	Field Duplicate	MS/MSD[1]	Trip Blank Required?
Discharge 001 Water-based drilling fluids and drill cuttings	Water-based drilling fluids and drill cuttings	SPP toxicity	E1619	Weekly and end of well	Duplicate collected each time a primary sample is collected[2]	NA	NA
		TAH	E624	Once per well	One duplicate per 20 or fewer samples	One MS/MSD per 20 samples	Yes
		TAqH	E625 SIM	Once per well	One duplicate per 20 or fewer samples	One MS/MSD per 20 samples	NA
		Diesel oil (Diesel-range organics)	SW8015C	Once per well, or if static sheen test fails	One duplicate per 20 or fewer samples	One MS/MSD per 20 samples	NA
	Diesel oil in storage	Diesel oil (Diesel-range organics)	SW8015C	If static sheen test fails	NA	NA	NA
Discharge 002 Deck Drainage	OWS effluent	TAH	E624	Once per discharge event (if conducted continuously)	One duplicate per 20 or fewer samples	One MS/MSD per 20 samples	Yes
	OWS effluent	TAqH	E625 SIM	Once per discharge event (if conducted continuously)	One duplicate per 20 or fewer samples	One MS/MSD per 20 samples	NA
Discharge 003 Sanitary Wastes	MSD effluent	BOD_5	SM5210-B	Weekly	NA	NA	NA
	MSD effluent	TSS	SM2540-D	Weekly	NA	NA	NA
	MSD effluent	Fecal coliform bacteria	SM9222-D	Weekly	NA	NA	NA

Notes:

[1] Triple volume of sample must be collected for MS/MSD for organic analyses. Two sample volumes must be collected for inorganic analyses.

[2] A duplicate sample volume will be collected with each primary sample. The duplicate volume will be retained in the rig compliance laboratory refrigerator until acceptable results are received for the sample transported to the laboratory. If a problem occurs with the original sample that invalidates the results, the duplicate volume of sample will be packaged and transported to the subcontract laboratory for analysis.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.6.2 Laboratory Quality Control

2.6.2.1 Analytical Method Quality Control Criteria

Quality control checks for sample collection will be accomplished by a combination of CoC protocols, field QA samples, and laboratory QC as prescribed in the sampling or analytical methods. Fixed laboratory QC samples will be prepared and analyzed as required by the analytical methods and laboratory QA Manuals. Results from LCS/LCSD and MS/MSD samples will be compared to criteria for accuracy and precision listed in Table 2-33.

Table 2-33 Analytical Method Quality Control Criteria

Analytical Method	Analyte	Matrix	Laboratory Control Limits (Accuracy)		RPD (Precision)
			LCL (%)	UCL (%)	
SM5210-B	BOD_5	Aqueous	84.6	115.4	20
SM9222-D	Fecal coliform	Aqueous	NA	NA	NA
SM2540-D	TSS	Aqueous	75	125	5
E624	Benzene	Aqueous	80	120	20
E624	Toluene	Aqueous	75	120	20
E624	Chlorobenzene	Aqueous	80	120	20
E624	Ethylbenzene	Aqueous	75	125	20
E624	P & M -Xylene	Aqueous	75	130	20
E624	o-Xylene	Aqueous	80	120	20
E624	1,3-Dichlorobenzene	Aqueous	75	125	20
E624	1,4-Dichlorobenzene	Aqueous	75	125	20
E624	1,2-Dichlorobenzene	Aqueous	70	120	20
E625 SIM	Acenaphthene	Aqueous	45	110	30
E625 SIM	Acenaphthylene	Aqueous	50	105	30
E625 SIM	Anthracene	Aqueous	55	110	30
E625 SIM	Benzo[a]anthracene	Aqueous	55	110	30
E625 SIM	Benzo[a]pyrene	Aqueous	55	110	30
E625 SIM	Benzo[b]Fluoranthene	Aqueous	45	120	30
E625 SIM	Benzo[g,h,i]perylene	Aqueous	40	125	30
E625 SIM	Benzo[k]fluoranthene	Aqueous	45	125	30
E625 SIM	Chrysene	Aqueous	55	110	30
E625 SIM	Dibenzo[a,h]anthracene	Aqueous	40	125	30
E625 SIM	Indeno[1,2,3-c,d] pyrene	Aqueous	45	125	30
E625 SIM	Fluoranthene	Aqueous	55	115	30
E625 SIM	Fluorene	Aqueous	50	110	30
E625 SIM	Naphthalene	Aqueous	40	100	30
E625 SIM	Phenanthrene	Aqueous	50	115	30

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Analytical Method	Analyte	Matrix	Laboratory Control Limits (Accuracy)		RPD (Precision)
			LCL (%)	UCL (%)	
E625 SIM	Pyrene	Aqueous	50	130	30
SW8015C	Diesel Range Organics	Aqueous	75	125	20
SW8015C	Diesel Range Organics	Oil	NA	NA	NA

Notes:
BOD5 = biochemical oxygen demand
LCL = lower control limit
RPD = relative percent difference
TSS = total suspended solids
UCL = upper control limit
WET = whole effluent toxicity

For operational discharge compliance sampling under the GP, the completeness goal is 100%. If a sample is determined to be invalid or unusable, the sample will be recollected as soon as practicable. The M-I SWACO NPDES Compliance Specialist will be responsible for ensuring that all samples are collected as required by the permit.

2.6.2.2 Toxicity Testing Quality Control Criteria

The test acceptability criteria and performance standards for the proposed toxicity tests are summarized in Tables 2-34 and 2-35. The toxicity tests incorporate standard QA/QC procedures to ensure that the test results are valid. Standard QA/QC procedures include the use of negative and positive controls, the use of testing replicates, and water quality monitoring. All limits established for this program meet or exceed those recommended by USEPA.

All data collected and produced will be recorded on approved data sheets, which will become part of the permanent data record of the program. If any aspect of a test deviates from protocol, the test will be evaluated to determine whether it is valid according to test acceptability criteria and performance standards.

Each toxicity test includes sample replication of 3 to 8 replicates, depending on the test. The data generated are checked by the responsible laboratory technician and reviewed independently by another analyst to assess precision. The maximum percent difference (MPD) for replicates and the reference toxicant tests are evaluated relative to the permissible bounds of the methods. Acceptable accuracy levels are also assessed by the calibration of water quality instruments, the use of certified standards, and the establishment of acceptable water quality testing parameters. For example, water quality is monitored and, adjusted if necessary, throughout testing in at least one test replicate. Parameters that fall outside of acceptable test ranges may require corrective action.

The sensitivity of test organisms will be evaluated using positive control reference toxicant tests. Reference toxicant tests will be conducted on each batch of test organisms either concurrently with project samples or monthly, as specified under the QA requirements for each test. The reference toxicant test will consist of an exposure to at least five concentrations of a reference substance (known toxicant) used to assess the health and sensitivity of the test organisms. The test duration and endpoint will mimic those of the corresponding bioassay. Dilutions will be selected to bracket laboratory historical LC_{50}/EC_{50}.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

The LC_{50}/EC_{50} results will be compared with historical data from definitive bioassays with the reference substance. The reference toxicant substances will be copper sulfate, ammonium chloride, or other toxicants as appropriate for evaluating the sensitivity of test organisms.

Table 2-34 Water Quality Criteria and Performance Standards

Analyte	Water Quality Test Parameters Acceptability Criteria			
	Dissolved oxygen	Temperature	pH	Salinity
Drilling Fluid (Mud) SSP Mysid Acute Survival Toxicity Test	Aeration to maintain DO > 5.3 mg/L	20 ± 2°C	6 – 9[3]	20 ± 2 ppt
Chronic Toxicity Echinoderm Fertilization Test	DO > 4.0 mg/L	12 ± 1°C	6 – 9	34 ± 2 ppt
Larval Topsmelt 7-Day Chronic Survival and Growth Test	Aerate if DO < 4.0 mg/L	20 ± 1°C	6 – 9	5 – 34 ppt[1]
Larval Menidia 7-Day Chronic Survival and Growth Test	Aerate if DO < 4.0 mg/L	25 ± 1°C	6 – 9	5 – 32 ppt[1]
Mysid Shrimp 7-Day Larval Survival, Growth and Fecundity Test	Aerate if DO < 4.0 mg/L	26 ± 1°C	6 – 9	20 – 30 ppt[1]
Echinoderm Larval Survival and Development Test	Aerate if DO < 4.0 mg/L[2]	15 ± 1°C	6– 9	34 ± 2 ppt

Notes:

[1] Target should not deviate by ± 2 ppt during test period.
[2] No aeration during testing.
[3] 7.8 ± 0.1 (at initiation in the 100% elutriate).

Table 2-35 Toxicity Test Acceptance Criteria and Performance Standards

Test Organism (Protocol – SOP)	Test Acceptability Criteria
Drilling Fluid (Mud) SPP Mysid Acute Survival Toxicity Test (40 CFR Part 435, EPA-821-R-11-004, EPA-821-R-02-012)	1. Survival in the controls ≥ 90%
Initial Toxicity Screening Test	
Chronic Toxicity Echinoderm Fertilization Test (*Strongylocentrotus purpuratus* or *Dendraster excentricus*) (EPA/600/R-95/136, WDOE WQ-R-95-80 – SOP No. TOX045)	1. At least 70% fertilization in controls 2. The dilution water and the effluent egg blanks have essentially no eggs with fertilization membranes. 3. Minimum significant difference (MSD) of <25% 4. Final sperm stock concentration must be ≤33,600,000 sperm/mL *AND* one of the following conditions: a. Trial fertilization used – final sperm stock must not exceed double the target density selected that would provide 70-<100% fertilization without oversperming b. Sperm/egg ratio kept at ≤500:1 (without trial fertilization) and confirmation of sperm stock ≤5,600,000 sperm/mL c. Use any reasonable sperm stock density and run two extra sets of controls (high and low density). The high density control (0.200 mL of sperm stock) must have at least 5% higher fertilization than the low density control (0.050 mL of sperm stock)

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Test Organism (Protocol – SOP)	Test Acceptability Criteria
WET Tests:	
Larval Fish 7-Day Chronic Survival and Growth Test Topsmelt (*Atherinops affinis*) (EPA/600/R-95/136 – SOP No. TOX002)	1. Survival in the controls ≥ 80% 2. 0.85 mg average weight of control larvae (9 days old)
Larval Fish 7-Day Chronic Survival and Growth Test Inland Silverside (*Menidia beryllina*) (EPA-821-R-02-014 – SOP No. TOX012)	1. Survival in the controls ≥ 80% 2. 0.50 mg average weight of control larvae (7 days old)
Mysid Shrimp 7-Day Larval Survival, Growth, and Fecundity Test (EPA/821-R-02-14 – SOP No. TOX014B)	1. Survival in the controls ≥ 80% 2. 0.20 mg average weight of control larvae (7 days old) 3. MSD for growth ≤ 37% 4. Egg production in ≥ 50% of females
Echinoderm Larval Survival and Development Test (EPA/600/R-95/136 – SOP No. TOX043)	1. Normal development in the controls ≥ 80% 2. MSD for growth < 25%

Notes:

EPA = U.S. Environmental Protection Agency
mL = milliliter
MSD = minimum significant difference
SPP = suspended particulate phase
SOP = standard operating procedure

2.7 Documents and Records

2.7.1 Responsibilities

The M-I SWACO NPDES Compliance Supervisor or designee establishes and maintains the central files for project records, training records, qualified subcontractor files, and other important documentation. Each M-I SWACO NPDES Compliance Specialist is responsible for assembling supporting documentation generated in his or her task and forwarding the documentation to the Shell Environmental Compliance Engineer and the M-I SWACO NPDES Compliance Supervisor at the end of the season. In addition, the M-I SWACO NPDES Compliance Specialist is responsible for providing the rig compliance laboratory reports to the permittee.

The M-I SWACO NPDES Compliance Supervisor and other signatories shall approve revisions of controlled documents such as the QAPP and associated SOPs and LWIs. The M-I SWACO NPDES Compliance Supervisor is responsible for determining, through consultation with technical staff, the activities that require SOPs or LWIs, and for working with the appropriate technical experts to develop the SOPs and LWIs. The M-I SWACO NPDES Compliance Supervisor is responsible for obtaining technical review and approval of SOPs and LWIs, for maintaining control of QAPP and revisions, and for maintaining an up-to-date distribution list for written procedures.

M-I SWACO NPDES Compliance Specialists are responsible for performing tasks in accordance with applicable written procedures, except as explicitly directed by the relevant contract or Health and Safety policy. M-I SWACO NPDES Compliance Specialists are responsible for maintaining copies of applicable written procedures at the rig compliance laboratory locations, performing the procedures defined in the written procedures, maintaining documentation as required by the written procedures, and

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

notifying management of deviations from written procedures. M-I SWACO NPDES Compliance Specialists are also responsible for assisting the Shell Environmental Compliance Engineer and/or the M-I SWACO NPDES Compliance Supervisor in designing accurate and practical written procedures, and in keeping the written procedures up-to-date.

2.7.2 Field and Laboratory Records

M-I SWACO shall retain copies of observations, calculations and derived data, calibration records, and a copy of the test report in accordance with the BMP and permit requirements. Records that are generated or stored by computers shall have hard copy or write-protected backup copies. Field notebooks shall be assigned an identification number and each page of the notebook shall be sequentially numbered. The M-I SWACO NPDES Compliance Supervisor shall maintain completed notebooks, hard copy electronic records, write-protected backup records, and test reports. Records that are expected to be generated to document compliance with drilling fluid and effluent monitoring requirements are provided in Table 2-36.

The records shall include the identity of the personnel involved in sampling, sample receipt, preparation calibration, and testing. Data, except those generated by automatic data collection systems, shall be recorded directly, promptly, and legibly in permanent ink.

Changes to records shall be signed or initialed by responsible staff. Entries shall not be obliterated by methods such as erasures, overwritten files, or markings. Corrections to recordkeeping errors shall be made by one line marked through the error. The individual making the corrections shall sign (or initial) and date the correction. This requirement also applies to electronically maintained records.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 2-36 General Permit Compliance Records by Location

Record	Shell Quality Assurance/ Central Project Files	Compliance Specialist Notebook	M-I SWACO Area Office
Quality Assurance Project Plan (QAPP)	Original	Copy[2]	
Audit Reports	Original	Copy	
HSE Manual	Copy	Copy [2]	
Material Safety Data Sheet (MSDS)	Copy	Copy [2]	
SOPs and LWIs	Copy	Copy [2]	Original
Personnel Qualifications	Copy		Original[1]
Training Documentation Form	Copy		Original[1]
Demonstration of Capability	Copy	Copy	Original[1]
Computer Program Verification	Original		
Equipment Manuals	Original	Copy	
Reference Material Certificates	Original	Copy	
Equipment Log	Original	Copy	
Field Notebook	Archive Copies[3]	Copy	
Daily Activity Report	Archive Copies[3]	Copy [2]	
Equipment calibration forms	Archive Copies3	Copy	
Sample chain-of-custody forms	Archive Copies	Copy	
Analytical reports from rig compliance laboratory	Archive Copies[3,4,5]	Copy	
Fixed analytical laboratory data packages	Archive Copies[3,4,5]		
Certification of Analysis – mercury and cadmium content in Barite	Archive Copies[3]	Copy	
Drilling Fluid Inventory	Archive Copies[3]		
Monthly Discharge Flow Volume Report	Archive Copies[3]		
Static Sheen Results	Archive Copies[3]	Copy	

Notes:

[1] Certified copy.

[2] Electronic copy.

[3] Rig compliance laboratory records will be retained in accordance with the permit requirements. Fixed laboratories shall maintain originals of their analytical data in accordance with their internal QA programs.

[4] Including QC results, if applicable.

[5] Copy of CoC document, with recipient's signature at sample transfer to be filed. Sample transfer is defined as the point at which the sample is delivered to any third party.

[6] Originals provided to permittee at required frequency (e.g., at end of drilling season).

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.7.2.1 Deviations

Deviations from SOPs, if any, shall be documented on Corrective Action Report Forms (Table 2-37).

CAR No. _____

Date: _____

Table 2-37 Service Quality Non-Conformance Report

To:	From:
Findings or Deviations	
Answer Due Date	Signature
Review and Comments	
Date	Signature
Review and Comments	Follow up Actions

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2.8 Reporting

2.8.1 Notifications

If any of the discharge limits are exceeded or if other suspected BMP Plan noncompliance or modification occurs, the Shell Compliance Duty Officer (907-830-7435) must be called immediately. Noncompliance of the NPDES GP that may endanger health or the environment (if any) must be reported to the EPA by telephone within 24 hours from the time of occurrence. This includes any unanticipated bypass or upset that exceeds discharge limitations in the permit or any violation of maximum daily discharge limitations for any of the pollutants listed in Part 1 of the GP requiring 24-hr reporting.

If NPDES GP noncompliance occurs, the Shell Environmental Compliance Engineer will complete and file the necessary reports to the EPA in accordance with permit requirements.

2.8.2 Discharge Monitoring Reports

All discharge monitoring results and effluent sampling will be summarized in the Discharge Monitoring Report (DMR) form EPA No. 3320-1 or equivalent. Monitoring data and other reports will be submitted electronically using NetDMR (http://www.epa.gov/netdmr). DMRs will be submitted to EPA no later than the 20th of the month following the completed reporting period.

All permit records are submitted to Shell. Annual sampling results will be reported on the January DMR. All records of monitoring information shall be retained at least 5 years from the date of the sample, measurement, report, or application.

The permittee must ensure that records of monitoring information include:

- The date, exact place, time of sampling or measurements, and the name(s) of the individual(s) who performed the sampling or measurements;
- The date(s) analyses were performed and the names of the individual(s) who performed the analyses;
- The analytical techniques or methods used; and
- The results of such analyses.

Noncompliance reporting that is not required to be reported within 24 hours is to be included with the Discharge Monitoring Reports and submitted monthly. Shell is to preserve all reports and records for a period of at least five years from the date of sample, measurement, report, or application, or for the term of this permit, whichever is longer.

2.8.3 TAH/TAqH Reporting

Total aromatic hydrocarbons, or TAH, is determined by summing the results of EPA Method 602 (plus xylenes) or EPA Method 624 to quantify monoaromatic hydrocarbons. Total aqueous hydrocarbons, or TAqH, are determined by summing the results for TAH and EPA Method 610 or EPA Method 625 (to quantify PAHs listed in EPA Method 610). For samples where one or more analytes has a detectable result, TAH and TAqH will be presented as the sum of the detectable results. Detectable results include results that are reported as estimated (e.g., J-flagged) because the result is greater than the detection limit

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

and less than the reporting limit. If all results for the sample are nondetect, one-half the reporting limits for all nondetect results will be summed.

2.9 Data Reporting

A group of samples submitted to the subcontract laboratory at the same time and included on the same CoC form will be considered a sample delivery group. The results for this sample delivery group will be reported as one analytical data package. The analytical data package must contain adequate information to verify the quality of the data and be presented in a clear and concise manner. Data packages must include, at minimum, the following elements:

- Cover sheet, which identifies the project;
- Table of contents;
- Case narrative, which documents all discrepancies with the data contained in the report, including (but not limited to) sample receipt, holding time(s), documentation of QC discrepancies and corrective action, matrix interferences;
- Preparation and analytical methods used;
- Sample identification;
- Analytical results, including detection limits, reporting limits, and dilution factors;
- Laboratory qualifiers;
- Date(s)/time(s) of collection, receipt, preparation, analysis;
- Sample receipt and management records; and
- QA/QC sample results and supporting information.

The toxicity testing laboratory is required to report results that include all information recommended by the test protocols for quality assurance review and data validation, as follows:

- Test methods used for toxicity testing and statistical analyses;
- Source of testing water including a description of any pretreatment, and results demonstrating survival and growth of test organism in test water;
- Source, history, and age of test organisms and if appropriate culturing information, or collection information. Records should include information regarding taxonomic identification of test organisms;
- Source of food composition and procedures used to prepare and dispense food to test chambers;
- Description of experimental design including test setup, test monitoring, and test termination. Water quality and observation records should be summarized and included in report;
- Methods used for physical and chemical characterization of test matrices;
- A table of biological data for each sample, including negative and positive control information;

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

- Methods used for statistical analysis;
- A description of any deviations from the methodology or problems with the process and procedures of analyses;
- Original data sheets for water quality, survival, growth, abnormalities, reference toxicant, and statistics as applicable by test protocol;
- Chain-of-custody records; and
- References and literature.

2.10 Data Review and Qualification

All analytical data that the laboratory generates shall be verified before submittal to the permittee. This internal data review process, which is multi-tiered, shall include all aspects of data generation, reduction, and QC assessment. All definitive data shall be reviewed first by the analyst, and then by the supervisor of the respective analytical section using the same criteria. Elements for review or verification at each level must include, but are not limited to, the following:

- Sample receipt procedures and conditions;
- Sample preparation;
- Appropriate analytical SOPs and methodologies;
- Accuracy and completeness of analytical results;
- Correct interpretation of all raw data, including all manual integrations;
- Appropriate application of QC samples and compliance with established control limits;
- Verification of data transfers;
- Documentation completeness; and
- Accuracy and completeness of data deliverables (hard copy and electronic).

2.10.1 Laboratory Data Evaluation

The calibration, QC, corrective actions, and flagging requirements will be performed in accordance with the laboratory QA Manual and the analytical methods. The laboratory shall apply data qualifiers as part of its internal validation activities. Flagging criteria apply when acceptance criteria are not met and when corrective actions are not successful or not performed. The supervisor of the respective analytical sections shall review the data qualifiers.

The laboratory's QA section shall perform internal review prior to issuance of the final data packages. The laboratory project representative shall complete a final review on all of the completed data packages and issue the final reports.

2.10.2 Data Review and Verification

Staff reviewing permit compliance data will conduct a QA/QC review and assessment of laboratory data deliverables, including an evaluation of:

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

- The information provided on the analytical data sheets, including QC sample results;
- The laboratory case narrative and any flags that the laboratory applied as part of its data validation and usability assessment;
- The sample collection documentation, including CoC records; and
- Field laboratory data sheets and supporting documentation.

This review will also verify the accuracy and completeness of field activities, including the adherence to the procedures as described in the cited SOPs and the specified analytical methods. In general, analytical data that have been reviewed by the laboratory QA section and permit compliance staff will be considered acceptable for use, including results that were flagged as part of the laboratory QA review and validation. Laboratory flags and case narratives will be reviewed as part of the data quality review and assessment to confirm that the quality of the data is acceptable for its intended purpose.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

This page intentionally left blank

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

3.0 Environmental Monitoring Program

3.1 Introduction and Overview

In the management of its activities, Shell has contracted with Olgoonik Fairweather, LLC for the implementation of the Environmental Monitoring Program (EMP) portion of its exploration program in the Chukchi Sea. This section addresses the GP compliance tasks that will be performed by Olgoonik Fairweather LLC under contract to Shell during offshore drilling exploration.

Table 3-1 defines the roles and responsibilities of the EMP implementation team. The specific details of responsibilities may change during project execution. Changes will be documented and communicated to the project team to ensure that project personnel are aware of appropriate points of contact and to avoid any gaps in responsibilities.

Table 3-1 Roles and Responsibilities of the EMP Implementation Team

Role	Responsibilities
Shell Science Lead (SL)	• Technical input on and review of project scope and equipment specifications • Participation in identification of risks, opportunities, and hazards
Shell Project Lead (PL)	• Ultimate program responsibility and management • Project execution • Permitting • Accounting • Stakeholder communication
Shell Representative (Shell Rep)	• Offshore based single point accountability for operations and oversees the projects assets and contractors in regards to program delivery, health, safety, security and environment (HSSE), reputation, stakeholder and regulatory compliance requirements established for the project • Coordination of operational implementation in the field • Sample shipping logistics • Day to day communication with Shell
Vessel Master (VM)	• Is the primary operator of the vessel • In United States (US) waters, must comply with US Coast Guard (USCG), state, and local regulations • Is responsible for all aspects of boating operations, regardless of any senior personnel present on the boat. These responsibilities include, but are not limited to: o Safety of the vessel and all persons on board o Safe transport of the vessel to and from her berth, if applicable o The safe operation of all shipboard equipment o Ensuring that all required operational and safety equipment is on board and that crew and passengers know the location and how to operate safety/survival equipment o Report all accidents, incidents, boardings, citations, safety concerns according to USCG regulations
Olgoonik Fairweather Project Manager (PM)	• Planning, coordination, and execution of the program as defined by Shell • Oversight of project assets and subcontractors
Olgoonik Fairweather Lead Scientist (LS)	• Development of EMP design and quality assurance project plan (QAPP) • Coordination and approval of study reports • Oversight of field and analytical activities

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Role	Responsibilities
Sr Marine Technician (MT)	• Field Instrument/Equipment Calibration, Maintenance, and Operation • Works with VM to determine if conditions are acceptable for deployment of sampling tools • Oversight and coordination (e.g., between VM and CS) of deployment and retrieval of sampling gear
Principle Investigator(s) (PI)	• Onshore based lead scientist for particular scientific field or subcontractor • Contribute expertise to development of sampling design, EMP, QAPP, and final reports. • Plan field sampling and execute post-field processing activities • Review laboratory data for reasonableness and usability • Communication of quality assurance (QA) and quality control (QC) requirements to project personnel
Chief Scientist (CS)	• Offshore based overall field scientific lead • Ensures field sampling procedures comply with QAPP and Standard Operating Procedures (SOPs) are being followed • Documents sample collection and processing activities, and initiates sample custody and/or additional sampling • Maintain custody of field records during ship-board activities • Review field records at the end of each sampling day
Field Team(s) (FT)	• Collect the samples after the sampling equipment is retrieved • Take control of the collected samples once determined to be acceptable and maintain custody of samples collected for chemical analysis • Process and preserve samples according to the QAPP, including all field documentation • Prepare and ship samples under custody to the appropriate analytical laboratories
Laboratory Manager(s) (Lab Manager)	• Conduct all sample analysis, reporting, analytical activities, as well as all activities related to sample custody records and processing in accordance with their contracts and the QAPP and SOPs • Review/QC data, assign laboratory qualifiers, and implement corrective action • Ensure independent QA oversight • Communicate any issues that could affect sample integrity, data quality, or schedule to contracting Laboratory QA/QC Officer • Perform internal verification and validation of all reported data • Submit data packages and electronic data deliverables (EDDs) that conform to QAPP requirements
Laboratory QA/QC Officer (Lab QA/QC)	• Review analytical data to verify that QAPP and SOP requirements were achieved • Ensure data are traceable to raw data, calculations are accurate • Ensure data qualifiers are applied to any data that do not meet the QAPP measurement quality objectives (MQO) requirements • Report the results of audit to management

3.2 Data Quality Objectives

The data quality objectives of the EMP are to address the following NPDES GP requirements:

1) Complete an initial site assessment, including a physical sea bottom survey, to ensure the exploratory facility is not located or anchored in a sensitive biological area or habitat;

2) Evaluate water-quality characteristics of the receiving water and potential effects of the specified discharges;

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

3) Evaluate sediment characteristics of the seafloor and potential effects of the discharges on the sediment characteristics;

4) Evaluate potential effects to the benthic community structure due to deposition of Discharge 001 (water-based drilling fluids and drill cuttings) and Discharge 013 (muds, cuttings, cement at the seafloor), which includes both spatial and temporal changes in community diversity and abundance; and

5) Evaluate the plume(s) in the vicinity of the discharges

3.3 EMP Technical Approach: (Phase I through IV)

The technical approach for the EMP requires collection of data during four different phases shown in Table 3-2. The types of analysis for the four phases are shown in Table 3-3. The sampling design described in Section 3.5 will describe each of the four phases and how they meet the DQOs of the EMP.

The sampling design is based on and intended to meet the data quality objectives (DQOs) of the EMP.

Table 3-2 Summary of Field Sampling for the Four Monitoring Phases

EMP Component	Matrix	Permit Reference	Existing Baseline Data (Phase I replacement) (pre-drill baseline)[1]	Phase II (during)	Phase III (post-drill)	Phase IV (no later than 15 months post drill)
Physical Oceanography/ Meteorology	Physical Characteristics (water)	II.A.f.2.	(X)[2]			
	Plume Monitoring (water)	II.A.j.4		X		
Biology	Benthic Community Structure (benthos/epibenthos)	II.A.f.4 II.A.i.2	X			X
	Physical Sea Bottom Survey	II.A.f.1. II.A.h.1. II.A.i.1	X		X	X
Chemistry	Water-based Drilling Fluids/Drill Cuttings	II.A.j.1		X		
	Sediment Characteristics (surface sediment)	II.A.j.2	X		X	X
	Benthic Community Bioaccumulation Monitoring (tissue)	II.A.j.3	X		X	X
Chemistry (continued)	Receiving Water Chemistry	II.A.f.3.	(X)[3]	X		
	Plume Monitoring (water)	II.A.j.4		X		

Notes:

[1] As indicated in the EMP, Appendix A, Phase I data includes historical data within the previous 5 years, sampling completed in 2012, 2013, additional samples of opportunity , and samples that may be collected concurrent with Phase II.

[2] Water column physical characteristics have historically been collected and additional data may be collected during Phase II.

[3] Reference samples will be collected outside the plume during Phase II as the most representative baseline (Phase I) data during drilling.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

3.3.1 Phase I Assessments

The Phase I data collected from the previous 5 years was compiled and analyzed to determine the variability within and among the data sets from the same region and to establish whether historical data from a larger geographical area may be predictive of current baseline data at site-specific locations. The results demonstrate that baseline data are available and are sufficient for replacement of Phase I permit requirements; therefore, Phase I sampling requirements are not addressed in this QAPP. The results of this analysis are presented in the EMP Appendix A.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 3-3 Summary of Analytical Parameters by Matrix

Parameter	Water Total	Water Particulate Phase	Water Dissolved Phase	Sediment	Tissue	Drilling Fluids/Cuttings[1]
Volatile Organic Carbon (VOC)/ Total Aromatic Hydrocarbons (TAH)[2,3]	(Phase II)[4]					Phase II
Saturated Hydrocarbons (SHC)	(Phase II)			Phase III Phase IV	Phase III Phase IV	Phase II
Total Petroleum Hydrocarbons (TPH)	(Phase II)			Phase III Phase IV	Phase III Phase IV	Phase II
Polycyclic Aromatic Hydrocarbons (PAH)	(Phase II)			Phase III Phase IV	Phase III Phase IV	Phase II
Petroleum Biomarkers				Phase III Phase IV	Phase III Phase IV	Phase II
Percent Lipid					Phase III Phase IV	
Particulate Organic Carbon (POC)	(Phase II)					
Total suspended solids (TSS)	(Phase II)					
Grain Size				Phase III Phase IV		
Total organic carbon (TOC)				Phase III Phase IV		
Sediment profile imaging (Sea Bottom) or ROV camera survey				Phase III Phase IV		
Benthic Community Structure (benthos/epibenthos)				Phase IV		
Aluminum (Al)		Phase II	Phase II	Phase III Phase IV	Phase III Phase IV	Phase II
Antimony (Sb)		Phase II	Phase II	Phase III Phase IV	Phase III Phase IV	Phase II

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Parameter	Water Total	Water Particulate Phase	Water Dissolved Phase	Sediment	Tissue	Drilling Fluids/Cuttings[1]
Arsenic (As)			Phase II	Phase III Phase IV	Phase III Phase IV	Phase II
Barium (Ba)		Phase II	Phase II	Phase III Phase IV	Phase III Phase IV	Phase II
Beryllium (Be)			Phase II	Phase III Phase IV	Phase III Phase IV	Phase II
Cadmium (Cd)			Phase II	Phase III Phase IV	Phase III Phase IV	Phase II
Chromium (Cr)		Phase II	Phase II	Phase III Phase IV	Phase III Phase IV	Phase II
Copper (Cu)			Phase II	Phase III Phase IV	Phase III Phase IV	Phase II
Iron (Fe)		Phase II	Phase II	Phase III Phase IV	Phase III Phase IV	Phase II
Lead (Pb)			Phase II	Phase III Phase IV	Phase III Phase IV	Phase II
Manganese (Mn)				Phase III Phase IV	Phase III Phase IV	Phase II
Mercury (Hg)			Phase II	Phase III Phase IV	Phase III Phase IV	Phase II
Methyl mercury			Phase II	Phase III Phase IV	Phase III Phase IV	Phase II
Nickel (Ni)			Phase II	Phase III Phase IV	Phase III Phase IV	Phase II
Selenium (Se)			Phase II	Phase III Phase IV	Phase III Phase IV	Phase II
Silver (Ag)			Phase II	Phase III Phase IV	Phase III Phase IV	Phase II
Tin (Sn)			Phase II	Phase III Phase IV	Phase III Phase IV	Phase II

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Parameter	Water Total	Water Particulate Phase	Water Dissolved Phase	Sediment	Tissue	Drilling Fluids/Cuttings[1]
Titanium (Ti)			Phase II	Phase III Phase IV	Phase III Phase IV	Phase II
Thallium (Tl)			Phase II	Phase III Phase IV	Phase III Phase IV	Phase II
Vanadium (V)				Phase III Phase IV	Phase III Phase IV	Phase II
Zinc (Zn)		Phase II	Phase II	Phase III Phase IV	Phase III Phase IV	Phase II
Total metals		6	19	19[5]	19[5]	19[5]

Notes:

[1] Analyses for total recoverable [metals] concentrations must be conducted and reported for each metal using EPA methods. The results must be reported in "mg/kg of whole mud (dry weight) and moisture content (percent by weight) of the original drilling fluid sample."

[2] TAH "as determined by EPA Method 602 (plus xylenes)".

[3] Total Aqueous hydrocarbons (TAqH) is the sum of TAH + PAH.

[4] As indicated in the EMP, Appendix A, Phase I data includes historical data, sampling completed in 2012, 2013 additional samples of opportunity, and samples that may be collected concurrent with Phase II.

[5] All required metals (Table A, NPDES GP) are included in the 19 metals. Manganese and vanadium are also included in sediments, muds and cuttings, and tissue sample analyses bringing the total metals for those matrices and phases to 21.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

This page intentionally left blank

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

3.3.2 Phase II Plume Monitoring and Observations

The objective of the plume-monitoring component is to measure metals, organics, turbidity and total suspended solids throughout the water column during periods of maximum discharge of water-based drilling fluid and drill-cuttings (Discharge 001). Additionally, the objective is to focus characterization efforts on areas of expected deposition of water-based drilling fluid and drill-cuttings based on model predictions. Plume monitoring will also serve as a check/verification of modeled effluent behavior.

Phase II plume monitoring will be conducted from a vessel configured to conduct environmental monitoring. Safety, operational and navigational issues could limit the ability to delineate plumes in the immediate vicinity of the drilling operations. Within these logistical constraints, efforts will be made to safely locate and sample the plume(s) during the drilling process. In order to assess maximum discharge of metals, hydrocarbons, turbidity, and total suspended solids, two primary time periods will be targeted.

(1) Drilling of the largest casing interval after the BOP stack is set; this time period represents the expected maximum discharge rate over the longest time interval of water-based drilling fluids and drill-cuttings during the drilling process.

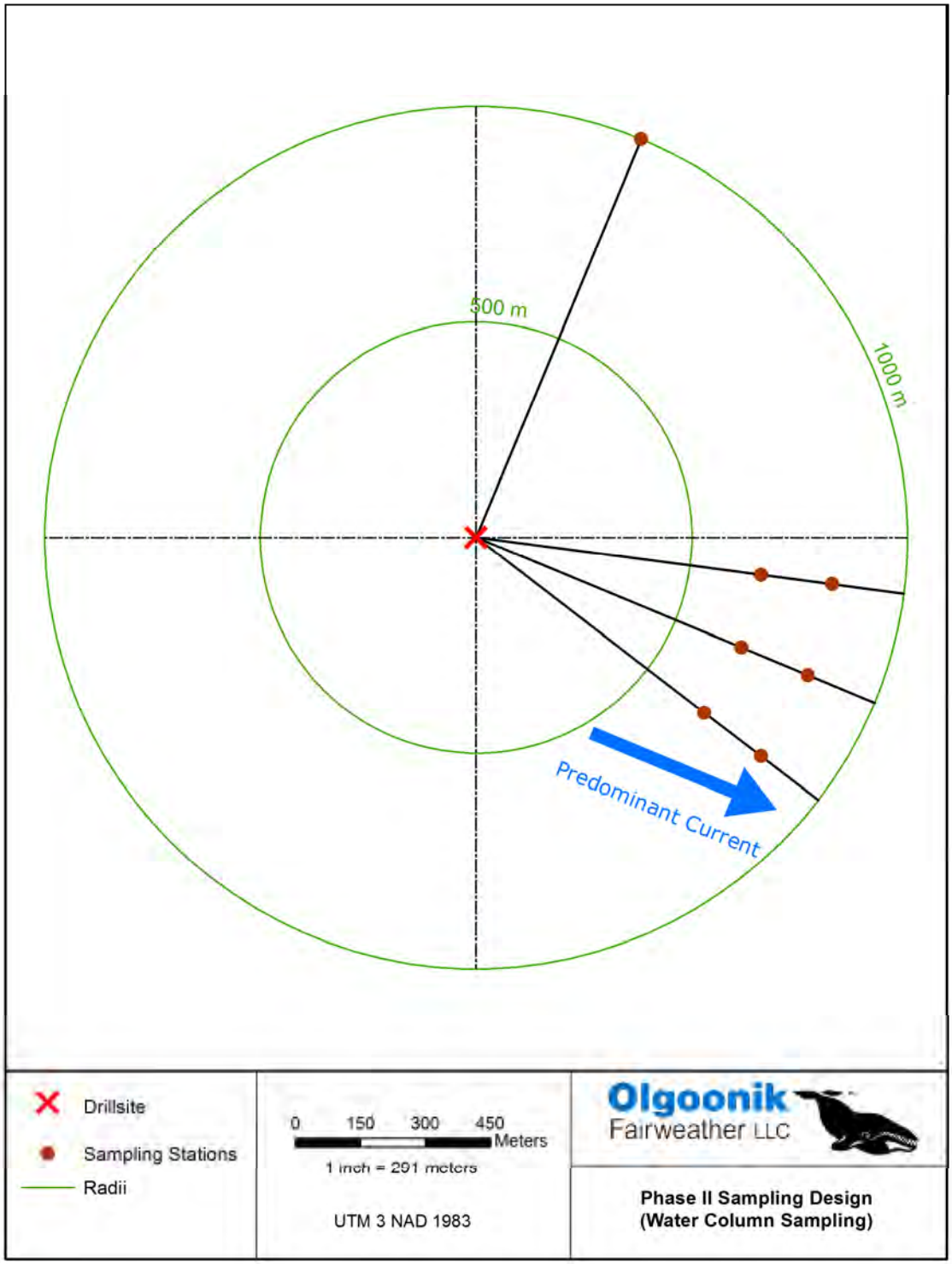
(2) During and/or immediately following bulk drilling fluid discharge; this discharge represents a period when only water based drilling fluid (with some finer entrained drill cuttings) is discharged and total suspended solids could be higher due to the small particle size of the material (barite and bentonite).

In the event that sampling during these time points cannot be conducted in the field, secondary options are presented in the EMP. During the two discharge events listed above, up to seven sampling stations will be targeted for sample collection (Figure 3-1). A total of up to 70 water samples will be targeted for collection plus 6 samples of drill cuttings and drilling mud will be collected during Phase II (Table 3-4). The direction of the predominant currents will be measured with the ADCP system and will be used to inform actual sampling stations during field activities.

The data collected during the Phase II monitoring will be used to assess the location of the plume(s), to refine model inputs, and to help inform the Phase III and IV monitoring efforts.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Figure 3-1 Phase II Water Sampling Stations



CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 3-4 Number of Samples Slated for Collection during Phase II

Sampling Water Depth[1]	Transect Type	Number of Samples (Estimated)			
		Phase – Largest Casing Interval	Phase – Bulk Drilling Fluids[2]	Other Intervals[4]	Total Number of Samples
1 m below surface	Plume	6	6	---	12
	Reference	1	1	---	2
10 m below surface	Plume	6	6	---	12
	Reference	1	1	---	2
20 m below surface	Plume	6	6	---	12
	Reference	1	1	---	2
30 m below surface	Plume	6	6	---	12
	Reference	1	1	---	2
2 m above bottom	Plume	6	6	---	12
	Reference	1	1	---	2
Drill-Cuttings	Drilling Rig	2	0[3]	2	4
Drilling Fluid	Drilling Rig	2	2	2	6
Subtotal		**Up to 39**	**Up to 37**	**Up to 4**	**Up to 80**

Notes:

[1] Sampling water depth may vary depending on in-field measurements of turbidity during plume monitoring, weather conditions, or operational parameters.

[2] If bulk discharge event occurs.

[3] No separate drill cuttings samples will be collected because they are not present at significant concentrations in the bulk drilling fluids.

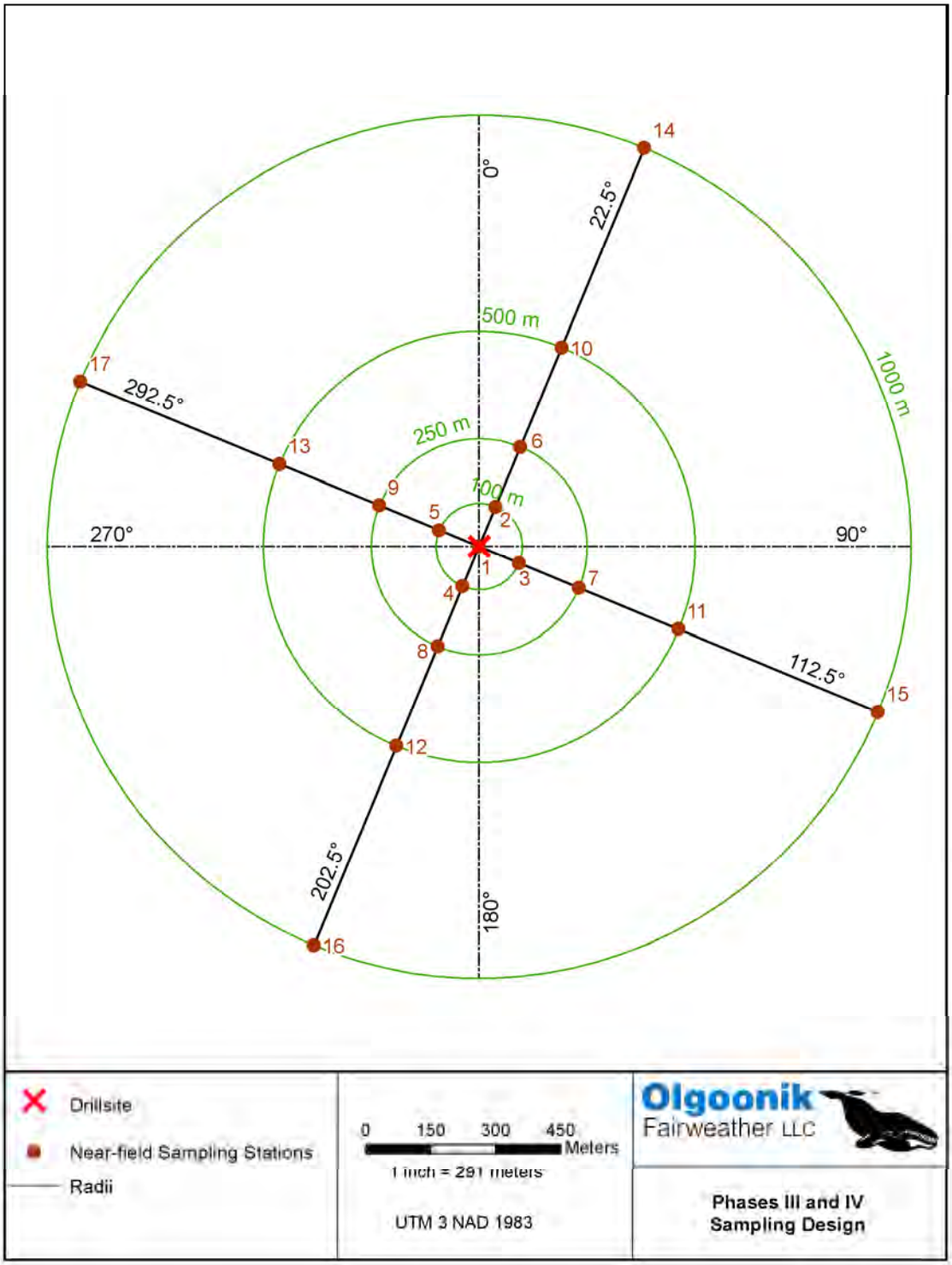
[4] Drill-cuttings and drilling fluids will be collected at each interval beyond the top hole as specified in the Drilling Fluids Plan.

3.3.3 Phase III Assessment

Phase III incorporates the post drill sampling immediately (as soon as practicable) following cessation of drilling at a well site. In the event that unforeseen circumstances occur preventing the environmental sampling of data immediately after drilling, the EPA will be notified immediately to determine the next course of action. A four-transect design (N, E, S, and W) off-set 22.5 degrees in line with the annual mean current direction, in conjunction with four different radii at 100 m, 250 m, 500 m, and 1000 m from the drill site location, will be used (Figure 3-2; Table 3-5).

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Figure 3-2 Phase III and IV Sampling Stations



CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

These transect orientations may be modified in the field, depending on observations made during the field effort (e.g., the Phase II ADCP data indicate a different trajectory for the predominant downstream current direction), and/or sediment profile imaging or ROV survey, and sediment grab samples will be used to also help determine the depositional area of the muds and cuttings.

Table 3-5 Summary of Near-Field and Far Field[1] Phase III and IV Samples Slated for Collection

Discipline	Number of Sample Design Near-field stations	Number of Far-Field[1] stations	Number of samples
Sediment Profile Imagery	Up to 17	Up to 2-4	Up to 19-21[2]
Benthic ecology (Phase IV only)	Up to 17	Up to 2-4	Up to 57-63 (3 reps, possibly 5 reps, depending on field conditions and operational limitations)
Chemistry—sediments	Up to 17	Up to 2-4	Up to 19-21
Chemistry—biota (clams)	Up to 4	Up to 1-2	Up to 5-6
Chemistry—biota (amphipods)	Up to 4	Up to 1-2	Up to 5-6

Notes:

[1] Far-field samples will be collected at 2-4 stations contemporaneous with the near-field stations. Far-field stations will be consistent with a subset of stations from the CSESP, where possible.

[2] Multiple photographs will be taken at each station (plan-view and cross-sectional) to ensure at least one high-quality photograph per station.

3.3.4 Phase IV Assessment

The sampling that occurs for the Phase IV monitoring must follow the same sampling design as for the Phase III sampling, as per the NPDES permit (Figure 3-2; Table 3-5). Sediment profile imaging (or similar technology), sediment chemistry, and tissue chemistry sample collection for Phase IV, if possible (e.g., if organisms are present for sample collection for chemical analysis), will be identical to the Phase III sampling design. Benthic community structure will be added for the Phase IV assessment to measure and assess any potential long term impacts to the benthic community as a result of the exploratory drilling operations. Three to five replicate sediment samples for identification and enumeration of benthic infauna will be collected from up to17 near-field stations and 2-4 far-field reference locations.

3.4 Field Sampling

3.4.1 Sampling Methods

The following section summarizes the field sampling procedures that will be used to implement the environmental monitoring plan. Details are provided in field SOPs provided in Appendix B.

3.4.1.1 Navigation

The Shell vessel navigation system will be used to track vessel and sampling locations during environmental monitoring if the accuracy of the system meets the EMP requirements (±10 m). If the

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

vessel navigation system cannot meet this level of accuracy, an auxiliary system will be provided to define sampling locations. The location of each sample is marked as a waypoint when the FT communicates to the VM that a sample is about to be collected. The milestone number is documented in the field log by the FT and the pre-assigned sample identification (ID) number is recorded with the waypoint number, creating a link between each sample and the station coordinates.

3.4.1.2 Acoustic Doppler Current Profiler (ADCP)

An ADCP will be mounted on the environmental sampling vessel. Real time water velocity data from this ADCP system will be used to determine the water speed and direction to estimate the probable trajectory of the plume. In addition, backscatter data from the ADCP will be used if adequate strength backscatter data are present, to determine the three dimensional shape of the plume and influence sampling locations and depths. Integrating the ADCP data with the sampling XYZ locations is done to maximize the effectiveness of the Phase II plume-sampling component.

After determining the XY sampling locations based on ADCP data, the Z component (water depth) will ultimately be determined by review of the turbidity and transmittance downcast data from the Sea-Bird SBE25*plus* system (Section 3.4.1.3). Discrete samples will be collected during the upcast at depths selected to cover the maximum and minimum range of turbidity observed in the downcast. Review of ADCP data will be ongoing throughout the discharge sampling event to maintain sampling focus within the observed plume (if a plume is observed). Sample XY and Z positions may change during the sampling as water velocities change.

3.4.1.3 Conductivity, Temperature, and Depth (CTD)

A Sea-Bird Electronics, Inc., SBE25*plus* (or similar) CTD profiler with (at a minimum) a turbidity sensor (e.g., Nephelometric Turbidity Units (NTU)) and a transmissometer will provide real-time multi-dimensional data on suspended solids to optimize water-sampling locations. The CTD may be mounted on the carousel water sampler and may be used to collect hydrographic data at each water station, depending on the apparatus used to collect water samples.

Twenty-five (25) carousel sensor measurements will be collected during the downcast from near surface (approximately 1 meter) to within approximately 2 m of the sea floor at each station. Salinity and density (as sigma-t) will be calculated using Sea-Bird software from the conductivity, temperature and depth data. Navigational position and time will be recorded concurrently with the hydrocast measurements. CTD profiles and the presence of suspended solids detected by the turbidity sensor(s) and transmissometer will indicate the presence of the plume in addition to ADCP water column velocity data and real-time weather conditions. Water samples will be collected during the upcast or downcast (depending on rosette type, to minimize sample contamination) within the depth zones indicating plume characteristics. CTD operation will follow the guidance of Battelle SOP 5-367-01 *Sea-bird Electronics SBE 25plus Sealogger and SBE 32 Carousel Water Sampler System.*

3.4.1.4 Water Samples

A total of up to 70 water samples representing the five different sampling depths in the water-column will be targeted for collection during Phase II using a multiple bottle carousel sampler (e.g., example pictured in Figure 3-3) or similar system. Samples will be collected in the carousel using GO-FLO or OTE Niskin

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

bottles (C Free). The sampling layout is depicted in Figure 3-1. Table 3-4 summarizes the sampling design. Sampling collection using the carousel sampler will follow the guidance of Battelle SOP 5-367-01 *Sea-bird Electronics SBE 25plus Sealogger and SBE 32 Carousel Water Sampler System.*

Transect locations will maximize the plume coverage in response to discharge and plume dynamics. The general procedure during each sampling event is proposed as follows:

1) The field team will use the real-time or near-real time ADCP data (if available) along with recent water column velocity data to determine the current direction and speed near the drilling operation.
2) Prior to initiation of plume sampling, whole-water samples and CTD/turbidity data will be collected along the reference transect located at least 1,000 m away and perpendicular to the up-current end of the downstream plume transect (Figure 3-1).
3) The plume-monitoring transect will be conducted across the plume (laterally) at intervals from as close to the release point as it is safe to occupy and down-current until evidence of the plume (e.g., turbidity measurements above background levels) disappears (Figure 3-1). ADCP data will be used to help locate the plume vertically and horizontally based on water volume velocity data and acoustic backscatter data. Modifications to the transect scheme may be made at the discretion of the CS in response to conditions encountered in the field.
4) Additional vessel transects along the plume (axially) may be made at the discretion of the field leader to help locate plume boundaries, pending vessel logistical considerations and priorities in the field.
5) Water samples will be collected with a sampling carousel within the plume at up to six stations along three transects (two stations per transect) oriented in the direction of the predominant current at each of five depths. The main plume transect will be positioned along the primary current direction. Two additional transects will be set at approximately ±10-15 degrees from the primary current direction (Figure 3-1). All plume-transect sampling stations will be attempted within 1000 m from the drilling location, with the near-field stations being as close to the discharge as logistically possible. The sampling vessel will be equipped with a laboratory supporting on-board water filtration for collection of water samples for analysis of dissolved metals. Water samples will be filtered as soon as practical on-board the vessel laboratory.
6) ADCP and CTD data will be used in an adaptive manner to optimize the location and depth for discrete water sample collection to capture the densest portion of the plume when possible. General target sample depths are approximately 1 m (near-surface), 10 m, 20 m, 30 m below the surface of the water, and 2 m above the sea bottom.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Figure 3-3 Example Carousel Water Sampler with Go-Flow Bottles and CTD Sensors

3.4.1.5 Muds and Cuttings

Two samples of used water-based drilling fluids and two samples of drill cuttings will be collected during drilling of the largest casing interval (after the blowout preventer (BOP) is set), and two samples of used water-based drilling fluids will be collected during bulk-mud discharge (if applicable), in Phase II of the monitoring program, for a total of 6 samples (Table 3-4). In addition, Permit No.: AKG-28-8100 Section II.A.13.j.1 requires metals analysis of each drilling fluid system. Different weight drilling systems are utilized in each drilling interval as described in the Drilling Fluids Plan. A sample from each drilling interval beyond the top hole (as specified in the Drilling Fluids Plan, i.e., 17 ½", 12 ¼", and 8 ½" hole sizes) will be collected and analyzed for the metals identified in Table A of Permit No.: AKG-28-8100 (Additional 4 samples shown in column termed "Other Intervals" in Table 3-4). Drilling-fluid

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

compositions and monitoring records will be obtained from the Daily Mud Report and Well Mud recap (done at end of well) to the degree possible.

The water-based drilling fluids and drill cuttings will be collected by personnel on the Shell drilling rig (e.g., M-I SWACO NPDES Compliance Specialists) and placed in clean glass jars. Sample handling and analysis will be performed in accordance with Section 3.5.2.

3.4.1.6 Sediment Samples

Sediments will be sampled at up to 17 near-field stations and up to two to four far-field stations during Phases III and IV with a double van Veen grab sampler (Table 3-5). Analytical chemistry samples will be collected from the top 2 cm (i.e., the surficial layer) of sediment. Depending on sediment observations from van Veen grab collections, gravity-core samples also may be collected in the field to obtain truly undisturbed cross-sectional samples of the sediment layer and to provide information on the depth/thickness of solids deposition caused by Discharges 001 and 013. The thickness of any overlying materials (water-based drilling fluids and drill cuttings) will be estimated by the CS or appropriate FT lead at the time of sample collection and recorded as part of the field documentation efforts.

<u>Van Veen Grab Sampler</u>

The double van Veen grab sampler is designed to be deployed from a vessel equipped with a power winch and A-frame or boom system and to collect undisturbed surface sediment samples to a maximal depth of approximately 15 cm. The double van Veen grab sampler enables chemistry and benthic infaunal samples to be co-collected from the same deployment. Fairweather Science (FWS) SOP 06 *Surface Sediment Sampling Using a Modified van Veen Grab Sampler* describes the operation of the grab sampler. Based on the sediment surface, the penetration depth of the grab sampler will be modified for softer or denser sediments. Weight will be added for dense, stiff sediment or removed for soft sediments. A sheet of material (e.g., plastic, plywood) may be fastened to the grab frame to slow the descent rate into the sediment to prevent over-penetration. In addition, the grab sampler can be used in a variety of sea conditions.

Upon return of the grab sampler to the deck of the vessel, the sampler will be placed on a table to enable sediment collection from the buckets. The hinged access doors on the top of the sampler are opened to determine whether the sample is acceptable for collecting material for analysis. The discipline specific FT lead makes this determination. An acceptable sample collection is one that displays the following characteristics:

- Sampler is not overfilled with sediment, the jaws are fully closed and the top of the sediment is below the level of the open doors.
- Overlying water must be present and must not be excessively turbid.
- No significant leakage of water from the sampler of the bucket used for collecting a sample, unless sediment is very coarse grained (e.g., gravel or coarse sand).
- The sampler is at least 80% full of sediment or the desired penetration has been achieved.
- The sediment is level on at least one side.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Overlying water with no excessive turbidity indicates that the sediment sample is undisturbed and that surface sediments remain intact (i.e., there was no significant leakage of water and, hence, fine sediment remains in the sampler). If unacceptable, the grab sampler will be redeployed at a slightly different location to avoid disturbance of the sediment layer from previous unacceptable grabs and drops of unwanted sediment.

If the grab sample is acceptable then samples will be collected according to the following steps:

1) Remove overlying water from the grab by siphoning or pumping through a pre-cleaned Teflon tube. (See Section 3.5.1.11 for equipment decontamination procedures).
2) Collect samples through the access doors into stainless steel bowls and/or clean glass sample jar, avoiding sediment that contacts the metal sides of the grab.
3) Collect the top 2 cm of sediment in the grab using a Kynar®-coated (or equivalent) scoop pre-marked with a 2-cm marking. This surficial sediment layer represents recent accumulation (in this case, potentially drilling muds and cuttings discharged as a result of the drilling operations) and incorporates the primary biogenic zone.

Once the top 2 cm have been removed from the grab into the homogenizing container, it will be gently but thoroughly mixed to a homogeneous color and consistency and subsampled into the appropriate containers for analysis of organics, metals, grain size, and total organic carbon (See Table 3-6). Any rocks, large shells, or rock debris will be removed from the sample.

<u>Gravity Core</u>

If collected, the sediment-core samples would be obtained most likely in the immediate vicinity of the drilling location and at the stations located within the 100 m and 250 m concentric radii from the drill site. If evidence exists in the field of muds or cuttings thicker than expected beyond the 100 m radii, additional core samples may be taken. Core samples would be collected only if/when sediment samples collected by grab or other data indicated substantial thickness of drilling muds or cuttings. Decisions regarding additional coring will be made at the discretion of the CS. Any sediment core samples would be in addition to the scope of the surface sediment sampling described earlier (e.g., in Table 3-5).

Battelle SOP 5-342 *Collecting Sediment Cores with a Piston Push/Hammer Corer* describes the operation of the gravity core. After collection, the core liner with sediment will be removed from the outer core tube. Following penetration and removal, the core will be examined for integrity and volume. The core is acceptable if the appropriate length is collected and the sediment recovered is relatively undisturbed throughout its depth. Disturbed cores will be rejected; a new core liner installed; and the station will be resampled. If not immediately processed, the core liner will be sealed at each end with electrical tape or an equivalent system (e.g. cable tie) and stored upright in ice for up to 6 hours prior to processing. Pre-cleaned core liners will be used to collect each sample; a new liner will be used for each station. The cores must be chilled (Table 3-6) and stored upright until processing.

Core sample processing will be conducted in the field on the vessel as follows:

1) Store the core liner with sample vertically prior to extraction.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

2) Insert a piston (constructed from Teflon®, plastic, or aluminum) attached to a post that is longer than the core into the bottom of the core tube.

3) Push the core tube down by hand, pushing adequate sediment (~4cm to satisfy laboratory requirements) out of the top of the core.

4) Using a clean utensil (plastic or Kynar® covered), scrape the outside of the core away and discard (this removes any material smeared along the sides of the core liner).

5) Using a second clean utensil (plastic or Kynar® covered), cut the sediment even with the top of the core tube and transfer to a clean collection jar.

6) Continue to extrude, scrape off the edges, and sample the core until completed. The length of each core segment will be based on observed horizons identified by the CS. It is anticipated that segment thicknesses could range from 4 – 10 cm.

7) Gently but thoroughly mix the sediment to a homogeneous color and consistency and subsample sediment into the appropriate containers for analysis of organics, metals, grain size, and total organic carbon (See Table 3-6).

Table 3-6 Sample Containers, Sample Sizes, Preservative Requirements, and Holding Times for Sediments, Tissue, and Water

Compound Class	Minimum Sample Size	Container[1]	Preservation	Holding Time[2]
Sediment/Water-Based Drilling Fluids/Cuttings				
Hydrocarbons[3]	8oz	Glass with Teflon lid	Frozen –20°C	1 year to extraction/40 days to analysis
VOC, muds and cuttings only	10g	Glass with Teflon lid	Cool <6ºC	14 days
Metals	2oz	Glass with Teflon lid	Frozen –20°C	1 year
Mercury	4oz (1/2 filled)	Glass with Teflon lid	Frozen –20°C	1 year
Methylmercury	4oz (1/2 filled)	Glass with Teflon	Frozen –20°C	1 year
TOC	2 oz	Glass	Cool <6°C, above freezing	6 months
Grain Size	4 qt	Plastic bag	Cool <6°C, above freezing	6 months
Benthic Animals	60ml	Whirl-Pak® plastic bags, various sizes	Buffered Formalin	1 month
Benthic Animals	60 mL	Glass jars	Transfer from formalin to ethanol	Indefinite
Tissue				
Hydrocarbons	8oz	Glass with Teflon	Frozen –20 °C	1 year to extraction/40 days to analysis
Metals	2oz	Glass with Teflon	Frozen –20 °C	1 year

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Compound Class	Minimum Sample Size	Container[1]	Preservation	Holding Time[2]
Tissue (continued)				
Mercury	4oz	Glass with Teflon	Frozen –20 °C	1 year
Methylmercury	4oz	Glass with Teflon	Frozen –20 °C	1 year
Water				
VOC[4]	3 x 40 ml vials	Glass with Teflon-lined lid	No head space. Acidified to a pH ≤2 with hydrochloric acid, above freezing	14 days
Hydrocarbons[5]	1 L (two 1-L bottles collected)	Glass with Teflon-lined lid	Acidified to a pH ≤2 with hydrochloric acid, above freezing	14 days to extraction/40 days to analysis
Metals (dissolved)	1L	HDPE	Acidified to a pH ≤2 with Nitric Acid	6 months
Metals (particulate filter)	1 mg on filter[6]	Plastic petri dish; double Ziploc bags	Dry	6 months
Mercury	0.5 L	Teflon	Acidified to a pH <2 with Hydrochloric Acid	90 days
Methylmercury	0.5 L	Glass with Teflon-lined lid	Acidified to a pH <2 with Hydrochloric Acid	180 days
POC	1	Glass Fiber filter in plastic petri dish	Frozen	1 year
TSS	1	Polycarbonate Filter	Frozen in sealed petri dish	6 months

Notes:

[1] Container Types: G = Glass/Teflon-lined lid; P=Plastic SPEX.
[2] "x" days/"y" days = maximum days from sampling to extraction/maximum days from extraction to analysis.
[3] PAH, SHC/TPH, petroleum biomarkers.
[4] Three 40-ml VOC vials w/ Teflon® septum and Zero head space.
[5] PAH, SHC/TPH.
[6] Volume filtered on 0.47-mm, 0.4-µm pore size polycarbonate filter based on the TSS concentration is typically 0.5 – 2.0 L.

3.4.1.7 Sediment Samples - Benthic Ecology Samples

Infaunal and epifaunal benthic invertebrates will be sampled with a double van Veen grab sampler at up to 17 near field stations and up to two to four far-field stations. Three to five replicate grab samples will be collected at each station (Table 3-5, Figure 3-2). Sediment samples for benthic ecology will be collected using the same protocol as for sediment samples collected for environmental chemistry. FWS SOP-06 *Surface Sediment Sampling Using a Modified van Veen Grab Sampler* describes the operation of the grab sampler. Photographs of the surface of the grab samples will be taken to compare to Plan View photographs taken during the SPI or ROV program.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Following the completion of the sediment sample collection at a particular station, a clean plastic bin will be placed underneath each side of the non-disturbed (no sediment removal for chemistry) grab samplers to empty the bucket with the remaining sediment for biota sorting (both for benthic ecology and biota chemical analysis samples). Samples will be rinsed using a 1.0-mm mesh stainless steel screen with water pressure sufficient enough to remove sediments but weak enough to minimize damage to the animals to isolate biological material (a stacked 0.5 mm sieve may also be placed beneath the 1.0 mm sieve to capture smaller organisms). The bucket that was used for sediment chemistry sampling may be used to obtain additional tissue mass for chemistry samples. Rinse water will be seawater filtered at least as low as the smallest sieve to remove any indigenous pelagic organisms that may be introduced into the benthic sample. Biological and sediment residues will be carefully removed from the sieve so that all visible animals, sediment particles, and fragments will be removed. The biological and sediment residue remaining in each sieve will be placed into separate pre-labeled plastic jars or Whirl-Pak® bags, preserved in 10% formalin buffered with borax or equivalent and securely stored for shipment to the laboratory. The sieving and sample preservation procedures for benthic ecology samples are described in Environ SOP SAM043.02 *Benthic Sample Collection and Processing for Shell Baseline Environmental Sampling Program – Chukchi Sea*.

3.4.1.8 Tissue Samples for Chemistry

Collection of biota samples (clams and amphipods) will be attempted at up to four (4) near-field stations and up to one to two additional reference stations each during both Phases III and IV (Table 3-5). Target locations for biota sampling will be stations 3, 7, 11, and 15 (stations along the mean current transect anticipated to be the area of potential plume) but the actual locations will be determined in the field based on the availability of clams and amphipods. Due to natural patchiness of the biota, it is unlikely that biota samples will be able to be collected at all specific proposed stations. Biota samples for tissue analysis will be collected by using a combination of a clam rake and double van Veen grab sampler at the same station for clams and by using baited modified minnow traps for amphipods. Previous efforts at collecting bivalves and other benthic organisms in the Chukchi Sea (J. Hardin, Battelle, San Diego, CA, pers. obs.) indicated that clams are not obtained in numbers large enough for tissue volumes required for chemical analyses with the double van Veen grab sampler. Alternatively, the use of a clam rake towed for a few minutes often provides adequate numbers of bivalves. Because sample size is important for chemical analysis in order to have enough sample mass to meet target detection limits for all analyses, the use of the clam rake is warranted for bivalve collection. Battelle SOP 5-365-01, *Collecting Benthic and Epibenthic Invertebrates with a Towed Clam Rake* and SOP 5-368-01, *Collecting Amphipods for Chemical Analysis Using Baited Traps* describe the collection procedures.

For bivalves, following the clam rake sample collection, the catch is brought aboard and emptied into large plastic tubs. The contents of the tubs then are sorted by trained personnel using clean-gloved hands. Target bivalve species include *Astarte* spp. and *Macoma* spp. If numbers are sufficient to provide the required tissue mass, one and the same species will be collected at each station; however, if this is not possible then it is more important to collect sufficient tissue mass for the analyses. Preliminary identification of the bivalve species will be determined in the field and verified by taxonomic identification. Collected bivalves are placed in a clean sieve and gently rinsed with seawater to remove external sediment and debris prior to being counted and photographed. Clams will be placed into pre-cleaned glass containers, and frozen. For amphipods, traps are recovered to the ship. Traps are opened up

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

and amphipods are gently rinsed from the trap and screens into a clean plastic sieve. Amphipods are separated from any visually adhered materials and sediment, then transferred into pre-cleaned glass containers, photographed, then frozen (Table 3-6). Chemical analysis will be conducted separately on whole body clams and on whole body amphipods (i.e., the organisms will not be dissected prior to chemical analysis).

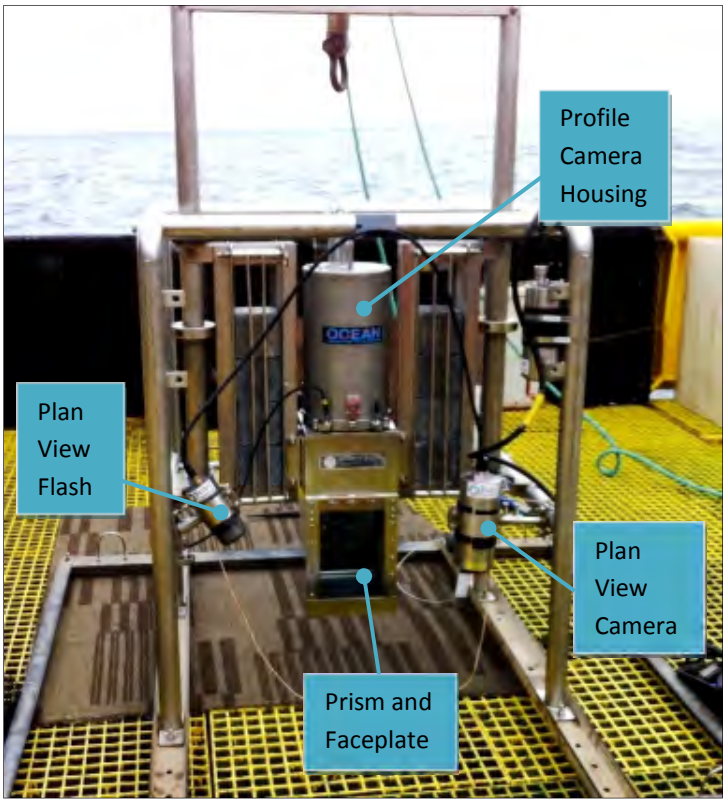
3.4.1.9 Sediment Profile Imaging

Plan-view digital photographs of the seafloor and sediment profile images (cross-sectional digital photographs of the sediment-water interface) will be obtained using SPI technology at up to 17 near field stations per drill site and up to two to four reference stations. Images will be assessed to characterize baseline seafloor conditions. Operation of the SPI will follow the guidance of NewFields SAM044.02 *Sediment Profile Imaging (SPI) and Plan View (PV) Photography Collection.*

The SPI system consists of a camera enclosed in a waterproof, pressure-resistant housing, a 45° prism that penetrates the sediment, and a mirror that reflects an image of the sediment profile through the camera lens to a digital camera (Figure 3-4). The camera frame also supports a downward-looking camera to view the surface of the seafloor. These images are viewed onboard the vessel after the system has been retrieved and permit the scientific crew to view conditions of the seafloor and the ability to provide near real-time guidance of sampling activities and strategy. The two independent camera systems are triggered by mechanical switches. The plan-view camera is triggered first at a pre-determined elevation above the sea bottom. When the system hits the sea bottom and the prism begins to penetrate the sediment, the SPI camera switch initiates time-delay electronics that trigger the camera to collect an image when the prism has completed penetration (~15 seconds). At each station, the camera is lowered to the seafloor a minimum of three times to ensure that replicate images suitable for analysis are obtained. At any station where difficulties are encountered, additional camera drops can be made. The date, time, station, water depth, photo number, and estimated prism penetration are recorded in a field log, with each drop of the camera also logged. The digital images are transferred to an onboard computer after each station for back-up. Images are transferred to a third location (e.g., an on-vessel external hard-drive) at least 1 time/day.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Figure 3-4 Sediment Profile Imaging and Plan View Camera Systems



Alternatively, photography of the ocean floor can be accomplished by the use of an ROV equipped with a downward-facing central digital camera with two flashes on both sides. The device may be placed in a sealed titanium housing with a window allowing for wide angle photographs, depending on water depth and pressure considerations. The distance between the sea floor bottom and the camera is known through the use of an altimeter on the ROV. If used, the ROV system provides both digital photographs and video recordings of sea bed characteristics and the epibenthic infaunal community structure only.

The ROV is powered through a hydraulic propulsion system which is supplied with power from the surface vessel through an electrical control umbilical. The ROV is deployed from the vessel or rig via an electrical winch that is attached to a tether management system (TMS). Once deployed, the TMS is suspended vertically below the surface vessel at an altitude above the seafloor of approximately 10 m. The ROV is then able to exit the TMS and make access to the seafloor to conduct its visual inspection of the sampling stations. Dependent on the ROV system in use, a lateral offset (maximum flying distance) between the ROV and TMS would be no greater than 100m. A video system consisting of multiple cameras allows the operators to direct the ROV and manipulate both mechanical arms and other systems. The ROV will be lowered to within 1-2 meter of the seafloor or to a distance such that the sea bed is not disturbed by the ROV propulsion system. Photographs and video footage at each sampling site will be collected for approximately 30 minutes at each sampling station visited or as required by the onboard science crew. Imagery is recorded in real time onto digital hard drives that are located onboard the vessel or rig. The digital images are transferred to an external hard drive after each station for back-up. Images are transferred to a third location (e.g., an on-vessel external hard-drive) at least 1 time/day.

3.4.1.10 Contamination Prevention

Extreme care will be taken to avoid cross-contamination of sampling equipment and samples during collection and processing. FWS SOP-04 *Decontamination of Equipment – Sediment, BRL SOP-01 Field Go Flo Bottle Decontamination,* and FWS SOP-07 *Decontamination of Tissue Sampling Equipment* describe general procedures for decontamination of field sampling equipment. Other procedures include the following:

- Avoid contact with hydrocarbon sources and any possible metals contamination during the collection of samples.
- Use only clean stainless steel, Kynar® or similar coating, and/or plastic equipment and utensils for sample collection.
- Decontaminate all components of the sampling equipment prior to use.
- Store sampling equipment away from grease drips from winches and winch wire, diesel smoke, and other potential airborne contaminants (e.g., smoking) when it is not being used to sample.
- Process samples in a clean area outside the influence of gasoline or diesel engines fumes and exhaust gases.

Rigorous decontamination procedures will be used to ensure that sampling equipment is clean and comply with the QAAP. The CS will be responsible for assuring SOPs are followed.

To the extent possible, non-contaminating, pre-cleaned materials (glass, stainless steel, Teflon™) will be used for sample collection. When this is not possible (steel equipment, core liners), the sampling equipment will be cleaned as described below; 1% Alconox® solution (or equivalent) will be used as soap. The use of solvents as part of the equipment decontamination process will be avoided, if possible, to limit the generation of solvent waste. However, if any oily sheen is noted or if oil contamination is suspected, then the affected equipment will be rinsed three times with methanol. The methanol must be completely evaporated prior to use of the equipment.

- Any utensils that will contact samples for chemical analysis (e.g., Kynar® coated, stainless steel, or plastic utensils, screens and forceps) will be scrubbed with soap and water and rinsed three times with deionized water.
- During the sample collection and processing, field personnel will wear nitrile (or equivalent) gloves that will be changed between stations.
- Sample coring equipment will be cleaned prior to use and between samples. A new core liner will be used for each station. Other components of the core will be thoroughly scrubbed with a stiff brush and soapy water and thoroughly rinsed with site water at the beginning of each day and between each sampling station.
- All sources of contamination (airborne sources, fingers, unclean equipment) should be avoided.
- The core liner will be sealed at both ends to contain the sediment and keep contamination out. The core sample will not be removed from the liner until it is ready for processing under controlled conditions.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

3.4.2 Sample Handling and Custody

The procedures described in this section are designed to ensure that sample integrity and custody are maintained at all times. If the sampling labeling, preservation, holding times, or custody requirements are not met, Shell will be notified. The laboratory may proceed with testing with client approval and the data will be qualified by including a discussion of any protocol deviations in the analysis report. If deemed feasible, the client may elect to provide a replacement sample for the out-of-specification sample and the initial sample rejected for further testing.

3.4.2.1 Sample Labeling

A unique sample identification (ID) number must be assigned to each sample. The sample ID must be documented by the CS in the field logbook and communicated to the ship navigation system so that sample location and collection information are definitively linked to a specific sample container. The sample ID is a concatenation of the sample year, station ID, replicate number, sample type in the form as shown in Table 3-7. For example, a sample collected from Burger A drill site, station BA001a, which is replicate 3 for benthic ecology would be identified as: 14-BA001a-03-BE. Each sample will also include a designation to include analysis type (eg. Hydrocarbons or metals in sediment, water or tissue).

Table 3-7 Sample Identification Scheme

Character Position in Sample ID	Description	Example
1,2	Year	14 (i.e., 2014)
3-8	Station ID	BA001a
9,10	Replicate Number	03
11,12	Sample Type	BE
Sample Identification Code Definitions		
Codes for Sample Types	QC Sample Types	Visit Number
AC = Amphipod chemistry BC = Bivalve chemistry BE = Benthic ecology CC = Cuttings chemistry DC = Drilling fluid chemistry GS = Grain size LC = Water (liquids) chemistry PV = Sediment Profile Imaging plan view camera photograph SC = Sediment chemistry SP = Sediment Profile Imaging photograph TOC = Total organic carbon	EB = Equipment blank FB = Field blank TB = Trip blank (VOCs)	A unique sample ID if re-sampling is needed. The default is 01, and is incremented each time a sample is recollected.

Each sample must be labeled with the unique sample identification number as soon as it is containerized. Sample labels must provide sufficient detail to uniquely identify each sediment sample and allow tracking to field activities. An example label is shown in Figure 3-5.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Figure 3-5 Example Sample Label

Project Chukchi Sea_____ **Sample ID**_____

Collection Date (YYMMDD)_____ Time (2400) **Station ID**_____

Matrix (Circle one): Sediment / Water / Tissue / Drilling Fluid / Cuttings

Water Type (Circle one): Whole / Particulates / Dissolved

Tissue Type (Circle one or enter other): Macoma / Astarte / Other: _____

Analysis Type: Organics Metals POC TSS TOC Grain size Biology

Preservation (Circle): Chill Freeze Acidify Formalin None Other_____

Sample Collector Initials:_____

Container ___ of ___ (*e.g.*, 1 of 2, 2 of 2) if the sample is contained in more than one container.

3.4.2.2 Sample Preservation and Packing for Shipment

Once samples are transferred to sample containers for analysis, they will be preserved as specified in Table 3-6 and maintained at the required temperature/conditions until packaged for shipment to the laboratories. FWS SOP-03 *Sample Packaging and Shipping* describes these procedures. Every effort will be made to deliver the samples to the analytical laboratories in a timely manner to meet the sample holding times.

To prepare samples for shipment,

- Protect the sample jars with shock insulation such as bubble wrap. The cooler should have insulation placed on the bottom of the cooler and the samples should be wrapped in insulation if breakable or crushable containers are used.
- For coolers containing samples for chemical analysis, add gel ice or cubitainers of frozen water to achieve the proper temperature and to ensure that the samples stay at a constant temperature for their entire trip.
- Pack samples tightly so that they cannot move freely in the cooler; they must be secure.
- An upper weight limit of 50 pounds per cooler is suggested.
- For coolers containing samples for chemical analysis, place a temperature blank container in each cooler.
- Record the contents of the coolers and list them on the chain-of-custody (CoC) forms.
- Affix two CoC seals on each cooler with samples. Packing and labeling will conform to IATA regulations for the sample preservative.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

3.4.2.3 Holding Times

Sample holding conditions and holding times are defined in Table 3-6. Holding times are determined from the time of sample collection. Documentation must be sufficient to track sample holding, processing, and analysis times to ensure that holding times are met. Samples must be held in a controlled area with limited access. Some data results with short holding times may be flagged due to the logistics of transporting the samples from the remote site to the analytical laboratories. These data are expected to still be usable within the confines of the data quality objectives presented in this QAPP.

Field samples collected for organics or metals analysis will be held for six months after delivery of final data; sample extracts and digestates will be held for one month. Disposal records for unextracted samples, extracted samples, sample containers, and sample extracts must be sufficient to provide tracking from collection, through laboratory receipt, to sample disposal.

3.4.2.4 Chain-of-Custody Records

Sample custody records are the administrative records associated with the physical possession and/or storage history of each individual sample from sample collection to the final analytical result and sample disposal. FWS SOP-02 *Sample Custody* and FWS SOP-03 *Sample Packaging and Shipping* describe these procedures. Sample custody will be initiated by the sample collection records that identify for each unique sample identification number the date, time, collection location, and collector.

During the survey, samples will be in the custody of the FT(s), who will store samples securely under the preservation requirements defined in Table 3-6. When samples are packaged for shipment to the analytical laboratories, the FT(s) will verify that each sample is recorded on the appropriate custody form. Each sample custody form will be signed by the FT(s), relinquishing the samples once he/she has verified that the custody form is accurate; that all samples present in the shipping container are listed on the form, and that the sample descriptions, requested analytical methods, and sampling dates are accurate. The sample custody form provides a record of the samples collected and analyses requested. The custody form should be sealed in a plastic bag and taped to the inside lid of the cooler. The original sample custody forms accompany the samples; the shipper will keep a copy.

If more than one cooler is sent in one shipment to the laboratory, then each cooler will contain a separate custody record for the samples in that cooler. In addition, the outside of the coolers will be marked to indicate the number of coolers in the shipment (*e.g.*, 1 of 2, 2 of 2). Two custody seals will be placed on each cooler lid on opposite sides and will be signed and dated.

Upon receipt at the designated laboratory, sample custody forms will be signed by the person receiving the samples once that person has verified that all samples identified on the custody forms are present in the shipping container. Any discrepancies will be noted on the form (in addition to any internal laboratory documentation policy) and the sample receiver will immediately contact the Lab Manager to report missing, broken, or compromised samples.

Each analytical laboratory must have a formal, documented system designed to provide sufficient information to reconstruct the history of each sample, including preparation of sampling containers, sample collection and shipment, receipt, distribution, analysis, storage or disposal, and data reporting within the

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

laboratory. Laboratory documentation must provide a record of custody for each sample throughout processing, analysis, and disposal.

Field custody of electronic data, including all data on navigation, CTD, dissolved oxygen, ADCP acoustic backscatter, and optical-backscatter turbidity will be the responsibility of the field survey's CS. The field custody of the electronic data consists of creating external hard-drive backups of all electronic data generated each day. The label on the backup media will include a survey ID, date, and name of person creating the backup files. The data will be transferred to a software system capable of physical oceanographic processing upon completion of the survey.

3.4.2.5 Sample Archiving

Samples must be archived under the conditions specified in Table 3-6 until the final analytical data have been received, reviewed, and approved by the scientific field specific PI.

3.4.3 Field Instrument/Equipment Calibration, Maintenance, and Operation

Field equipment must be tested, maintained, and calibrated according to SOPs and the manufacturers' instructions prior to use in the field to avoid breakdowns that could impact schedule or loss of data. The instruction manuals and SOPs must be available for all field equipment so that trouble-shooting and routine repairs can be conducted in the field. Spare parts recommended by the manufacturer should be stocked on the vessel. Major maintenance should be documented in the field logbook. Maintenance must be documented to track instrument performance or problems. Documentation should include the name of the person performing the maintenance, date maintenance was performed, a description of the maintenance activity, and (if the maintenance was performed in response to a specific instrument performance problem) the result of re-testing to demonstrate that the instrument performance had been returned to acceptable standards prior to re-use. Calibration, maintenance, testing, and inspection requirements for field equipment are defined in Table 3-8 and is the responsibility of the MT.

3.5 Laboratory Analysis

3.5.1 Analytical Methods

Laboratory-specific detection limits and reporting limits have been evaluated against the EMP objectives, and have been deemed sufficient for their intended uses.

Table 3-9 summarizes the methods that will be utilized by matrix and parameter. As noted on the table, more than one method may be used for trace metals. Analytical laboratory SOPs and QA/QC data will be provided to the EPA upon request.

Table 3-8 Field Equipment Calibration, Maintenance, Testing, and Inspection

Equipment	Activity	Frequency
Carousel- Sea Bird SBE25*plus* CTD and sensors (or equivalent)[1]	Calibration	Prior to survey
	Maintenance	Prior to survey; as necessary
	Testing	After any modifications/changes
	Inspection	Visual inspection before and after each cast, data reviewed after each cast

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Equipment	Activity	Frequency
GPS[2]	Calibration	NA
	Maintenance	As necessary (GPS systems do not require scheduled maintenance)
	Testing	As necessary (GPS systems do not require scheduled testing)
	Inspection	As per Ship's standard procedures, data accuracy will be continuous during critical navigation operations
Sediment Profile Imaging System[3]	Calibration	Prior to survey
	Maintenance	Prior to survey; as necessary during survey (no scheduled maintenance)
	Testing	After each cast
	Inspection	Visual inspection before and after each cast; photographs reviewed after each cast
ADCP	Calibration	Prior to survey
	Maintenance	Prior to survey and deployment
	Testing	Prior to survey and deployment.
ROV System	Maintenance	Ongoing as required for continued operations

Notes:

[1] Samples/direct measurements collected: Conductivity/salinity, temperature, depth, fluorescence, turbidity, transmissivity.

[2] Samples/direct measurements collected: Location of sampling equipment at time of sample or direct measurement.

[3] Samples/direct measurements collected: Sediment profile images, sediment characterization.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 3-9 Laboratory Analytical Methods

Compound Class (Units)	Method (EPA Citation)	Possible Laboratory[1]	Laboratory SOP Analysis Method
Water			
VOCs	EPA 8260[2]	Battelle – Norwell	5-245 GC/MS purge and trap
PAH	EPA 8270	Battelle – Norwell	5-157 GC/MS
SHC/TPH	EPA 8015 (Mod)	Battelle – Norwell	5-202 GC/FID
Metals (Dissolved): As, Be, Cd, Cr, Cu, Ni, Pb, Sb, Se, Tl, Zn	EPA 1640, (Mod)	Brooks Rand Laboratory	BR-0066/BR-0060
Metals (Dissolved): Ag, Al, Ba , Fe, Mn, Sn, Ti, V	EPA 1638, (Mod)	Brooks Rand Laboratory	BR-0060
Mercury (Dissolved)	EPA 1631E	Brooks Rand Laboratory	BR-0006
Methylmercury (Dissolved)	EPA 1630	Brooks Rand Laboratory	BR-0011
Metals (Particulates): Al, Ba, Cr, Fe, Zn, Sb	EPA 1638, (Mod)	Brooks Rand Laboratory	BR-0060
POC (Particulates)	EPA 9060/Lloyd Kahn	Brooks Rand Laboratory	EPA 9060/Lloyd Kahn
TSS (Particulates)	SM 2540 D (Mod)	Brooks Rand Laboratory	BR-1500 (Mod)
Sediment and Drilling Fluids/Cuttings			
VOCs, muds and cuttings only	EPA 8260	Battelle – Norwell	5-245 GC/MS purge and trap
PAH	EPA 8270	Battelle – Norwell	5-157 GC/MS
Petroleum Biomarkers	EPA 8270 (Mod)	Battelle – Norwell	5-157 GC/MS
SHC/TPH	EPA 8015 (Mod)	Battelle – Norwell	5-202 GC/FID
Metal: Ag, As, Ba, Be, Cd, Ni, Pb, Sb, Se, Sn, Tl, V	EPA 6020A	Florida Institute of Technology	FIT-2012 Series ICP-MS
Metals: Al, Cr, Cu, Fe, Mn, Ti, Zn	EPA 7000B	Florida Institute of Technology	FIT-2010 Series FAAS
Total Mercury	EPA 7473	Battelle – Sequim	FIT-2014 CVAAS
Methylmercury	EPA 1630M	Battelle – Sequim	MSL-I-015 CVAF
TOC	Modified EPA 415.1	Florida Institute of Technology	FIT-2015 TOC Analyzer
Grain Size	NA	Florida Institute of Technology	FIT-2010-GS

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Compound Class (Units)	Method (EPA Citation)	Possible Laboratory[1]	Laboratory SOP Analysis Method
Tissue			
PAH/Petroleum	EPA 8270	Battelle – Norwell	5-157 GC/MS
Petroleum Biomarkers	EPA 8270 (Mod)	Battelle – Norwell	5-157 GC/MS
SHC/TPH	EPA 8015 (Mod)	Battelle – Norwell	5-202 GC/FID
Metal: Ag, As, Ba, Be, Cd, Ni, Pb, Sb, Se, Sn, Tl, V	EPA 6020A	Florida Institute of Technology	FIT-1012 Series ICP-MS
Metals: Al, Cr, Cu, Fe, Mn, Ti, Zn	EPA 7000B	Florida Institute of Technology	FIT-1013 Series FAAS
Total Mercury	EPA 7473	Battelle – Sequim	MSL-I-034 CVAAS
Methylmercury	EPA 1630M	Battelle – Sequim	MSL-I-015 CVAF
Percent Lipid	NA	Battelle – Norwell	SOP 5-190 Gravimetric

Notes:

[1]Possible analytical laboratories are listed. Laboratories may change prior to project implementation and may include ALS Global (Kelso, WA for hydrocarbons, TOC, Grain Size analysis) and Brooks Rand Laboratory (Seattle, WA for metals analysis) or other contract analytical laboratory/laboratorie(s).

[2] VOC compounds are the Method 602 compounds plus o, m, p-xylene.

[3] Inductively-coupled plasma-mass spectrometer (ICP-MS) following preconcentration using method of Nakashima et al. (1988).

[4] Inductively-coupled plasma-mass spectrometer (ICP-MS) following preconcentration using a SeaFast system (Hathorne et al. 2012).

[5] USEPA SW-846 Method Series [6]010C with analysis by inductively coupled plasma/mass spectrometry (ICP-MS) according to FIT SOP 6005.

3.5.2 Samples for Metals Analysis

Samples of drill cuttings, mud samples, water, sediments, and tissues will be analyzed for a suite of metals. The analyses will be conducted following protocols that have been developed specifically for reliable trace-level analysis of the target metals in complex marine environmental samples. The analytical protocols have been used extensively for baseline characterization and monitoring the potential impact of offshore oil and gas activities in Alaska, including in the CSESP, Chukchi Offshore Monitoring In Drilling Area – Chemistry and Benthos (COMIDA-CAB), Arctic Nearshore Impact Monitoring In Development Area (ANIMIDA), and Continuation of Arctic Nearshore Impact Monitoring In Development Area (cANIMIDA) programs. Table 3-10 lists the metals that will be analyzed for each phase of the EMP and the applicable analytical instrument.

3.5.2.1 Metals in Water (Phase II) Samples

Dissolved metals in water samples collected during drilling activities (Phase II) will be analyzed for the list of 19 metals (Table 3-10). The dissolved-phase metal samples will be pre-concentrated prior to analysis. Particulate-bound metals in water samples collected during the plume-monitoring component in Phase II will be analyzed for 6 metals (Table 3-10) known to be indicators of particles derived from drilling muds and cuttings; the suspended particles will be air-dried (at ~50% humidity). The samples will be analyzed by inductively coupled plasma/mass spectrometry (ICP/MS) for determination of the

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

different metals. Mercury concentrations will be measured by Cold Vapor Atomic Fluorescence Spectrometry (CVAFS). These methods are based on USEPA methods described for Series 1630 and 1631E (CVAFS), and Series 1638 (ICP/MS), with optimization to address the required detection limits and the sample matrices.

3.5.2.2 Metals in Sediment (Phases II, III, and IV) Samples

Sediment samples and muds and cuttings samples will be analyzed for a suite of 19 metals (see Table 3-10). The well-mixed mud/cuttings and sediment will be freeze-dried and then totally digested in Teflon® beakers using concentrated high-purity hydrofluoric acid (HF), nitric acid (HNO_3) and perchloric acid ($HclO_4$). The liquid-phase and clear samples will be diluted with distilled deionized water (DDW) prior to analysis. The dissolved-phase water samples will be concentrated prior to analysis. Sediment samples to be analyzed for mercury will be digested by heating with HNO_3 and sulfuric acid (H_2SO_4). The samples will be analyzed by FAAS, CVAF, cold vapor atomic absorption spectrometry (CVAAS), or ICP/MS for determination of the different metals. Total mercury concentrations will be measured by CVAAS and methylmercury by CVAF. These methods are based on USEPA methods described for Series 7000 (FAAS and ICP-MS), Series 7473 (CVAAS), Series 1630M (CVAF), and Series 6010A (ICP/MS, with optimization to address the required detection limits and the sample matrices). Analyses of muds and cuttings for concentrations of total recoverable metals will be conducted following EPA methods, and results will be reported in mg/kg of whole mud (dry weight) and moisture content (percent by weight) of the original drilling-fluid sample. Laboratory limits of quantitation (LOQ) and limits of detection (LOD) are defined in Table 3-10.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 3-10 Metals and Analytical Instruments for Each Phase of Environmental Monitoring with Laboratory Limits[1]

Analyte	Analytical Instrument[2]	Dissolved Metals Water		Particulate Metals Water		Sediment &Drilling Mud/Cuttings		Tissue	
		MDL (µg/L)	MRL (µg/L)	MDL (µg/g)	MRL*Est (µg/g)	LOQ (µg/g)	LOD (µg/g)	LOQ (µg/g)	LOD (µg/g)
Aluminum (Al)	ICP-MS	50	150	TBA	3.00	0.015%	0.003%	10	2
Antimony (Sb)	ICP-MS	0.004	0.015	-	-	0.005	0.0014	0.005	0.001
Arsenic (As)	ICP-MS	0.030	0.100	-	-	0.10	0.02	0.06	0.012
Barium (Ba)	ICP-MS	1.00	3.00	TBA	0.01	0.05	0.01	0.05	0.01
Beryllium (Be)	ICP-MS	0.006	0.013	-	-	0.005	0.001	0.005	0.001
Cadmium (Cd)	ICP-MS	0.004	0.012	-	-	0.025	0.005	0.005	0.001
Chromium (Cr)	ICP-MS, FAAS	0.040	0.100	TBA	0.03	8	1.6	0.05	0.01
Copper (Cu)	ICP-MS,FAAS	0.04	0.12	-	-	8.5	1.7	0.01	0.002
Iron (Fe)	ICP-MS, FAAS	12.0	50.0	TBA	1.00	0.05%	0.01%	12.5	2.5
Manganese (Mn)	ICP-MS, FAAS	0.75	3.00	-	-	15	3	5	1
Mercury (Hg), Total	CVAF (Dissolved) CVAAS (other)	0.10 ng/L	0.40 ng/L	-	-	5 ng/g	2 ng/g	5 ng/g	1.9 ng/g
Methylmercury (MeHg)	CVAF	0.02 ng/L	0.05 ng/L	-	-	0.05 ng/g	0.01 ng/g	5 ng/g	1.5 ng/g
Nickel (Ni)	ICP-MS	0.04	0.14	-	-	0.20	0.04	0.05	0.01
Lead (Pb)	ICP-MS	0.003	0.013	-	-	0.10	0.02	0.015	0.003
Selenium (Se)	ICP-MS	0.070	0.210	-	-	0.1	0.02	0.075	0.015
Silver (Ag)	ICP-MS	0.011	0.036	-	-	0.015	0.003	0.02	0.004
Tin (Sn)	ICP-MS	2.50	7.50	-	-	0.05	0.01	0.01	0.002
Titanium (Ti)	ICP-MS, FAAS	2.50	10.00	-	-	0.1%	0.02%	0.1%	0.02%
Thallium (Tl)	ICP-MS	0.003	0.010	-	-	0.015	0.003	0.005	0.001
Vanadium (V)	ICP-MS	1.05	3.00	-	-	0.01	0.01	0.05	0.01
Zinc (Zn)	ICP-MS, FAAS	0.26	0.75	TBA	0.20	2.5	0.5	2	0.4

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Notes:

[1] Actual detection limits (e.g., LOD, MDL) may be higher or lower, depending on the specific analytical laboratory under contract at the time of project implementation.

[2] CVAAS = Cold Vapor Atomic Absorption Spectrometry; CVAF = Cold Vapor Atomic Fluorescence; FAAS = Flame Atomic Absorption Spectrometry; GFAAS = Graphite Furnace Atomic Absorption Spectrometry; and ICP/MS = Inductively Coupled Plasma/Mass Spectrometry.

[3] Laboratory detection limits are verified and updated periodically according to FIT's quality system. Detection limits current at the time of analysis may vary from those defined in this QAPP. The actual laboratory LOQs and LODs will be reported with the laboratory data.

[4] To be determined (TBD). Laboratory LODs will be developed and reported with the study data.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

3.5.2.3 Metals in Tissue (Phases III and IV) Samples

Tissue samples will be analyzed for a suite of 19 metals (Table 3-10). Tissue samples for all metals, with the exception of Hg, will be freeze-dried and then digested by sequential addition of concentrated, high-purity nitric acid (HNO_3), hydrogen peroxide (H_2O_2), and hydrochloric acid (HCl). The solution will be diluted with distilled/deionized (DDW). Mercury analyses will be conducted following digestion with concentrated, high-purity HNO_3 and H_2SO_4

The samples will be analyzed by FAAS, CVAF, or ICP/MS for determination of the different metals. Mercury concentrations will be measured by CVAF and CVAAS. These methods are based on USEPA methods described for Series 7000B (FAAS), Series 1630M (CVAF), Series 7473 (CVAAS), and Series 6010C (ICP/MS, with optimization for particular sample matrices).

3.5.3 Samples for Hydrocarbon Analysis (Phases II, III, and IV)

Samples of drilling mud, cuttings, sediment, and tissues will be analyzed for a suite of PAH, petroleum biomarkers (sterane/triterpanes; St/Tr), TPH, and SHC compounds. Water samples collected during Phase II monitoring will be analyzed for VOCs, TPAH, SHC and TPH; but, petroleum biomarkers will not be measured in the water samples. The analyses will be conducted following SOPs (e.g., 5-157, see Table 3-9) that have been developed specifically for reliable trace-level analysis of the target parameters in complex marine environmental samples (e.g., Trefry et al. 2003 and 2012). The analytical protocols have been used extensively for baseline characterization and monitoring the potential impact of offshore oil and gas activities in Alaska, including in the CSESP, ANIMIDA, and cANIMIDA programs for hydrocarbon analysis.

The instrumental analysis will be conducted following methods that are modified from USEPA Methods 8015 (SHC) and 8270 (PAH and biomarkers), to obtain improved sensitivity and specificity, to include a number of additional key target parameters (e.g., alkyl PAHs and petroleum biomarkers), and to ensure that the analysis is appropriate for complex samples of drilling mud/cuttings, sediments, and biological tissues. The sample analyses are summarized below.

3.5.3.1 Hydrocarbons in Water Samples (Phase II)

Water samples will be extracted for PAH, SHC, TPH, and VOC compounds (Table 3-11, Table 3-12, and Table 3-13) following laboratory SOPs. Briefly, water samples will be prepared by fortifying a 1–2 L sample with surrogate internal standard (SIS) compounds, serially extracting the analytes of interest with dichloromethane (DCM), and preparing the samples for instrumental analysis. The sample extract will be dried and concentrated over anhydrous sodium sulfate and then will be purified with an alumina clean-up column. The extract will be concentrated and spiked with internal standards (IS) and split for instrumental analysis. One split will be submitted for SHC and TPH analysis by modified EPA Method 8015 by using gas chromatography with flame-ionization detection (GC/FID). The other split will be submitted for PAH analysis that uses a modified EPA Method 8270 gas chromatography/mass spectrometry (GC/MS) method with the detector operating in the selected ion-monitoring (SIM) mode. Target compounds will be quantified by using the method of internal standards using the SIS compounds resulting in surrogate

recovery-corrected data generated to represent the native sample concentrations. Laboratory reporting limits (RL) and method detection limits (MDLs) are reported in Table 3-11, Table 3-12 and Table 3-13.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 3-11 List of Polycyclic Aromatic Hydrocarbon and Alkyl PAH Target Analytes with Reporting Limits and Method Detection Limits[1]

Parameter	Whole Water (ng/L)		Sediment (ng/g dry)		Tissues (ng/g dry)	
	RL	MDL[2]	RL	MDL	RL	MDL
Naphthalene[3]	5.0	3.28	1.2	0.531	2.9	2.98
C1-Naphthalenes	5.0	3.28	1.2	0.531	2.9	2.98
C2-Naphthalenes	5.0	3.28	1.2	0.531	2.9	2.98
C3-Naphthalenes	5.0	3.28	1.2	0.531	2.9	2.98
C4-Naphthalenes	5.0	3.28	1.2	0.531	2.9	2.98
Biphenyl	5.0	1.43	1.2	0.162	2.9	1.25
Acenaphthylene	5.0	1.02	1.2	0.186	2.9	1.04
Acenaphthene	5.0	1.17	1.2	0.150	2.9	1.06
Dibenzofuran	5.0	1.36	1.2	0.201	2.9	2.29
Fluorene	5.0	1.02	1.2	0.138	2.9	3.02
C1-Fluorenes	5.0	1.02	1.2	0.138	2.9	3.02
C2-Fluorenes	5.0	1.02	1.2	0.138	2.9	3.02
C3-Fluorenes	5.0	1.02	1.2	0.138	2.9	3.02
Anthracene	5.0	1.27	1.2	0.225	2.9	0.726
Phenanthrene	5.0	1.20	1.2	0.246	2.9	2.62
C1-Phenanthrenes/Anthracenes	5.0	1.20	1.2	0.246	2.9	2.62
C2-Phenanthrenes/Anthracenes	5.0	1.20	1.2	0.246	2.9	2.62
C3-Phenanthrenes/Anthracenes	5.0	1.20	1.2	0.246	2.9	2.62
C4-Phenanthrenes/Anthracenes	5.0	1.20	1.2	0.246	2.9	2.62
Retene	5.0	0.681	1.2	0.174	2.9	0.600
Dibenzothiophene	5.0	1.23	1.2	0.144	2.9	1.28
C1-Dibenzothiophene	5.0	1.23	1.2	0.144	2.9	1.28
C2-Dibenzothiophene	5.0	1.23	1.2	0.144	2.9	1.28
C3-Dibenzothiophene	5.0	1.23	1.2	0.144	2.9	1.28

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Parameter	Whole Water (ng/L)		Sediment (ng/g dry)		Tissues (ng/g dry)	
	RL	MDL[2]	RL	MDL	RL	MDL
C4-Dibenzothiophene	5.0	1.23	1.2	0.144	2.9	1.28
Fluoranthene	5.0	0.682	1.2	0.444	2.9	0.944
Pyrene	5.0	0.531	1.2	0.537	2.9	0.848
C1-Fluoranthenes/Pyrenes	5.0	0.531	1.2	0.537	2.9	0.848
C2-Fluoranthenes/Pyrenes	5.0	0.531	1.2	0.537	2.9	0.848
C3-Fluoranthenes/Pyrenes	5.0	0.531	1.2	0.537	2.9	0.848
C4-Fluoranthenes/Pyrenes	5.0	0.531	1.2	0.537	2.9	0.848
Benzo(a)anthracene	5.0	0.610	1.2	0.369	2.9	0.752
Chrysene	5.0	0.710	1.2	0.333	2.9	0.606
C1-Chrysenes	5.0	0.710	1.2	0.333	2.9	0.606
C2-Chrysenes	5.0	0.710	1.2	0.333	2.9	0.606
C3-Chrysenes	5.0	0.710	1.2	0.333	2.9	0.606
C4-Chrysenes	5.0	0.710	1.2	0.333	2.9	0.606
Benzo(b)fluoranthene	5.0	0.883	1.2	0.390	2.9	0.723
Benzo(k)fluoranthene	5.0	0.839	1.2	0.201	2.9	0.663
Benzo(e)pyrene	5.0	0.798	1.2	0.303	2.9	0.642
Benzo(a)pyrene	5.0	1.14	1.2	0.411	2.9	0.468
Perylene	5.0	2.48	1.2	0.354	2.9	0.612
Indeno(1,2,3-cd)pyrene	5.0	0.808	1.2	0.462	2.9	0.543
Dibenz(a,h)anthracene	5.0	1.09	1.2	0.285	2.9	0.279
Benzo(g,h,i)perylene	5.0	0.990	1.2	0.450	2.9	0.417

Notes:

[1] Actual detection limits (e.g., LOD, MDL) may be higher or lower, depending on the specific analytical laboratory under contract at the time of project implementation.

[2] Laboratory MDLs are verified and updated periodically according to the organization's quality system. MDLs current at the time of analysis may vary from those defined in this QAPP. The actual laboratory MDLs and RLs will be reported with the laboratory data. Water MDL/RL based on a 1L sample size with a dilution factor of 1 and a PIV = 500uL. Sediment MDL based on a 20g sample size (wet weight; 16.63 g dry weight) with a dilution factor of 2 and PIV = 1000uL. Tissue MDL based on 20 g sample size (wet weight; 3.58 g dry weight) with a dilution factor of 2.05L and PIV = 500uL.

[3] Bolded compounds are the 16 priority PAH pollutants.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 3-12 List of Saturated Hydrocarbons Target Analytes with Reporting Limits and Method Detection Limits[1]

Parameter	Whole Water (ng/L)		Sediment and Drilling Mud/Cuttings (ng/g dry)		Tissues (ng/g dry)	
	RL	MDL[2]	RL	MDL	RL	MDL
n-Nonane	500	43.1	120	7.46	305	28.7
n-Decane	500	54.2	120	5.70	305	90.2
n-Undecane	500	31.4	120	5.93	305	35.8
n-Dodecane	500	31.9	120	6.42	305	30.4
n-Tridecane	500	24.1	120	7.57	305	21.5
Isoprenoid RRT 1380	NA[3]	NA	NA	NA	305	NA
n-Tetradecane	500	22.7	120	5.66	305	29.6
Isoprenoid RRT 1470	NA	NA	NA	NA	305	NA
n-Pentadecane	500	26.5	120	5.49	305	56.3
n-Hexadecane	500	36.3	120	12.9	305	30.1
Norpristane (1650)	NA	NA	NA	NA	305	NA
n-Heptadecane	500	35.5	120	5.71	305	48.0
Pristane	500	31.3	120	25.0	305	95.3
n-Octadecane	500	50.5	120	8.06	305	23.9
Phytane	500	33.2	120	9.23	305	24.9
n-Nonadecane	500	38.5	120	4.91	305	26.9
n-Eicosane	500	46.8	120	10.1	305	30.6
n-Heneicosane	500	54.1	120	3.07	305	29.3
n-Docosane	500	58.9	120	17.6	305	36.3
n-Tricosane	500	43.5	120	6.97	305	25.8
n-Tetracosane	500	63.6	120	17.4	305	25.1
n-Pentacosane	500	69.8	120	15.4	305	16.2
n-Hexacosane	500	72.6	120	10.2	305	15.4
n-Heptacosane	500	69.5	120	8.97	305	25.9

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Parameter	Whole Water (ng/L)		Sediment and Drilling Mud/Cuttings (ng/g dry)		Tissues (ng/g dry)	
	RL	MDL[2]	RL	MDL	RL	MDL
n-Octacosane	500	78.9	120	9.62	305	19.7
n-Nonacosane	500	58.3	120	6.26	305	23.0
n-Triacontane	500	57.7	120	6.85	305	21.1
n-Hentriacontane	500	55.6	120	4.05	305	40.0
n-Dotriacontane	500	52.7	120	5.74	305	25.7
n-Tritriacontane	500	58.1	120	2.87	305	23.9
n-Tetratriacontane	500	47.0	120	4.99	305	30.6
n-Pentatriacontane	500	50.0	120	5.19	305	26.8
n-Hexatriacontane	500	45.4	120	4.44	305	31.1
n-Heptatriacontane	500	48.1	120	9.92	305	40.0
n-Octatriacontane	500	43.2	120	5.65	305	44.3
n-Nonatriacontane	500	49.9	120	9.26	305	52.6
n-Tetracontane	500	52.4	120	10.0	305	60.6
SHC Total (C9-C40)	NA	NA	NA	NA	NA	NA
TPH Total (C9-C40)	NA	9200	NA	694	NA	267,000

Notes:

[1] Actual detection limits (e.g., LOD, MDL) may be higher or lower, depending on the specific analytical laboratory under contract at the time of project implementation.

[2] Laboratory MDLs are verified and updated periodically according to the organization's quality system. MDLs current at the time of analysis may vary from those defined in this QAPP. The actual laboratory MDLs and RLs will be reported with the laboratory data. Water MDL based on 1L sample with a dilution factor of 1 and pre-injection volume (PIV) = 500uL. Sediment MDL based on a 20g sample size (wet weight; 16.63 g dry weight) with a dilution factor of 2 and PIV = 1000uL. Tissue RL is estimated based on 20 g sample size (wet weight; 3.36 g dry weight) with a dilution factor of 2.05L and PIV = 500uL.

[3] NA = standards not available for this compound; the RL and MDL of the compound which elutes prior to the isoprenoid compound is applied.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Water samples will be analyzed for VOCs using gas chromatography by purge-and-trap techniques (Table 3-13). Samples are spiked with SIS and RIS and an inert gas is bubbled through the water samples. The VOCs are purged from the aqueous phase to the gas phase, which is swept through a sorbent trap where the VOCs are trapped, heated and back flushed with inert gas to desorb the components onto a non-polar fused silica capillary chromatographic column, separated via capillary gas chromatography, and identified and quantified using electron ionization mass spectrometry in the Full Scan mode. Target compounds will be quantified by using the method of internal standards using the SIS compounds resulting in surrogate recovery-corrected data generated to represent the native sample concentrations.

Table 3-13 List of VOC Target Analytes with Reporting Limits and MDLs[1]

Parameter	Whole Water (ng/L)		Drilling Muds and Cuttings (ng/g)	
	RL	MDL[2]	RL	MDL
1,4-Dichlorobenzene[3]	5.0	0.984	1.2	0.0737
1,3-Dichlorobenzene[3]	5.0	0.984	1.2	0.0737
1,2-Dichlorobenzene[3]	5.0	0.984	1.2	0.0737
Benzene	2950	564	11.8	1.21
Chlorobenzene[3]	TBD[2,3]	TBD	TBD	TBD
Ethylbenzene	2860	506	11.4	1.62
Toluene	1930	348	7.69	1.08
m-xylene	938	227	3.70	0.603
p-xylene	1990	311	7.94	1.20
o-xylene	957	180	3.82	0.528
Total Aromatic Hydrocarbons (TAH)	NA	NA	NA	NA

Notes:

[1] Actual detection limits (e.g., LOD, MDL) may be higher or lower, depending on the specific analytical laboratory under contract at the time of project implementation.

[2] Laboratory MDLs are verified and updated periodically according to the organization's quality system. MDLs current at the time of analysis may vary from those defined in this QAPP. The actual laboratory MDLs and RLs will be reported with the laboratory data. Water MDL based on a 0.02 L sample size and a dilution factor of 1. Sediment MDL based on a 5g sample size and a dilution factor of 1.[3] These parameters may be analyzed by GC/MS purge and trap (SOP 5-245) or GC/MS SIM (SOP 5-157). MDLs are for GC/MS SIM using 20 g wet wt sediment (16 g dry weight) and 1L of water.[3] To be determined (TBD). Laboratory MDLs will be developed and reported with the study data.

3.5.3.2 Hydrocarbons in Sediment Samples (Phases III and IV)

Samples of sediments, drilling muds, and cuttings will be extracted for PAH (Table 3-11), SHC and TPH (Table 3-12), and petroleum biomarkers St/Tr (Table 3-14), following laboratory SOPs. Muds and cuttings will also be analyzed for VOCs. Briefly, approximately 30 g of wet sediment will be fortified with SIS compounds and serially extracted with DCM. Less material may be used for the analyses of used drilling mud and cuttings because they may contain higher hydrocarbon concentrations than native sediment.

The sample extract will be dried and concentrated over anhydrous sodium sulfate. The extract will be purified with activated copper to remove any sulfur that is present and then will be purified further with an alumina clean-up column. The extract then will be purified further using silica gel column fraction to

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

isolate the TPH/SHC fraction and petroleum biomarker fraction (F1) from the aromatic hydrocarbon fraction (F2). The resulting extracts will be concentrated and spiked with IS compounds. The TPH/SHC and petroleum biomarker F1 extracts will be submitted for TPH and SHC analysis by modified EPA Method 8015 using GC/FID and for petroleum biomarkers analysis by modified EPA Method 8270 using GC/MS-SIM. The F2 extract will be submitted for PAH analysis also using the modified EPA Method 8270 by GC/MS-SIM analysis. Target compounds will be quantified by using the method of internal standards using the SIS compounds resulting in surrogate recovery-corrected data generated to represent the native sample concentrations. The laboratory also will determine the sediment grain size and the total organic carbon (TOC) content of the sediments. Sediments will be processed by the sieve and pipette methods to determine sediment grain size with data for the following four fractions: gravel, sand, silt, and clay. For organic matter, the TOC content will be measured at 900ºC with a total-carbon analyzer.

Table 3-14 List of Petroleum Biomarker (St/Tr) Target Analytes with Reporting Limits and Method Detection Limits[1]

Compound	Synonym	Sediment (ng/g dry)		Tissue (ng/g dry)	
		RL	MDL[2]	RL	MDL
C_{23} Diterpane	T4-C23Diterpane	1.8	0.318	7.6	1.39
13β,17α-diacholestane(20S)	S4-Diacholestane	0.60	0.114	2.5	0.402
13β,17α-diacholestane(20R)	S5-Diacholestane	0.60	0.114	2.5	0.402
C_{29} Tricyclictriterpane(20S)	T9-C29Tricyclictriterpane	1.8	0.318	7.6	1.39
C_{29} Tricyclictriterpane(20R)	T10-C29Tricyclictriterpane	1.8	0.318	7.6	1.39
5α,14α,17α-cholestane(20R)	Cholestane	0.60	0.114	2.5	0.402
18α(H)-22,29,30-trisnorhopane(TS)	T11-Trisnorhopane(TS)	1.8	0.318	7.6	1.39
17α(H)-22,29,30-trisnorhopaneI	T12-TrisnorhopaneI	1.8	0.318	7.6	1.39
5α,14α,17α,24-methylcholestane(20R)	S24-Methylcholestane	0.60	0.114	2.5	0.402
5α,14α,17α,24-ethylcholestane(20S)	S27-Ethylcholestane(S25)	0.60	0.114	2.5	0.402
5α,14α,17α,24-ethylcholestane(20R)	S28-Ethylcholestane(S28)	0.60	0.114	2.5	0.402
17α(H),21β(H)-30-norhopane	T15-Norhopane	1.8	0.318	7.6	1.39
18α(H)-oleanane	T18-Oleanane	1.8	0.318	7.6	1.39
17α(H),21β(H)-hopane	T19-Hopane	1.8	0.318	7.6	1.39
22S-17α(H),21β(H)-30-homohopane	T21-Homohopane	1.8	0.318	7.6	1.39
22R-17α(H),21β(H)-30-homohopane	T22-Homohopane	1.8	0.318	7.6	1.39
17β(H),21β(H)-hopane	17β(H),21β(H)-hopane	1.8	0.318	7.6	1.39

Notes:

[1] Actual detection limits (e.g., LOD, MDL) may be higher or lower, depending on the specific analytical laboratory under contract at the time of project implementation.

[2] Laboratory MDLs are verified and updated periodically according to the organization's quality system. MDLs current at the time of analysis may vary from those defined in this QAPP. The actual laboratory MDLs and RLs will be reported with the laboratory data. Sediment MDL based on a 20g sample size (wet weight; 16.63 g dry weight) with a dilution factor of 1 and PIV = 1000uL. Tissue RL was estimated based on a 20g sample size (wet weight; 4.03 g dry weight) with a dilution factor of 2.05L and PIV = 1000uL. In the event that additional petroleum biomarkers are included in analysis, RLs and MDLs can be provided by the laboratory upon request.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

This page intentionally left blank

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

3.5.3.3 Hydrocarbons in Tissue Samples (Phases III and IV)

Samples of biological tissues will be extracted for PAH (Table 3-11), SHC and TPH (Table 3-12), and petroleum biomarkers St/Tr (Table 3-14) following laboratory SOPs. About 20 g of wet tissue will be fortified with SIS compounds and serially extracted with DCM. The tissue will be extracted by maceration using a TissueMizer® or equivalent, with stainless-steel probes. The sample extract will be dried and concentrated over anhydrous sodium sulfate. The extract will be purified with an alumina clean-up column. The extract then will be purified further with silica-gel column fraction to isolate the TPH/SHC fraction and petroleum biomarker fraction (F1) from the aromatic hydrocarbon fraction (F2). The resulting extracts will be concentrated and spiked with IS compounds. The TPH/SHC and petroleum biomarker F1 extracts will be submitted for TPH and SHC analyses by modified EPA Method 8015 using GC/FID and for analysis of petroleum biomarkers by modified EPA Method 8270 using GC/MS-SIM. The F2 extract will be submitted for PAH analysis using the modified EPA Method 8270 by GC/MS-SIM analysis. Target compounds will be quantified by using the method of internal standards using the SIS compounds resulting in surrogate recovery-corrected data generated to represent the native sample concentrations. The laboratory also will determine the lipid content of the tissue, based on the total extractable material (TEM).

3.5.4 Macrofaunal Analysis

Sediment samples will be processed shipboard by sieving according to methods outlined in Section 3.5.1.8, and taxonomic analysis will be conducted on infaunal invertebrates to determine community composition. In the laboratory, receipt of benthic samples will be logged and processing steps recorded in a notebook to track each sample. Samples will be kept in formalin for a minimum of 1 month, and preferably no longer than 4 months, to prevent decalcification of small bivalve shells. After 1–3 months, the formalin in benthic samples will be decanted and the samples rinsed and then preserved in isopropyl alcohol (or 70% ethanol). Decanted formalin and rinsing water will be poured through a 0.5-mm mesh screen or smaller to capture any specimens that otherwise would be lost. Biological tissues in the 1.0-mm mesh sieve samples will be sorted from the sediment remains into major taxonomic units, and the invertebrate animals will be identified to the lowest practical taxonomic category. A small sample "tag" will be created on waterproof paper for each group of specimens of similar taxonomic determination to follow that group through identification and weighing. Samples will be weighed for wet-weight biomass and stored in alcohol in a glass container along with the specimen tags. Data will be entered into a computer with a database program. After analysis, samples should be moved to glass containers for long-term storage and archival. Lids will be sealed with plastic liners, electrical tape or parafilm to reduce the rate of evaporation of fluids.

Resulting metrics include taxonomic identification, abundance (individuals m^{-2}), and biomass (g m^{-2}). The data on benthic density and biomass resulting from taxonomic analysis will be used for statistical analysis. A small subset of samples employed for community analysis should be reprocessed by a different technician or multiple technicians, when appropriate. Where questions arise, specimens will be compared with the authoritative voucher sets or sent to an appropriate taxonomic expert. Quality-control

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

methods for benthic taxonomic analysis will follow guidelines outlined in SOP SAM043.02 *Benthic Sample Collection and Processing for Shell Baseline Environmental Sampling Program – Chukchi Sea.*

3.5.5 Sediment Profile Imaging Analysis

Table 3-15 below identifies the range of parameters that may be evaluated from the sediment photos. Further descriptions of the parameter groups are provided below.

Table 3-15 Sediment Profile Imaging Parameters

Parameter	Units	Method	Description
Sediment grain size	Modal phi φ interval	Visual analysis (V)	An estimate of sediment types present. Determined from comparison of images of known grain size.
Prism penetration	cm	Computer analysis (CA)	A geotechnical estimate of sediment compaction. Average of maximal and minimal distances from sediment surface to bottom of prism window.
Sediment surface relief	cm	CA	An estimate of small-scale bed roughness. Maximal depth of penetration minus minimal depth.
Apparent Redox Potential Discontinuity depth (from color change in sediment)	cm	CA	Estimate of depth to which sediments appear to be oxidized. Area of aerobic sediment divided by width of digitized image
Thickness of sediment layers	cm	CA	Measure thickness above original sediment surface
Methane/Nitrogen Gas Voids	number	V	Count
Epifaunal Occurrence	number	V	Count, identify
Tube Density	number/cm^2	V	Count
Tube Type			
Burrow Structures	—	V	Identify
Pelletal Layer	cm	V	Measure thickness, area
Bacterial Mats	—	V	Determine presence and color
Infaunal occurrence	number	V	Count, identify
Feeding Voids	number	V	Count, measure thickness, area
Apparent Successional Stage	—	V,CA	Estimated based on all of the above parameters

Sediment Grain Size—This parameter is a textural feature of the sediment used to describe the type of sediment present. Based on grain-size distribution, the nature of the physical forces acting on a habitat can be inferred. Grain size is determined by comparison of collected images with a set of standard images for which mean grain size has been determined in the laboratory.

Prism Penetration—This parameter provides an indication of sediment stiffness, with the profile camera prism acting as a penetrometer. The further the prism enters into the sediment, the softer the sediment is and typically indicates higher water content. Penetration is measured as the distance from the leading

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

(deeper) edge of the prism to the sediment-water interface, up the length of the face plate. If the weight of the camera frame is not changed during image collection, the prism penetration provides a means for assessing the relative compaction between stations. In the unlikely event adjustments to weight and/or flotation are made, a minimum of three replicate drops with both system weight/flotation setups will be made to provide corrections for prism penetration calculations.

Surface Relief—Surface relief is measured as the difference between the maximal and minimal penetration measurements recorded from the sea bottom in one image. Another way to describe this measurement is the distance between the 'peaks' and 'valleys' of the sea bottom within the image. This parameter provides an estimate of small-scale bed roughness, on the order of the width of the prism's face plate (15 cm).

Apparent Color Redox Potential Discontinuity (SPI RPD) Layer—This parameter is used as an estimator of benthic habitat quality. It is the depth to which sediments are oxidized. The term "apparent" is used in describing this parameter because no actual measurement is made of the redox potential. An assumption is made that, given the complexities of iron and sulfate reduction-oxidation chemistry, reddish-brown sediment color tones (Diaz and Schaffner 1988) are indications that the sediments are oxic or at least are not intensely reducing. This assumption is in accordance with the classical concept of RPD depth, which associates it with sediment color (Fenchel 1969, Lyle 1983). The depth of the apparent color RPD is defined as the area of all the pixels in the image discerned as being oxidized divided by the width of the digitized image.

Surface Features—A variety of physical and biological features can be seen at or on the sediment surface. These features can range from SAV, worm tubes, fecal pellets, epibenthic organisms, bacterial mats, algal mats, shells, mud clasts, and bed forms to feeding pits and mounds. Each of these features provides information on the type of habitat and its quality. Surface features are evaluated visually from each slide and compiled by type and frequency of occurrence.

Subsurface Features—Subsurface features include a wide variety of features (such as infaunal organisms, burrows, water-filled voids, gas voids, or sediment layering) and reveal information about physical and biological processes influencing the sea floor. Subsurface features also provide data about the physical–biological control occurring in a habitat.

Successional Stage—Sediment profile data can be used to estimate successional stage of the fauna in a habitat (Rhoads and Germano 1986). Successional stage is based on the theory that organism-sediment interactions follow a predictable sequence after a major seafloor disturbance (Rhoads and Germano 1982). Characteristics that are associated with pioneering or colonizing (Stage I) assemblages (Pearson and Rosenberg 1978), such as dense aggregations of small polychaete tubes at the surface and shallow apparent RPD layers, may be readily visible in sediment-profile images. Advanced or equilibrium (Stage III) assemblages also have characteristics that can be seen in profile images, such as deep apparent RPD layers and subsurface feeding voids. Stage II is intermediate between Stages I and III and has characteristics of both (Rhoads and Germano 1986).

ROV Images-Once the survey is complete, the photos and video data will be sorted, analyzed and archived by the science crew. The videos and photos are directly interpreted by benthic scientists and observations recorded on forms provided for this purpose. A data sheet is filled out for each video.

3.5.6 Laboratory Instrument/Equipment Calibration, Maintenance, and Operation

Laboratory instruments and equipment must be tested, maintained, and calibrated according to SOPs and the manufacturers' instructions prior to use. The manufacturer manuals and SOPs must be readily available at the bench so that trouble-shooting and routine repairs can be performed correctly. All routine maintenance and non-routine repairs are to be documented in a permanent location (e.g., electronically or in bound logbooks). The return to analytical control is demonstrated by successful calibration. Instruments and equipment that are out-of-calibration must be tagged or removed from the laboratory to prevent inadvertent use. Calibration requirements are defined in Table 3-16.

- Certified calibration standards will be used for instrument calibration. Where possible, standards will be traceable to National Institute of Standards and Technology (NIST).
- Stock solutions for spiking solutions, surrogate compounds, and other organic or inorganic compound mixes will be made from reagent-grade chemicals or as specified in the SOPs. All analytical stock solutions will be prepared using Class-A volumetric ware.
- Preparation of stock solutions must be documented including the parent material used (lot number and concentration), the amount used, the final solution volume, and the final solution concentration. Specific handling and documentation requirements for the use of standards will be defined in laboratory SOPs.
- All new calibration or spiking solutions must be analyzed against a previously accepted standard to verify that the concentrations are acceptable.

Prior to analysis, a calibration curve must be verified through the analysis of a check solution prepared from a source (or at least a lot) independent of that used for the initial calibration curve. The calibration check solutions must include all targeted analytes.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 3-16 Calibration Procedures for Laboratory Instruments

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)
Battelle, Hydrocarbons/Metals (sediment and biota)				
Gas Chromatography/ Mass Spectrometry (GC/MS)	Initial Calibration (ICAL) Standard	Prior to samples	≤25% relative standard deviation (RSD) for each analyte and average RSD for all analytes ≤ 15%, R≤0.995	Reanalyze, if failure repeats, take remedial action, if failure continues, a new ICAL is performed
	Independent Calibration Check (ICC)	After ICAL or if failure of continuing calibration verification (CCV)	PD must be ≤ 25% for each analyte and internal standard (IS) area has not changed by more than a factor of two from the area in level 3 ICAL	Evaluate and re-analyze, if this ICC fails, perform remedial action and reanalyze. If a second ICC fails, a new ICAL is performed or justify results.
	CCV	Beginning and end of 10 injections, or 24 hr period	≤25% from true check std. conc. For each analyte and average difference for all analytes ≤ 15%, and IS area has not changed by more than a factor of two from the area in level 3 ICAL	Re-injection of samples prior to a CCV may be warranted. Evaluate samples, sample extracts must be bracketed by an acceptable CCV
GC-Flame Ionization Detection (FID)	ICAL Standard	Prior to samples	≤25% relative standard deviation (RSD) for each analyte and average RSD for all analytes ≤ 20%, R≤0.995	Evaluate, re-analyze if necessary, discuss with PM
	ICC	After ICAL	RSD must be ≤ 25% for each analyte and ≤ 25% for the mean, the IS area must be within a factor of 2 from the Level 3 ICAL and mass discrimination must be ≥0.8	Reanalyze, if failure repeats, take remedial action, if failure continues, a new ICAL is performed
	CCV	After every 10 injections, or 24 hr	≤25% from true check standard conc. For each analyte and average difference for all analytes ≤ 20%	Reanalyze, if failure repeats, take remedial action, if failure continues, a new ICAL is performed. Samples must be bracketed by an acceptable CCV

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)
Purge and Trap GC/MS	ICAL Standard	Prior to samples	≤30% RSD for each analyte and average RSD for all analytes ≤ 15%, R≤0.995	Recalibrate if >10% of target analytes exceed %RSD or R^2 criteria If ≤ 10% of target compounds exceed criteria, recalibration is not required provided %RSD is < 40% or R^2 >0.98. If failure repeats, take remedial action, if failure continues, a new ICAL is performed
Purge and Trap GC/MS (continued)	ICC	After ICAL	PD must be ≤ 30% for most analytes (40-60% for oxygenates) and the IS area must be within a factor of 2 from the Level 3 ICAL	Recalibrate if >10% of target analytes exceed criteria. Reanalyze, perform remedial action as necessary, reanalyze if second ICC fails, a new ICAL is performed
	CCV	beginning and end of each 12 h period	≤30% PD for each analyte, average difference for all analytes ≤ 15% and the IS area must be within a factor of 2 from the Level 3 ICAL	Reanalyze if >10% of target analytes exceed criteria. If ≤ 10% of target compounds exceed criteria, affected sample re-analysis is not required if the % difference for exceeding analytes is < 40% (or 60% for oxygenates) Evaluate and re-analysis of samples analyzed after failed CCV, if necessary. Samples must be bracketed by an acceptable CCV
CVAAS	5 point curve	Before, during, and after analysis of 20 samples	R^2>0.995	Recalibrate
Total Hg cold vapor atomic fluorescence spectrophotometer (CVAFS)	5 point curve using two standards	Daily	RSD<15%	Recalibrate
Methylmercury CVAF	5 point curve using two standards	Daily	RSD<15%	Recalibrate
ICP-MS	3-5 point curve depending on metal; r≥0.999 for all metals	Recheck standards every 8-10 samples	Continuing calibration with %RSD <15%	Rerun samples
FAAS	3-5 point curve depending on metal; r≥0.999 for all metals	Recheck standards every 8-10 samples	Continuing calibration with %RSD <15%	Rerun samples

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)
Brooks Rand Lab, metals (water and particulates)				
Total Hg cold vapor atomic fluorescence spectrophotometer (CVAFS)	6 point curve using two standards	Daily	RSD<15% and low calibration point recovery 75-125%	Reanalyze suspect calibration standard. If criteria still not met, then re-prepare standards and recalibrate the instrument
Methylmercury CVAFS	7 point curve using two standards	Daily	RSD<15% and low calibration point recovery 65-135%	Reanalyze suspect calibration standard. If criteria still not met, then re-prepare standards and recalibrate the instrument
ICP-MS (waters and particulates)	5 point curve	Daily	Correlation coefficient 0.995, 1st standard MRL with ± 20% rec.	Reanalyze suspect calibration standard. If criteria still not met, then re-prepare standards and recalibrate the instrument
Total Carbon Analyzer, Shimadzu (POC) SSM-TOC	4 pt curve, r≥0.999	Recheck standards every 8-10 samples	Continuing calibration %RSD <15%	Rerun Calibration

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

This page intentionally left blank

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

3.6 Quality Assurance/Quality Control

Personnel performing QA activities within each organization must be trained and independent of the technical work they are reviewing. QA staff will monitor the technical components of the project according to organizational SOPs to ensure the accuracy, integrity, and completeness of the data. Analytical staff members will be responsible for ensuring that sample tracking, sample preparation, and analytical instrument operation all meet the quality-control criteria detailed in the applicable analytical SOPs.

The project design incorporates SOPs to ensure consistency (Table 3-17) and QC procedures and checks in both the field and laboratory in order to assess data quality. The study design and QC samples are intended to assess the major components of total study error, which facilitates the final evaluation of whether environmental data are of sufficient quality to support the related decisions. The QC sample requirements are designed to provide information on measurement error that can be used to initiate corrective actions with the goal of limiting the total measurement error. Note: Possible analytical laboratories and associated SOPs are listed in Table 3-17. Laboratories may change prior to project implementation and may include other contract analytical laboratories (and subsequently slightly different SOP numbers and titles).

Table 3-17 Standard Operating Procedures

SOP Number	SOP Title
Field	
FWS SOP-01	Field Documentation
FWS SOP-02	Sample Custody
FWS SOP-03	Sample Packaging and Shipping
FWS SOP-04	Decontamination of Equipment – Sediments
FWS SOP-05	Preparation of Field Quality Control Samples
FWS SOP-06	Surface Sediment Sampling Using a Modified van Veen Grab Sampler
FWS SOP-07	Decontamination of Sampling Equipment
FWS SOP-08	Preparation of Field Quality Control Samples – Tissues
BRL SOP-01	Field Go Flo Bottle Decontamination
SOP 5-365-01	Collecting Benthic and Epibenthic Invertebrates with a Clam Rake
SOP 5-368-01	Collecting Amphipod for Chemical Analysis using Baited Traps
SAM043.02	Benthic Sample Collection and Processing
SAM044.02	Sediment Profile Imaging and Plan View Photography Collection
SOP 5-367-01	At-Sea Collection of Hydrographic Data Using CTD and Carousel System
SOP 5-342-01	Collecting Sediment Cores with a Piston Push/Hammer Corer
FIT-0001	Field Collection of Seawater Samples for Dissolved Trace Metals
FIT-6001	Filter Preparation for Suspended Matter Collection and Trace Metal Analysis

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

SOP Number	SOP Title
FIT-6002	Collection and Digestion of Particulate Samples for Trace Metal Analysis
Laboratory	
SOP 5-157	Identification and Quantification of Semi-Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry
SOP 5-190	Tissue Extraction for Trace Level Semi-Volatile Organic Contaminant Analysis
SOP 5-191	Size Exclusion high performance liquid chromatography (HPLC) Cleanup of Sample Extracts for Semi-Volatile Organic Pollutants
SOP 5-192	Soil/Sediment Extraction Using an Orbital Shaker Table Method for Trace Level Semi-Volatile Organic Contaminant Analysis
SOP 5-200	Water Extraction for Trace Level Semi-Volatile Organic Contaminant Analysis
SOP 5-202	Determination of Low Level Total Petroleum Hydrocarbons and Individual Hydrocarbon Concentrations in Environmental Samples
SOP 5-245	Preparation and Analysis of Volatile Hydrocarbons in Environmental Samples
SOP 5-328	Removal of Sulfur from Environmental Sample Extracts
SOP 5-330	Silica Gel Fractionation of Environmental Extracts for the Separation of Saturated Hydrocarbons and Aromatic Compounds
SOP 5-329	Alumina Clean-up of Environmental Sample Extracts
SOP 6-010	Sample Receipt, Custody, and Handling
FIT-2010-GS	Grain size by sieve and pipette
BR-0066	Reductive Precipitation of Total Recoverable and Dissolved Metals from Brackish and Seawater Samples
BR-0060	Determination of Trace Elements by Inductively Coupled Plasma - Mass Spectrometry using a Perkin-Elmer ELAN DRC II
FIT-1012 Series	Determination of (Metals) in Tissues ICP-MS
FIT-1013 Series	Determination of (Metals) in Tissues by FAAS
FIT-2010 Series	Determination of (Metals) in Sediments by FAAS
FIT-2012 Series	Determination of (Metals) in Sediments by ICP-MS
BR-0060 (Mod)	Determination of Trace Elements by Inductively Coupled Plasma - Mass Spectrometry using a Perkin-Elmer ELAN DRC II (Particulates)
BR-0006	Procedure for EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry (CVAFS)
BR-0011	Determination of Methyl Mercury by Aqueous Phase Ethylation, Trap Pre-Collection, Isothermal GC Separation, and CVAFS Detection
FIT 2015	Determination of Total Organic Carbon
MSL-I-015	Methylmercury in Tissues and Sediments by Cold Vapor Atomic Fluorescence (CVAF)
MSL-I-034	Determination of Mercury in Tissues and Sediments by Direct Thermal Decomposition and Cold Vapor Atomic Absorption Spectrometry (CVAAS)
MSL-I-034-02	Determination of Mercury in Tissues and Sediments by Direct Thermal Decomposition and Cold Vapor Atomic Absorption Spectrometry (CVAAS)
SAM043.02	Benthic Sample Collection and Processing

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

3.6.1 Field Quality Control

Field QC samples will be collected in the same type of sample containers and in all other ways handled in the same manner as other field samples. The field QC samples will be assigned unique sample numbers and will be submitted to the analytical laboratory as routine samples. If abnormalities are detected in field QC samples, the data associated with the QC samples will be assessed to determine if project data are affected. FWS SOP-05 *Preparation of Field Quality Control Samples* and FWS SOP-08 *Preparation of Field Quality Control Samples – Tissue* describe specific procedures for preparing field QC samples.

The following field QC samples will be collected:

- Trip blanks will be prepared and submitted for analysis at the frequency of one per shipping container of VOC samples.
- Temperature blanks will accompany each cooler that contains samples with a temperature preservative requirement. The temperature blank will be created either in the field or laboratory by filling polyethylene bottles with deionized water or sediment, depending on the matrix being shipped.
- Field duplicates will be collected as separate co-located sample and will be analyzed for the same chemical and physical parameters as the other samples from its location. At a minimum, field duplicates are collected at 5% each of the sediment, water, and tissue samples.

Field QC samples that will be collected specific to the EMP are described in the following sections.

3.6.1.1 Equipment (Rinsate) Blank (EB)

An equipment blank is a sample of contaminant-free medium (typically reagent-grade water) that has been passed through or over the sampling equipment used to collect field samples. An equipment blank is collected in the same type of sample containers and in all other ways is handled in the same manner as other field samples. The equipment blank must be collected during the sampling event, after collection of at least one field sample, after normal equipment decontamination procedures, and prior to collection of the next field sample. Sampling devices for sediment include the grab, stainless steel spoons or spatulas, bowls, and flexible tubing. EB will be collected at a frequency of 5% of the total number of field samples collected for sediment and water.

3.6.1.2 Field Blanks

Field blanks will be collected in the field, depending on the type of associated analysis. For example, a sample of analyte free water poured into the container in the field, preserved and shipped to the laboratory with field samples serves to assess contamination from field conditions during sampling. Additionally, filter blanks will be collected for the dissolved metals to estimate any contamination associated with the field filtering process. Field blanks are prepared at a frequency of 5% of the total number of field samples collected for sediment and water.

3.6.1.3 Laboratory Duplicates (Laboratory Splits)

Laboratory duplicates (also called laboratory splits) are used to assess the precision of the analytical method and laboratory handling. For the laboratory duplicate analysis, one sample will be split by the

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

analytical laboratory into two portions and each analyzed. When collecting samples to be analyzed for laboratory duplicates, typically double the normal sample volume is required. This requires filling a larger size sample bottle, or filling two normal size sample bottles and labeling one with the site name and the second with the site name plus "laboratory duplicate". Laboratory duplicate samples are collected, handled, and delivered to the analytical laboratory in the same manner as environmental samples. In some cases, laboratory duplicates may be replaced by matrix spike and matrix spike duplicate samples, which also are indicative of precision of the analytical method and laboratory handling.

3.6.1.4 Benthic Samples

For benthic samples, every effort will be made to use only grabs that have demonstrated no wash-out of the sediment surface. The quantity of sediment retained in the van Veen grab buckets should range from full to minimum penetration depth regardless of the material type and/or coarseness. Samples with insufficient penetration and low-volume of sediment recovery are rejected for community comparison samples. Samples will be carefully dropped into buckets and transported and poured into the sieves without significant spillage. A substantial spillage will require a new sample. Samples will be rinsed over a 1.0-mm mesh with a water pressure strong enough to remove sediments, but weak enough to minimize damage to the animals (nested sampling with a stacked sieve with 0.5-mm mesh may also be used). Biological and sediment residues will be carefully removed from each sieve so that all visible animals, sediment particles, and fragments will be removed. Samples then will be placed into Whirl-Pak® bags or jars labeled with the date of collection, station name, replicate number, sieve mesh size, and initials of personnel packaging the samples. Pertinent information also will be recorded on sample collection sheets listing the collection date, station name, water depth, and gross sediment characteristics. This information will also be included on a waterproof sample tag that is placed inside the specimen jar or container. The pertinent information then will be entered by the field personnel into the shipboard database for managing workflow and data collections and will be checked by the field lead daily for accuracy.

3.6.1.5 Accuracy and Precision of the ADCP and CTD Sensor Arrays

Table 3-18 defines typical accuracy and precision of ADCP instrument sensors. Accuracy and precision are determined based on the pre-season calibration check and post-season calibration check. Table 3-19 defines typical accuracy and precision of the CTD instrument sensors. The accuracy and precision of the equipment deployed during the environmental monitoring will be similar to these values and will be documented and reported with the data.

Table 3-18 Typical Accuracy and Precision of Instrument Sensors (ADCP and OBS)

Sensor	Model (or equivalent)	Measurement	Units	Range	Accuracy	Precision
ADCP	Teledyne RDI Workhorse Sentinel 300khz (or equivalent)	Current velocity	cm/s	0 to 500	1	0.1
		Depth	M	0 to 40	2%	1 cm
		Waves	cm, sec	> 0 cm > 3.3 sec	1%, 1%	1cm, 0.5 sec
OBS	Seapoint Sensors Turbidity Meter (or equivalent)	Turbidity	NTU	0 to 25	Calibration Dependent	2%

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

Table 3-19 Typical Accuracy and Precision of Instrument Sensors (CTD)

Sensor	Model/Method (or equivalent)	Units	Range	Accuracy	Resolution
Depth (Pressure)	Sea-Bird SBE 25*plus* (or equivalent)	Meters	0 to 100	0.1% of range (0.1m)	0.002% of range (0.002m)
Temperature	Sea-Bird SBE 25*plus* (or equivalent)	ºC	-5 to +35	0.001	0.0003
Conductivity	Sea-Bird SBE 25*plus* V2 (or equivalent)	mS/cm	0 to 7000	0.0003	0.00004
Dissolved Oxygen	SBE43	% Saturation	0-120	± 2%	
pH	SBE18	pH units	0-14	± 0.1	± 0.02
Fluorescence/Turbidity	ECO-FLNTUrt	µg/L Chlorophyll	0-50	0.025	0.001
		NTU (Nephelometric Turbidity Unit)	0-25	0.013	0.001
Colored Dissolved Organic Matter (CDOM)	Wet Labs ECO-FLCDrt CDOM	µg/L	0.03-75-500	0.03 093	0.001
Turbidity	Seapoint Sensors Turbidity Meter (or equivalent)	NTU	0 to 25	Calibration Dependent	0.01
			0 to 125	5%	2%
			0 to 500	5%	2%
Light Transmittance	WET Labs C-Star Transmissometer 25cm (or equivalent)	m^{-1}	0 to 40	0.20	0.01
Altimeter	Valeport	Meter	0.1–100	0.01	
ADCP	Teledyne RDI Workhorse Sentinel 300khz (or equivalent)	Current velocity (cm/s)	0 to ± 2000	± 0.5% of water velocity relative to ADCP ± 0.5 cm/s	0.1
		Echo Intensity Profile (decibels)	0 to 80	1%	±1.5dB
		Depth(m)	0 to 165	2%	0.5m (bin size)

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

3.6.2 Laboratory Quality Control

Quality control is an integral part of the laboratory activities. It establishes methods for maximizing the quality of operations and analyses, provides analysts with metrics about method performance, and aids project managers in identifying and correcting systematic and random problems that can plague the laboratory operations.

Laboratory samples will be processed and analyzed in analytical batches or sample delivery groups (SDGs) of ≤20 field samples plus laboratory QC. A suite of QC samples that monitors the accuracy and precision of the methods will be incorporated into each batch as defined below. In addition to these QC samples, surrogate internal standards will be spiked into each sample analyzed for organic compounds. The acceptance criteria and corrective action for each QA sample is defined in Table 3-20.

Table 3-19 Measurement Quality Criteria[1]

QC Sample Type	Measurement Quality Objective	Corrective Action
Field Duplicate (DU)	No criteria defined. Results will be used to assess sample heterogeneity or inconsistent sample handling and analysis procedures	
VOC (water/drill mud/ cuttings)		
Method Blank (MB)	Target analyte concentration in MB <5x the MDL. Data are acceptable if field sample concentration >5x MB; data <5x the MB will be flagged regardless of MB concentration	Review with PI, possibly re-analyze and/or re-extract and reanalyze. If data fail MQO, report data with qualifiers; e..g., "B" data qualifier, unless "J" flagged.
Field Trip Blank (TB)	Target analyte concentration in TB <5x the MDL.	Review with PI. If data fail MQO, report data with qualifiers; e.g., "B" data qualifier.
Laboratory Control Sample (LCS)	Spiked target analytes must be recovered at 50-130%	Review with PI, possibly re-analyze and/or re-extract and reanalyze. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
Matrix Spike (MS)	Spiked target analytes must be recovered at 70-130%. Spike concentration must be >5x unspiked field sample concentration for MQO to apply.	Compare with LCS results. If the MS results are outside the LCS, review with the PI to determine if the difference is attributed to matrix effect or analytical error. Review all sample prep records, re-analyze as directed by the PI. If data fail MQO, report data with qualifiers; e.g., "MI" data flag.
Hydrocarbons (PAH/SHC/TPH/Biomarker)[2]		
Method Blank (MB)	Target analyte concentration in MB <5x the MDL, or MB result is N-qualified. Data are acceptable if field sample concentration >5x MB; however, field sample data <5x the MB will be B-qualified regardless of MB concentration.	Review with PI, possibly re-analyze and/or re-extract and reanalyze. If data fail MQO, report data with qualifiers; e..g., "B" data qualifier, unless "J" flagged.
Laboratory Control Sample (LCS)	Target analyte recoveries:70-130%; 50-130% for nonane.	Review with PI, possibly re-analyze and/or re-extract and reanalyze. If data fail MQO, report data with qualifiers; e.g., "N" data flag.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

QC Sample Type	Measurement Quality Objective	Corrective Action
Matrix Spike (MS)	Target analyte recoveries:70-130%; 50-130% for nonane. Spike concentration must be >5x unspiked field sample concentration for MQO to apply.	Compare with LCS. If the MS results are outside the LCS, review with the PI to determine if difference is due to matrix effects or analytical. Review sample prep records, re-analyze as directed by the PI. If data fail MQO, report data with qualifiers; e.g., "MI" data flag.
Matrix Spike Duplicates (MSD)	RPD ≤ 30%. Spike concentration must be >5x unspiked field sample concentration for MQO to apply.	Review with PI, possibly re-analyze and/or re-extract and reanalyze. If data fail MQO, report data with qualifiers; e.g., "MI" data flag.
North Slope Crude (NSC)	RPD ≤ 30%. Concentration must be >5x the MDL for MQO to apply.	Review with PI, possibly re-analyze and/or re-extract and reanalyze. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
Standard Reference Material (SRM)	PD ≤ 30% from target concentration and the 95% confidence level. Analyte concentration must be certified and >5x the MDL for MQO to apply.	Review with PI, possibly re-analyze and/or re-extract and reanalyze. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
Surrogate Internal Standard (SIS)	Recoveries: 40-120%.	Review with PI, possibly re-analyze and/or re-extract and reanalyze. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
Battelle Metals (Except Mercury and Methyl Mercury)		
MB	<5x the MDL, or field sample concentration >10x MB.	Review with PI, possibly reanalyze. If all samples are >10x the MB, no corrective action is required. If samples are <10x the MB, the batch is re-prepped and re-analyzed. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
MS	Target recoveries: 80-120%. Spike concentration must be >5x unspiked field sample concentration for MQO to apply.	Review with PI, possibly reanalyze. Failure of multiple MQOs requires re-preparation and reanalysis of batch. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
MSD	RPD ≤ 20%. Spike concentration must be >5x unspiked field sample concentration for MQO to apply.	Review with PI, possibly re-extract and reanalyze. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
SRM	Target recovery: 80-120% of certified value.	Review with PI, possibly reanalyze. Failure of multiple MQOs requires re-preparation and reanalysis of batch. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
Battelle Mercury		
MB	<5x the MDL, or field sample concentration >10x MB.	Review with PI, possibly reanalyze. If all samples are >10x the MB, no corrective action is required. If samples are <10x the MB, the batch is re-prepped and re-analyzed. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
OPR (mercury analysis only; one at start and one at end of batch; similar to LCS)	Target recoveries: 70-130% of (sediment and tissue).	Review with PI, possibly re-prepare and reanalyze with all samples in associated batch for failed analytes. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
MS	Target recoveries: 80-120% (sediment and tissue). Spike concentration must be >5x unspiked field sample concentration for MQO to apply.	Review with PI, possibly reanalyze. Failure of multiple MQOs requires re-preparation and reanalysis of batch. If data fail MQO, report data with qualifiers; e.g., "N" data flag.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

QC Sample Type	Measurement Quality Objective	Corrective Action
MSD	RPD ≤ 20% (sediment and tissue). Spike concentration must be >5x unspiked field sample concentration for MQO to apply.	Review with PI, possibly re-extract and reanalyze. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
SRM	Target recovery: 80-120% of certified value (sediment and tissue).	Review with PI, possibly reanalyze. Failure of multiple MQOs requires re-preparation and reanalysis of batch. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
Sensitivity	Low-level Check Sample analyzed at the MRL Target recovery: 80-120%. Concentration must be >5x the MDL for MQO to apply.	Review with PI, possibly re-extract and reanalyze. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
Battelle Methylmercury		
MB	<5x the MDL, or field sample concentration >10x MB.	Review with PI, possibly reanalyze. If confirmed and all samples are > 10x the blank, no corrective action is required. If samples are <10x the blank, the batch must be re-prepped and re-analyzed. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
OPR (one at start and one at end of batch; similar to LCS)	Target recovery: 67–133%.	Review with PI, possibly re-prepare and reanalyze with all samples in associated batch for failed analytes. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
MS	Target recovery: 65-135%. Spike concentration must be >5x unspiked field sample concentration for MQO to apply.	Review with PI, possibly reanalyze. Failure to meet criteria shall be reported in Data Summary. Failure of multiple MQOs requires re-preparation and reanalysis of batch. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
MSD	RPD ≤ 35%. Spike concentration must be >5x unspiked field sample concentration for MQO to apply.	Review with PI, possibly re-extract and reanalyze. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
SRM	Target recovery: 67-133% of certified value.	Review with PI, possibly reanalyze. Failure of multiple MQOs/OPRs requires redigestion and reanalysis of batch. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
Sensitivity	Low-level Check Sample analyzed at the MRL Target recovery: 80-120%. Concentration must be >5x the MDL for MQO to apply.	Review with PI, possibly re-extract and reanalyze. If data fail MQO, report data with qualifiers; e.g., "N" data flag.
TOC (Sediment)		
LCS	80 – 120% of certified value	Correct Problem, re-prepare and reanalyze LCS and all samples in associated batch for failed analytes. If problem persists, call PI.
QADU	RPD <10% at 10x detection limit	Review with PI, re-extract and reanalyze. If data continues to fail, report data with qualifiers.
SRM	±15% of certified value	Reanalyze. Failure to meet criteria shall be reported in Data Summary. Failure of multiple CRMs requires redigestion and reanalysis of batch.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

QC Sample Type	Measurement Quality Objective	Corrective Action
Completeness	>90%	Report results and assess impact
POC (Water Particulates)		
MB	All analytes in the method blank must be less than ½ the RL	Re-prepare and reanalyze the method blank and all samples processed with the contaminated blank. If problem persists, call PI.
LCS	80 – 120% of certified value	Correct problem, re-prepare and reanalyze LCS and all samples in associated batch for failed analytes. If problem persists, call PI.
LCSD	RPB<10%	Review with PI, re-extract and reanalyze. If data continues to fail, report data with qualifiers.
SRM	±15% of certified number	Reanalyze. Failure to meet criteria shall be reported in Data Summary. Failure of multiple SRMs requires redigestion and reanalysis of batch.
Completeness	>90%	Report results and assess impact.
TSS (Water)		
MB	No target analyte concentrations ≥ RL or ≥ 10% of the measured values of the samples (whichever is larger)	Reweigh and reanalyze the method blank and all samples processed with the contaminated blank. If problem persists, qualify or raise RL
Dup	RPD ≤ 15%	Reweigh and reanalyze the method blank and all samples. If problem persists, qualify.
Grain Size (Sediment)		
Laboratory Duplicate	RDP<20% of any individual values for gravel, sand, silt, or clay	Correct problem by re-homogenizing sediment to provide a more representative sample and repeat analysis.
Completeness	>90%	Assess impact and take corrective action.
Brooks Rand Metals in water and particulates (Except Mercury and Methylmercury)		
MB	Mean ≤ LOQ; SD ≤ MDL or MBs <1/10thsample result	Reanalyze to confirm results. MBs may be omitted if they meet the Grubb's Outlier test and if a minimum of 3 MB remain. If MBs are still high following rejection of any Grubb's outlier, then a batch specific MDL is estimated (EMDL) by multiplying the standard deviation of the remaining MBs by 3x. The batch specific MRL is estimated (EMRL) by multiplying the EMDL by 3x. All results are evaluated against the EMDL and EMRL, and data is qualified if necessary.
Filter Blank (for dissolved metals) (FB)	N/A	N/A
MS/MSD	Recovery = 70-130% and RPD ≤ 30%	If criteria not met, results must be qualified. If RPD criteria not met, then sample may be reanalyzed, but this is not required. Sample matrix may be inhomogeneous. A post-digestion spike (PDS) can be analyzed to evaluate instrument accuracy and also to determine if matrix interference is occurring at the prep stage or at the analytical stage. An MSA curve may be prepared and analyzed along with the samples to quantify and correct for interference.
SRM	Recovery = 70-130% unless limits set by SRM manufacturer are greater or element/SRM specific limits have been	If SRM true value is ≥5x the LOQ and if the recovery is outside of the control limit, then batch must be reprepared.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

QC Sample Type	Measurement Quality Objective	Corrective Action
	established	
Brooks Rand Mercury in water and particulates		
MB	Each MB ≤ 0.5 ng/L and StDev ≤ 0.1 ng/L or highest MB < 0.1 times the lowest reported result.	Reanalyze to confirm results. MBs may be omitted if they meet the Grubb's Outlier test and if a minimum of 3 MB remain. If MBs are still high following rejection of any Grubb's outlier, then a batch specific MDL is estimated (EMDL) by multiplying the standard deviation of the remaining MBs by 3x. The batch specific MRL is estimated (EMRL) by multiplying the EMDL by 3x. All results are evaluated against the EMDL and EMRL, and data is qualified if necessary.
OPR (CCV)	Recovery = 77 – 123%	Reanalyze samples bracketed by failing CCV unless QA Manager accepts a passing spike instead.
MS/MSD	Recovery = 71 – 125%; RPD ≤ 24%	If recoveries similar but fail recovery criteria, an interference is present in the sample and the result must be qualified. If RPD criteria not met, then the MS/MSD should be reanalyzed.
SRM	Recovery = 75-125%	Correct problem
Brooks Rand Methylmercury in water and particulates		
MB	Avg ≤ 0.045 ng/L StDev ≤ 0.015 ng/L or < 1/10th of associated samples	Reanalyze to confirm results. MBs may be omitted if they meet the Grubb's Outlier test and if a minimum of 3 MB remain. If MBs are still high following rejection of any Grubb's outlier, then a batch specific MDL is estimated (EMDL) by multiplying the standard deviation of the remaining MBs by 3x. The batch specific MRL is estimated (EMRL) by multiplying the EMDL by 3x. All results are evaluated against the EMDL and EMRL, and data is qualified if necessary.
OPR (CCV)	Recovery = 70-130%	Reanalyze samples bracketed by failing CCV unless QA Manager accepts a passing spike instead.
MS/MSD	Recovery = 65 – 135% (Recovery Criteria for Matrix Spike samples are based on recovery corrected results); RPD ≤ 35%	If recoveries similar but fail recovery criteria, an interference is present in the sample and the result must be qualified. If RPD criteria not met, then the system is not in control. Correct problem and reanalyze all associated samples.
SRM/BS	Recovery = 67 – 133% (Recovery Criteria for BS samples are based on recovery corrected results).	Reanalyze remaining volume. Correct problem prior to continuing analysis.
Sediment Profile Imaging		
Independent Check	Measurements ±1.0 cm and Counts ± 2 counts Pixel density (adequate focus, exposure, and detail)	Reanalyze all images for parameters out of QC range.
Benthic Organisms (Sediment)		
Laboratory report	>90% for Overall precision, analytical precision, analytical Accuracy/Bias	Correct problem, resort, reweigh all samples in batch.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

QC Sample Type	Measurement Quality Objective	Corrective Action
Taxonomy	100% of junior taxonomist samples verified. Questionable organisms of senior taxonomists verified	Discuss identifications with taxonomists.

Note:

[1] Table represents criteria for all matrices unless otherwise noted. [2] Hydrocarbon MQOs are based on the use of surrogate recovery corrected data.

The following laboratory QC samples will be analyzed:

- Method blank for each preparatory and analytical batch.
- LCS (prepared using contaminant-free matrix-specific sample, e.g., Ottawa sand or sodium sulfate [sediment] and clean Tilapia [tissue]).
- MS/MSD samples, prepared from the same parent sample and spiked with the analytes of interest at approximately 10X the MDL.
- A laboratory duplicate (QADU) is a second aliquot of a field sample processed and analyzed to monitor precision. It may be a second matrix-spike sample. As previously described, MS/MSD data may replace the laboratory duplicate sample analysis.

Additional laboratory QC specific to the EMP are described in the following sections.

3.6.3 Standard Reference Material

An SRM is characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability. A SRM is prepared with each processing batch for the appropriate sample matrix and analytical parameters (SRMs are not available for all parameters and sample types) to assess accuracy of the analytical procedures where applicable to a given matrix and analyte.

3.6.3.1 North Slope Crude Reference Oil

A NSC Reference Oil sample is used to evaluate the instrumental accuracy and also provide petroleum pattern information in the petroleum hydrocarbon analyses, aiding in the qualitative identification of target analytes. The NSC is analyzed for organics only.

The MQO for each QC sample in this project are presented in Table 3-20. Analytical results that do not meet the MQOs will be submitted to and/or reviewed with the PI for assessment of the potential impact of the results. Affected samples may be reanalyzed at the PI's discretion. QC sample data that are accepted outside the MQOs qualified, and the rationale for accepting the analysis will be documented.

3.6.3.2 Samples for Biological Community Analysis

A small subset of samples employed for community analysis will be reprocessed by a different technician or multiple technicians, when appropriate. Where questions arise, specimens will be compared with the authoritative voucher sets, sent to an appropriate taxonomic expert. Quality-control methods for benthic taxonomic analysis will follow guidelines adapted from the US EPA's Environmental Monitoring and Assessment Program (www.epa.gov/emap/html/pubs/docs/groupdocs/estuary/field/labman.html).

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

A substantial amount of data already exist for the outer continental shelf (OCS) Chukchi Sea as a result of extensive, multidisciplinary research programs (both industry and government) conducted over the past five years. These data are presented in the EMP Appendix A (OF, 2014) and will be used as part of the Phase I baseline characterization. Hence, baseline-characterization data already exist from empirical data collected in the past 5 years.

3.7 Data Management

During this study, both hard copy and electronic data records will be generated in the field by several principle investigators from different organizations. Each PI is responsible for ensuring that records generated by their field staff follow the requirements of this QAPP. Similarly, field samples will be analyzed in several fixed laboratories for a variety of parameters; the laboratory manager is responsible for ensuring that data management procedures are consistent with this QAPP. All the organizations that collect data in support of the EMP will maintain the original records that support their findings, report detailed results and provide copies of their records to OF at the end of each reporting phase.

3.7.1 Document Control

The QAPP and associated SOPs are controlled documents. The following procedures will be implemented to ensure that project personnel have the current versions of these documents.

- The document version number and effective date is defined in the header control block.
- Each organization will maintain a master list of current SOPs, which are approved by management and assigned an effective date.
- A distribution list is maintained for this QAPP and associated SOPs.
- SOPs that describe environmental data collection activities must be reviewed prior to use to ensure they are current and updated as needed.

Field and laboratory logbooks must be bound, dated, paginated and distinctly labeled.

3.7.1.1 Field Documentation

Field records must provide a detailed description of sample collection activities to ensure that samples and data are traceable and defensible. FWS SOP-01 *Field Documentation* describes these procedures. Field observations will be documented in real time in bound field logbooks and will provide a record of field activities, observations, and measurements during sampling. All field records and documentation must comply with the documentation requirements defined in this QAPP. Field forms required for this study will be included in the EMP project Sampling and Analysis Plan. The field logbooks will be reviewed and approved independently at the end of each survey day.

3.7.1.2 Laboratory Documentation

Documentation of all laboratory activities is critical for tracking data and evaluating the success of any activity. Laboratory documentation requirements must be defined in a laboratory QA Manual or specific SOPs. At a minimum, the laboratories will maintain the following documentation records:

- Calibration and maintenance of all instruments and equipment involved in the collection of environmental data
- Preparation of calibration standards, spiking solutions, and dosing solutions such that each unique preparation can be tracked to the original (neat) material
- Lot numbers for all standards, stock solutions, reagents, and solvents
- Sample processing or preparation for testing such that it is traceable to sample receipt records
- Sample analyses and results of analyses
- Rejected data, accompanied by explanations of the failure and the corrective action
- Data reduction formulas such that reported data are traceable to raw data.

3.7.2 Data Storage Requirements

Storage of project data must ensure that the integrity and traceability of data are maintained. In the field, electronic data will be backed up daily to a second media (e.g., separate hard drive, thumb drive, CD), labeled, and stored securely. Field logs must maintain an inventory of the location of electronic files. Each laboratory must have a documented system of daily incremental and at least monthly full data backups, storage and recovery. Electronic data files received from the laboratories will be stored on a networked project folder with incremental daily and full monthly backups. Storage locations must be appropriate for the media (paper or electronic) and limit access or availability of the data. Once the study is complete, original field records and copies of laboratory records will be submitted to Shell. All hardcopy and electronic project files will be archived by the organization that generated the data for at least 5 years.

3.7.3 Documentation Standards

All data generated during the course of this project must be able to withstand challenges to their validity, accuracy, and legibility. To meet this objective, data are recorded in standardized formats and in accordance with prescribed procedures. The documentation of all environmental data collection activities must meet the following minimum requirements:

- Data must be documented directly, promptly, and legibly. All reported data must be uniquely traceable to the raw data. All data reduction formulas must be documented.
- Handwritten data must be recorded in ink. All original data records include, as appropriate, a description of the data collected, units of measurement, unique sample ID and station or location ID (if applicable), name (signature or initials) of the person collecting the data, and date of data collection.
- Any changes to the original (raw data) entry must not obscure the original entry. The change must be initialed and dated by the person making the change.
- The use of pencil, correction fluid, and erasable pen is prohibited.

During the project, records will be maintained in a secure location that minimizes loss as follows:

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

- Hardcopy records will be maintained in the project files of the principle investigator at each organization. This includes administrative records, field logs, and other field raw data. Field logs and custody forms will also be scanned and saved in pdf format and saved in a networked project folder.
- Electronic records will be maintained on in a networked project folder. No project files may be maintained on personal computers except as temporary working files.
- The results of QA/QC reviews, audits, and assessments will be saved in the QA network folder. Hardcopy audit records will be maintained in the QA files.

3.7.4 Hardware and Software Requirements

The following computer hardware and software standards requirements are established:

- Software used to capture or transfer data electronically from analytical instruments to data management systems must be described in QA documentation, and validated prior to use.
- Data tracking from raw output to final values must be maintained. Data access and change control must be defined, limited, and traceable.
- Calculations performed by analytical instruments, data management software, and spreadsheets must be verified.
- All data and derived products will be stored in the laboratory computers and backed up on CDs.

3.7.5 Changes and Deviations

During the conduct of this study, it may be necessary to modify the planned activities. Modifications that are anticipated prior to field or laboratory work will be reported to the LS, who will assess the potential impact and contact the client if the changes are major (e.g., those that would affect the study objectives, design, or data quality). All modifications will be described in the final report.

Changes that are not anticipated prior to the planned activities are deviations and must be communicated and documented. Documentation will include an assessment of any impact that the deviation has on the study design and data quality, and any corrective action implemented. Minor deviations (e.g., those that would not impact the study objectives, design, or data quality) will be reported to and approved by the appropriate PI and the LS. Major deviations (e.g., those that could impact the study objectives, design, or data quality) will be reported to the LS and client. A discussion of major deviations and potential impact on the project objectives will be included in the final report.

3.7.6 Data Reporting

The reporting requirements for this project are defined by the analytical methods and intended use of the data.

Field measurements will be reported as follows:

- Water and sediment depth: feet
- Station location: WGS84 latitude and longitude (may change in field, system and units are always recorded with coordinates)

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

The concentrations of chemical compounds analyzed for this project will be reported in the units defined in Tables 3-10 through 3-15. Sediment concentrations will be reported on a dry weight basis and tissue concentrations will be reported on a dry weight basis. Additional data reporting requirements are as follows:

- Total PAH: the sum of all PAH compounds determined, including alkyl homologues, except retene (to ensure comparability to historical data)
- Total PAH16: the sum of the 16 priority pollutant PAHs (EPA method 610) Total TPH (SHC): the concentration based on the total resolved compounds and unresolved complex mixture in the SHC (F1) fraction (C9 – C40).
- Total SHC: the sum of the individual resolved SHC target compounds (C9 – C40)
- TAH: Method 602 volatiles +_o, m, p-xylene
- TAqH: TAH+PAH (sum of the 16 PAH, as defined above)
- Non-detect values in sums: Sum of EPA 16 priority pollutant PAH (Total PAH16) will include all detected compounds plus all non-detected compounds using ½ of the MDL reported for each non-detected compound. All other summations will use a zero value for non-detects when used to calculate summations.

3.7.7 Data Reduction

Data reduction is the process of converting raw numbers (*e.g.*, numbers of organisms per replicate) into data that can be displayed graphically, summarized in tables, or compared statistically for differences between mean values for sampling times or stations. The data discussed in this section are those data that require some manipulation before being submitted to the data management consultant for entry into the database.

3.7.7.1 Infaunal Analysis

Historical and new data will be assessed for two attributes. These include standardizing the taxonomy to equivalent 'species' taxa groups and identification and removal of non-benthic species (e.g., pelagic organisms). All original data will be provided but the analyses to be performed will be based on these two modifications to the data.

3.7.7.2 Organics and Metals

GC/MS and GC/FID data will be acquired on PC-based Chemstation® minicomputers with dedicated chromatography software and reduced using MS Enviroquant® software. All GC/MS and GC/FID data files will be transferred electronically to a PC so that the data can be incorporated into an electronic database or spreadsheets for final quantification and tabular results presentation. Data for metals analysis by CVAF, CVAAS, ICP-MS, FAAS, and ZGFAAS are collected and processed by the instruments' software systems. Processed data are electronically transferred to Excel™ spreadsheet format for EDD generation. The final reduction of analytical chemistry data will account for the size of the processed sample and dilution factors.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

3.7.7.3 Total Organic Carbon

Total organic carbon measurements are acquired on instrument software and downloaded onto Excel™ spreadsheets for final quantification and tabular results presentation. TOC results will be reported as percent total organic carbon on a dry weight basis.

3.7.7.4 Grain Size

Grain size will be reported as percent of the total for each size fraction measured. Silt content is determined by subtracting the total clay content from the mud content. Data are entered onto a spreadsheet for calculation of silt content. In addition to weight percent by size class, the Gravel: Sand: Silt: Clay ratio and a numerical approximation of mean size and sorting (standard deviation) are calculated.

3.7.7.5 Sediment Profile Imaging Analysis

After visual and computer image analyses are completed, a standard set of parameters (Table 3-15) taken from both analyses is combined and tabulated for reporting. If appropriate, statistical analyses can be done to test hypotheses by applying appropriate parametric (*e.g.*, *t*-test, ANOVA) and/or nonparametric techniques.

3.8 Data Review/Qualification

Data review conducted for this project is designed to ensure that reported data are accurate and traceable. Each organization generating data will perform the following data review:

- All data that are hand-entered from an original source to another location (e.g., from field logs to spreadsheets or from an instrument output to a spreadsheet) will be verified by the Lab Manager prior to use in calculations or entry into a database.
    - Manually transcribed data are highly susceptible to errors, which could include transposing numbers in the copying process, mis-associating data (e.g., assigning results to the wrong sample), and creating untraceable data by assumption, interpolation, extrapolation (e.g., adding information such as units, times or dates that are not recorded in the original entry). Hand-entered data must be verified 100%.
    - Electronically-transcribed data errors generally consist of an entire entry or record being copied into the wrong location or not copied over at all, resulting in missing data.
- All manual calculations will be performed by a second person to verify that calculations are accurate and appropriate.
- Calculations performed by software will be independently verified to ensure that the formulas are correct, appropriate, and consistent, and that calculations are accurately reported. .

Reported data will be independently reviewed to verify that reported data are accurate and traceable. The review will verify that data were generated according to the methods and MQC defined in this QAPP, including review of:

- Sample holding times and preservation requirements vs. the requirements of Table 3-6.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

- Initial and continuing calibration methods, frequency and results vs. the requirements of Table 3-16.
- Sample extraction and analysis procedures vs. the requirements of Table 3-9.
- Laboratory QC results vs. the requirements of Table 3-20.

Laboratory data that do not meet the requirements of this QAPP will be re-extracted and/or re-analyzed whenever possible. However, if it is not possible (e.g., sample consumed) or beneficial (sample exceeds holding time) to re-extract or re-analyze then data qualifiers will be added and reported with the data. Laboratory data qualifiers are defined in Table 3-21.

Table 3-20 Analytical Data Qualifiers

Laboratory Qualifiers[1]	
Organic Chemistry Data Qualifiers	
N	The QC result does not meet the accuracy, precision, or method blank MQO. The quality control result, not the related sample compound, is qualified.
n	The QC result does not meet the base accuracy or precision MQO, but meets the contingency criteria. Spiked sample (MS/MSD) and SRM result is less than 5X the native sample concentration or less than 5X the MDL (field sample replicate).
B	Blank contamination. The analyte was detected in the field sample at <5X the Method Blank concentration; the qualifier is applied to the field sample. The B qualifier is not applied if the sample data is J-qualified.
J	Estimated value: The analyte was positively identified but at a concentration less than the sample-specific RL.
U	Analyte was not detected at a 3-5:1 signal:noise ratio. The reported data value is the sample-specific MDL.
D	Dilution analysis value. The initial analysis was outside the calibration range of the instrument.
E	Estimated value. Result is greater than the highest calibration concentration.
ME	Estimated value. Significant matrix interference.
MI	Significant matrix interference. Value could not be determined or estimated.
T	Holding time (HT) exceeded.
H	Surrogate compound was diluted out. Qualifier used when surrogate recovery is affected by dilution of sample extract.
NA	Not applicable.
Metals Chemistry Qualifiers (including Mercury and Methylmercury)	
N	The QC result does not meet the accuracy, precision, or method blank MQO. The quality control result, not the related sample compound, is qualified.
J	Estimated value: The analyte was positively identified but at a concentration less than the sample-specific RL.
U	Not detected above the MDL: The associated reported value is the MDL, adjusted by any dilution factor used in the analysis (i.e., the sample-specific MDL).
D	Dilution analysis value. The initial analysis was outside the calibration range of the instrument.
NA	Not applicable
NS	Not spiked

Notes:

[1]MDL = method detection limit, as determined by EPA Method (USEPA 1997. 40 CFR part 136, Appendix B rev. 1.11); RL = reporting limit, the field sample concentration equivalent to a final extract concentration of that of the low calibration standard; MRL = method reporting limit, the MDL multiplied by 3.18 (based on an MDL determination using 7 replicates).

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

As a final review, the project principle investigator or laboratory manager at each organization will review and make professional judgments about the usability of data generated by that organization based on the field notes, field and laboratory QC results¸ and environmental reasonableness.

Data reported in tables or deliverables will be audited by, or under the direction, of the Project QA Officer. Errors noted in data audits will be communicated to analysts and project management and corrected data will be verified. No data measurements will be eliminated from the reported data or database and data gaps will not be filled through interpolation, extrapolation, or with other existing data. The loss of samples during shipment or analysis will be documented in the data reports.

CAUTION: All hardcopies of "Controlling Document" are uncontrolled. When using this document verify that the revision matches the revision in the controlled version found on Livelink®.

4.0 REFERENCES

Blake, J.A., Maciolek, N.J., Ota, A.Y., Williams, I.P. 2009. "Long-term benthic infaunal monitoring at a deep-ocean dredged material disposal site off Northern California." Deep-Sea Research I 56: 1775–1803.

Carr, S.R, E.R. Long, H.L.Windom, D.C. Chapman, G. Thursby, G.M. Sloanne, and D.A. Wolfe. 1996. Sediment Quality Assessment Studies in Tampa Bay, Florida. Environmental Toxicology and Chemistry. Vol. 15, No. 7, pp. 1218-1231.

Chapman, G.A., D.L. Denton, and J.M. Lazarchak (Eds). 1995. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms, 1st Edition. U.S. EPA Environmental Monitoring Systems Laboratory, Cincinnati, OH. EPA/600/R-95/136.

Code of Federal Regulations (CFR). 40 CFR 435. Appendix 2 to Subpart A of Part 435. Drilling Fluids Toxicity Test (EPA Method 1619).

40 CFR Part 136. Appendix A to Part 136, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater.

Diaz, R.J., Schaffner, L.C. 1988. "Comparisons of Sediment Landscapes in Chesapeake Bay as Seen by Surface and Profile Imaging." In: Lynch, M.P., Krome, E.C. (eds.) Understanding the Estuary: Advances in Chesapeake Bay Research. Chesapeake Research Consortium Publ. No. 129. CBP/TRS 24/88, p. 222-240.

Fenchel, T. 1969. "The Ecology of Marrine Microbenthos. 4. Structure and Function of the Benthic Ecosystem, It's Chemical and Physical Factors and the Microfauna Communities with Special Reference to the Ciliated Protozoa". Ophelia 6:1-182.

Folk, R.L. 1974. "Petrology of Sedimentary Rocks." Hemphill Publishing Co. Austin, Tx. 182 pp.

Fabiana D.C. Gallotta, Ragael A. Lourenco and Leandro F.M. de Araégo. 2010. "Evaluation of Holding Time for Polycyclic Aromatic Hydrocarbon (PAH) Analysis in Saline Water Samples." Environmental Forensics Vol.11, Issue. http://www.tandfonline.com/doi/full/10.1080/15275922.2010.494959

Hathorne, E.C., Haley, B., Stichel, T., Grasse, P., Zieringer, M., Frank, M. 2012. Online preconcentration ICP-MS analysis of rare earth elements in seawater. Geochem, Geophys, Geosyst. 13(1): 12pp.

Lewis, P.A., D.J. Klemm, J.M. Lazorchak, T.J. Norberg-King, W.H. Peltier, and M.A. Heber (Eds). 1994. Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms. U.S. EPA Environmental Monitoring Systems Laboratory, Cincinnati, OH. EPA/600/4-91/002.

Lyle, M. 1983. The brown-green color transition in marine sediments: a marker of the Fe(III)-Fe(II) redox boundary. Limnol. Oceanogr. 28:1026-1033.

Nakashima, S., Sturgeon, R.E., Willie, S.N., Berman, S.S. 1988. Determination of trace-elements in sea-water by graphite-furnace atomic-absorption spectrometry after preconcentration by tetrahydroborate reductive precipitation. Anal. Chim. Acta. 207: 291-299.

Odum, E. P. 1969. "The Strategy of Ecosystem Development." Science 164:262-270.

Olgoonik/Fairweather, 2014. "Environmental Monitoring Program (EMP) Plan of Study for the Shell Outer Continental Shelf Lease Chukchi Sea, Alaska."

Pearson, T.H. and Rosenberg, R. 1987. Macrobenthic succession in relation to organic enrichment and pollution of the marine environment. Oceanogr. Mar. Biol. Ann. Rev. 16:229-311.

Porebski L.H., K.G. Doe, B.A. Zajklik, D. Lee, P. Pocklington, and J.M. Osborne. 1999. Evaluating the Techniques for a Tiered Testing Approach to Dredged Sediment Assessment- A Study over a Metal Concentration Gradient. Environmental Toxicology and Chemistry. Vol. 18, No. 11, pp. 2600-2610.

Quinn, GP, Keough, MJ. 2002. "Experimental Design and Data Analysis for Biologists." Cambridge University Press, Cambridge.

Rhoads, D.C. and J.D. Germano. 1982. "Characterization of benthic processes using sediment profile imaging: An efficient method of remote ecological monitoring of the seafloor (REMOTS™ System)." Marine Ecology Progress Series 8:115-128.

Rhoads, D.C. and J.D. Germano. 1986. "Interpreting long-term changes in benthic community structure: A new protocol." Hydrobiologia 142:291-308.

Trefry, J.H., Rember, R.D., Trocine, R.P., Brown, J.S. 2003. Trace metals in sediments near offshore oil exploration and production sites in the Alaskan Arctic. Environmental Geology 45, 149-160.

Trefry, J.H., Trocine, R.P., Cooper, L.W. 2012. Distribution and provenance of trace metals in recent sediments of the Northeastern Chukchi Sea. In Chukchi Sea Offshore Monitoring in Drilling Area (COMIDA): Chemical and Benthos (CAB) Final Report. Prepared by K.H. Dunton, University of Texans Marine Science Institute for Bureau of Ocean Energy Management (BOEM), Anchorage, AK. March 2012.

U.S. Environmental Protection Agency (USEPA). 2011. Analytic Methods for the Oil and Gas Extraction Point Source Category. Office of Water, U.S. Environmental Protection Agency, Washington, D.C. 20460. EPA-821-R-11-004.

USEPA. 2002. Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine Organisms. Fourth Edition. Office of Water, U.S. Environmental Protection Agency, Washington, D.C. 20460. EPA-821-R-02-014.

USEPA. 2002. Guidance for Quality Assurance Project Plans. Office of Environmental Information, Washington, D.C. 20460. EPA/240/R-02/2009.

USEPA. 2001. EPA Requirements for Quality Assurance Project Plans. Office of Environmental Information, Washington, D.C. 20460. EPA/240/B-01/003.

Appendix A

Operational Discharge Compliance Sampling

Standard Operating Procedures

for the *Noble Discoverer*

APPENDIX A
OPERATIONAL DISCHARGE COMPLIANCE STANDARD OPERATING PROCEDURES
AND
LOCAL WORK INSTRUCTIONS

SOP/LWI Number	SOP/LWI TITLE
1001	Qualification and Documentation of Computer Programs
1002	Traceability of Reagents, Standards, and Reference Materials
1003	Equipment Tracking
1004	Balance Calibration
1005	Laboratory Refrigerators
1006	Field Logs
1008	Demonstration of Capability
2001	Chain-of-Custody (C-O-C) Procedures
2002	Sample Collection for Suspended Particulate Phase (SPP) Toxicity Test
2003	Packaging and Shipment of Samples
2004	Decontamination of Equipment
2005	Collection of QC Samples
2006	Collection of Oil and Grease Samples
2007	Sample Collection for Chromium VI, Silver, and Thallium in Water-Based Drilling Fluid
2008	Sample Collection for TAH and TAqH Analyses
2010	Sample Collection for Biochemical Oxygen Demand (BOD_5) Analysis
2011	Sample Collection for Fecal Coliform Analysis
2012	Field Measurement of pH
2013	Field Measurement of Total Residual Chlorine
2014	Sample Collection for Total Suspended Solids (TSS) Analysis
3001	Retort Inspection and Recalibration
3002	Base Fluids Retained on Cuttings Retort Test Procedure
3003	Reverse Phase Extraction Method for Detection of Oil Contamination in Non-Aqueous
3004	Free Oil by Static Sheen Method
3005	Visual Sheen Test Method
LWI-001	Continuous Temperature Monitoring
LWI-002	Chemical Inventory Management
ENV001	Chukchi Sea BES – Collection of Effluent Samples for Biological Testing
TOX002	7-Day Chronic Toxicity Study with *Atherinops affinis*
TOX012	7-Day Chronic Toxicity Study with *Menidia beryllina*
TOX014B	7-Day Chronic Toxicity Study with *Americamysis bahia* – Survival, Growth, and Fecundity
TOX043	Chronic Toxicity Test Using Echinoderm Larvae (*Strongylocentrotus purpuratus or Dendraster excentricus*)
TOX045	Chronic Toxicity Fertilization Test Using Echinoderms (*Strongylocentrotus purpuratus or Dendraster excentricus*)

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

This Standard Operating Procedure (SOP) provides consistent methodology for documenting that the software used to collect, analyze, process or maintain data is validated or verified. In addition, this SOP describes protocols for archiving historical software versions and manuals.

2.0 Definitions

2.1 Program – proprietary code developed, maintained, and controlled by a third-party vendor. An example of this would be Microsoft Excel® or the Discharge Tracking Application® by APEX.

2.2 Routine – spreadsheet or database templates developed by a third-party vendor or in-house that uses input and output capabilities as well as functional capabilities of the program to perform mathematical manipulations.

2.3 Verification – systematic methodology used to document the validity of adequacy, accuracy and reliability of program results and the validity of the models and algorithms used.

3.0 Interferences

3.1 No specific interferences are known for this procedure.

4.0 Health and Safety Considerations

4.1 No specific health and safety considerations are necessary other than the general procedures outlined in the Global HSE Manual.

5.0 Equipment and Supplies

5.1 Spreadsheet program such as Microsoft Excel®

5.2 Database program such as Microsoft Access®

5.3 Discharge Tracking Application® by APEX

5.4 Other software programs as may be necessary to meet the requirements of the General Permit.

5.5 Routines for performing calculations or data management.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

6.0 Reagents and Standards

6.1 No specific reagents and standards are specified in this SOP.

7.0 Sample Collection, Preservation, Shipment and Storage

7.1 Sample collection, preservation, shipment and storage requirements are not applicable.

8.0 Quality Control

8.1 This is a quality control procedure.

9.0 Calibration and Standardization

9.1 No specific calibration or standardization procedures are required for this SOP.

10.0 Procedure

10.1 All purchased software must be used in accordance with the terms of the software license.

10.2 Documentation is established and maintained to demonstrate the validity of software program results and the validity of the models and algorithms used in the software.

10.3 Verification is not required of the proprietary code that is the basis of commercial software programs such as Microsoft Excel® or Microsoft Access®. Verification is required of inputs/outputs and the calculations of routines.

10.4 Verification is required for industry-specific software programs, however Industry workgroup efforts to validate this software may be relied upon in lieu of a full verification.

10.5 Verification includes one or more of the following steps:

10.5.1 Performing hand calculations to verify key calculations within the routine.

10.5.2 Comparing the results to published technical papers.

10.5.3 Comparing the results of one program to a verified program that performs the same calculations.

10.5.4 Comparing the results to a previously completed project for which a verified program or hand-computations were used.

11.0 Calculations

11.1 Types of calculations appropriate for this procedure are described in Section 10.

12.0 Data Assessment and Corrective Action

12.1 Software or routines are removed from use if verification indicates that incorrect results are produced from the software or routine.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

13.0 Pollution Prevention and Waste Management

13.1 Wastes are not generated with this procedure.

14.0 References

14.1 Software manuals.

15.0 Documentation

15.1 Computer program documentation includes

15.1.1 A listing of algorithms and formulas.

15.1.2 The results of the verification checks in Section10.5.

15.2 The Quality Assurance Office or designee maintains the software verification documentation.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

This Standard Operating Procedure (SOP) provides consistent methodology for providing traceability of reagents, standards and reference materials. This SOP applies to all laboratory standards, reagents and reference materials that are used for the calibration of equipment, preparation of samples and standards and the analysis of samples.

2.0 Definitions

2.1 Reference materials - Materials or substances for which one or more properties are sufficiently well established to be used for the calibration of an apparatus, for assessment of methods or for assigning values to materials. Examples of reference materials include NIST thermometers and Class F weights.

2.2 Stock Standards – Certified standards received from a vendor and used as part of the analytical procedure or used to prepare calibration standards at appropriate concentrations. The NIST SRM 1582 is a stock standard material used to prepare positive controls for the RPE test.

2.3 Working Standards – Traceable standards prepared from certified stock standards.

3.0 Interferences

3.1 No specific interferences are known for this procedure.

4.0 Health and Safety Considerations

4.1 No specific health and safety considerations are necessary other than the general procedures outlined in the Global HSE Manual.

4.2 Consult Material Safety Data Sheets (MSDS) before handling reference materials or standards.

5.0 Equipment and Supplies

5.1 No specific equipment is specified in this SOP.

6.0 Reagents and Standards

6.1 No specific reagents and standards are specified in this SOP. Reagents and standards are specified in equipment calibration SOPs.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

7.0 Sample Collection, Preservation, Shipment and Storage

7.1 Sample collection, preservation, shipment and storage requirements are not applicable.

8.0 Quality Control

8.1 This is a quality control procedure.

8.2 Compliance Engineers are trained in the requirements of this procedure through the Compliance Engineer training program. Training on SOP revisions will be documented through completion of Form 2009-1, as described in M-I SWACO SOP 2009 (Compliance Engineer Training).

9.0 Calibration and Standardization

9.1 This SOP defines a methodology for tracing reagents, standards and reference materials used for the calibration of equipment, preparation of samples and standards and the analysis of samples.

10.0 Procedure

10.1 The traceability of reagents, standards and reference materials are the responsibility of the Compliance Supervisor.

10.2 Upon receipt of a reagent, standard or reference material, the Compliance Supervisor (or designee) assigns a unique identifier to the material. The same identification may be applied to multiple containers of the same lot of material received at the same time.

10.2.1 The material identification is placed on certificates that apply to the reference material. Certificates are maintained in the District Office with the Reagent, Standard and Reference Material Log.

10.2.2 The identification of the reagent, standard or reference material, and the expiration date of the material from the manufacturer's certificate and the M-I SWACO identification number are recorded in the Reagent, Standard and Reference Material Log (Figure 1).

10.2.3 Reference materials are removed from service upon expiration of the certificate and may only be placed back into service once the material is recertified.

10.3 Reagents and standards are only prepared from materials that have not expired. The expiration date of the prepared reagent or standard (working standard) is the earliest of the expiration dates of the materials used to prepare the working standard.

10.3.1 The identification number of the certified reagent or standard, the identification number of the reagent or standard prepared from the certified material, the methods used for preparation (volumes, masses, names of chemicals, etc.) and the expiration date (the earliest of the expiration dates of the materials used to prepare the new reagent or standard) are recorded in the Reagents and Standards Preparation Log (Figure 2).

© Copyright M-I L.L.C., 2012, All Rights Reserved.

10.3.2 Standards and reagents are removed from service at the expiration date.

11.0 Calculations

11.1 No calculations are necessary for this procedure other than those required to document reagent and standard preparation.

12.0 Data Assessment and Corrective Action

12.1 Reagents, standards and reference materials are removed from service upon expiration of the certificate.

13.0 Pollution Prevention and Waste Management

13.1 Expired standards and reagents are disposed of properly at the expiration date.

14.0 References

14.1 Appropriate equipment manuals.

14.2 M-I SWACO SOP 1004 – Balance Calibration

14.3 M-I SWACO SOP 1005 – Laboratory Refrigerators

14.4 M-I SWACO SOP 3001 – Retort Inspection and Calibration

14.5 M- I SOP 3002 – Base Fluids Retained on Cuttings Retort Procedure

15.0 Documentation

15.1 Figures 3 and 4 are examples of entries into the Reagents, Standards and Materials Log (Figure 3) and the Reagents and Standards Preparation Log (Figure 4).

15.2 The Equipment Coordinator maintains certificates for reagents, standards and reference materials in the District Office.

15.3 The Compliance Engineer maintains copies of reagents, standards and reference materials log and certificates with the mobile laboratory equipment.

15.4 Upon completion of the Drilling Interval, the copies of reagents, standards and reference material log and certificates are filed by the Records Custodian in the District Office.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Figure 1

Reagents, Standards and Reference Materials Log

Date:	M-I SWACO ID No:	Identification of Material	Expiration Date	Signature:

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Figure 2

Reagents and Standards Preparation Log

Date:	Working Standard ID:	Prepared from M-I SWACO ID No.:	Preparation Details	Expiration Date	Signature:

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Figure 3

Example Reagents, Standards and Reference Materials Log

Date:	M-I SWACO ID No:	Identification of Material	Expiration Date	Signature:
8-8-2003	0222554	10mL JP Tube	From Certificate (2 years from Cal. Date)	Toby Pierce
8-8-2003	0225778	20mL JP Tube	From Certificate (2 years from Cal. Date)	Toby Pierce
8-8-2003	21015846 (Serial number)	NIST Traceable Thermometer	From Certificate (2 years from Cal. Date)	Toby Pierce
8-8-2003	12222	F-Class Weights	From Certificate	Toby Pierce
8-8-2003	I12222	Isopropyl alcohol	02-05(3 years)	Toby Pierce
8-8-2003	N12222	NAF Calibration Fluid (NovaPlus B)	02-05(3 years)	Toby Pierce
8-8-2003	F12222	F Crude Oil Standard	02/05 (3 years)	Toby Pierce
8-8-2003	RPE110803	RPE Standard 1%	11-08-03	Toby Pierce

Example Form

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Figure 2

Example Reagents and Standards Preparation Log

Date:	Working Standard ID:	Prepared from M-I SWACO ID No.:	Preparation Details	Expiration Date	Signature:
1/31/02	W02-01	R02-01 / R02-02	87 mg dissolved into 10 ml methylene chloride	12/31/04	Toby Pierce
1/31/01	W02-02	W02-01 / R02-03	40 µl of W02-01 mixed into 10 ml IPA	12/31/03	Toby Pierce

Use Only If Standard is prepared on Rig

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Equipment Tracking

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

This Standard Operating Procedure (SOP) provides consistent methodology for tracking, maintaining and calibrating laboratory equipment. This SOP applies to all laboratory equipment that is used for the preparation of samples and standards and the analysis of samples.

2.0 Definitions

2.1 No specific definitions are necessary to complete this procedure.

3.0 Interferences

3.1 No specific interferences are known for this procedure.

4.0 Health and Safety Considerations

4.1 No specific health and safety considerations are necessary other than the general procedures outlined in the Global HSE Manual.

5.0 Equipment and Supplies

5.1 No specific equipment is specified in this SOP. Equipment is specified in equipment calibration and analytical SOPs.

6.0 Reagents and Standards

6.1 No specific reagents and standards are specified in this SOP. Reagents and standards are specified in equipment calibration SOPs.

7.0 Sample Collection, Preservation, Shipment and Storage

7.1 Sample collection, preservation, shipment and storage requirements are not applicable.

8.0 Quality Control

8.1 This is a quality control procedure.

9.0 Calibration and Standardization

9.1 This SOP defines a methodology for tracking and maintaining equipment calibrations. Calibration procedure details are described in SOPs for calibration and inspection.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

10.0 Procedure

10.1 The storage, preventive maintenance, issuing and tracking of equipment are the responsibility of the Compliance Supervisor.

10.2 Preventive Maintenance and Repair

10.2.1 Field equipment undergoes preventive maintenance in accordance with the manufacturers recommended schedule and procedures.

10.2.2 When a piece of equipment is sent to a vendor for repairs or maintenance, a log entry is made into the Equipment Log (Figure 1) giving the date, name of vendor, identification of the equipment, description of services required, and initials of the person sending the equipment. When the equipment is returned, a similar entry is made to document the return and a copy of the repair slip is placed in the Equipment Log (Figure 1).

10.2.3 Equipment that is overdue for scheduled maintenance or is in need of repair, is placed "Out of Service". This equipment shall be clearly identified as "Out of Service" until the repair work has been completed and the equipment is operating satisfactorily. Equipment that is not marked shall be considered in proper working order.

10.3 Storage of Equipment

10.3.1 Field equipment is kept in a designated, limited-access storage area. The Compliance Supervisor controls access to the storage area.

10.3.2 The Compliance Supervisor (or designee) issues equipment to each Compliance Engineer.

10.3.3 When equipment is issued to a project, an entry is made in the Kit Tracking Log (Figure 2) giving the date, project number, identification of the equipment, initials of the person issuing the equipment and the identity of the person to whom the equipment is issued. When the equipment is returned, a similar entry is made, noting date of return, and condition of the returned equipment.

10.3.4 A Compliance Kit Checksheet (Figure 3) is also filled out when a kit is sent to the field. It details the inventory of that kit.

10.4 Calibration Procedures

10.4.1 Equipment shall be calibrated at the frequency specified in the applicable SOPs.

10.4.2 Equipment shall be calibrated using the procedures specified in the applicable SOPs.

10.4.3 The status of equipment with regard to calibration needs to be readily available and clearly indicated on equipment and field logs.

10.4.4 Equipment calibration shall be verified by the analysis of appropriate reference materials before samples are collected/analyzed and at the required frequency throughout collection and/or analysis.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

10.4.5 The results of inspections and/or calibrations shall be documented on equipment inspection and/or calibration forms as specified in the applicable SOPs.

10.4.6 The results shall be within the acceptance limits for the applicable SOP in order to proceed with sample collection and/or analysis.

10.4.7 Records pertaining to calibration shall be safely stored for the period described in M-I SWACO's record retention policy. The following information shall be recorded:

10.5 Contingency Plan

- Date
- Time
- Instrument type and serial number
- Identification of calibration standard
- True value (numerical result, positive, negative) of calibration standard
- Response of instrument before repair or adjustment
- Response of instrument after repair or adjustment
- Signature of person performing the calibration

10.5.1 M-I SWACO shall maintain duplicate equipment for the RPE test (ultraviolet light) at the mobile lab.

10.5.2 Since the ROC procedure is performed daily, a duplicate retort shall be maintained in the mobile laboratory. If the backup retort is put into service due to malfunction of the primary retort, the Compliance Supervisor shall be notified immediately so that a replacement retort can be shipped to the mobile laboratory within 24-hours.

10.5.3 Duplicate glassware for the retort shall also be maintained at the mobile laboratory. If the glassware is unusable, the Compliance Supervisor shall be notified immediately so that replacements can be shipped to the mobile laboratory within 24-hours.

11.0 Calculations

11.1 No calculations are necessary for this procedure.

12.0 Data Assessment and Corrective Action

12.1 Equipment that is overdue for scheduled maintenance or is in need of repair, is placed "Out of Service".

© Copyright M-I L.L.C., 2012, All Rights Reserved.

12.2 Equipment that cannot produce an acceptable calibration is placed "Out of Service" until the appropriate corrective action is complete.

12.3 Notify the Compliance Supervisor and/or Quality Assurance Officer if equipment requires repair, maintenance or calibrations.

13.0 Pollution Prevention and Waste Management

13.1 Wastes are not generated with this procedure.

14.0 References

14.1 Appropriate equipment manuals.

14.2 SOP 1004 – Balance Calibration

14.3 SOP 1005 – Laboratory Refrigerators

14.4 SOP 3001 – Retort Inspection and Calibration

15.0 Documentation

15.1 The Compliance Supervisor keeps records of routine preventive maintenance, repairs and utilization of field equipment in an Equipment Log (Figure 1).

15.2 The Compliance Supervisor maintains original equipment manuals, reference material certificates and Equipment Logs in the District Office files.

15.3 The Compliance Engineer maintains copies of the applicable equipment manuals, reference material certificates and Equipment Logs with the mobile laboratory equipment.

15.4 The Compliance Supervisor completes the equipment inspection and/or calibration forms as specified in the applicable SOPs. Calibration data sheets are maintained in the Equipment Log and a copy accompanies the mobile laboratory equipment.

15.4.1 If the Compliance Engineer calibrates equipment during a fluids drilling interval, the form is maintained in the Drilling Interval notebook.

15.4.2 Upon completion of the Drilling Interval, copies of the equipment calibration records are returned to the Compliance Supervisor and placed in the project files.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Figure 1

Equipment Log

Equipment:		**Equipment ID No.:**	
Manufacturer:		**Serial No.:**	
Date In Service:			

Calibration Records (may reference Equipment Calibration/Inspection Logs if used)

Date:	**Time:**	**Calibration Std ID:**	**Std True Value:**	**Equipment Response**	**Signature:**

Maintenance Records

Date:	**Nature of Repair/Vendor and Services Required**	**Signature:**

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Compliance Kit Log (Figure 2)						
Kit Number						
Date In Service						
Date:	**Time:**	**Project**	**Issued To / Received From:**	**Condition of Equipment**	**Issuer Initials**	**Recipient Initials**
Date	**Comments:**					

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Equipment Tracking

Compliance Kit Checklist (figure 3)

Kit No.

Assembled By: _____

Date:

Retort Serial #	Orange Notebook#			Serial #	Exp. Date
1.	TB Balance #		RPE Std#		
2.	F-Class Weights #		Crude #		
3.	NIST Thermometer Serial #		IPA #		
	Printer Serial #				

Equipment	Quantity	Actual	Comment		Equipment	Quantity	Actual	Comment
Retorts	3				Beaker 100 ml	1		
JP Tube Stand	1				Marker	1		
JP Tubes 50 ml	6				IPA 1 Gal	1		
JP Tubes 20 ml	6				F Crude	1		
JP Tubes 10 ml	6				Nova Plus B	1		
Steel Brush	3				Black Light	2		
Wide Brush	3				View Box	1		
JP Brush	3				Calibration Wts.	1		
Pipe Cleaners	10				Accessory Wts.	1		
Fuse 5 amp	4				Labels	10		
Fuse 1 amp	4				TB Scale	1		
Legs	4				Glass Jars	12		
Rubber Plugs	2				IO Filter Discs	20		
O Rings	10				Cuttings Scale	1		
Reamer	3				Field Notebook	1		
Heat Sinks	2				Printer	1		
Never Seeze	3				Black Cartrdg.	2		
Condenser	3				RPE Bags	10		
Mitts	2				Waste Bottle	5		
Hook	1				1 Gal. Buckets	4		
Cells	6				Viscosity Cup	1		
RPE Standard1%	1				NIST Batteries	1		
Binder & Tabs	2				Contico	2		
Zipper Bags	2				RPE Box	1		
					NIST Thermometer	1		
					8 oz jars	8		
					Labels	10		

(Sheet 1 of 2)

Static Sheen Test Kit is to be supplied by the Permittee.

Steel wool is the responsibility of the Compliance Engineer.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Compliance Kit Checklist
(Continued)

Kit No.

Certificates and Paperwork

	Serial #	Cal. Date	Serial #	Cal. Date
Verification of Certification for 10 ml JP Tubes				
Verification of Certification for 20 ml JP Tubes				
Verification of Certification for 50 ml JP Tubes				

Certificate of Conformity for 10 ml JP Tubes	
Certificate of Conformity for 50 ml JP Tubes	
Traceable Certificate for Digital Thermometer	
Traceable Certificate for Weights	
32 oz. Glass Jar Cleanliness Certification	
Attachment Weights Sheet	
Equipment Tracking Sheet for Kit	
MSDS for F Crude Oil	
MSDS for IPA	
MSDS for Novaplus B	

(Sheet 2 of 2)

TOXICITY AND GC/MS KITS ARE TO BE ORDERED BY THE RIG FROM THE LAB OF CHOICE OF THE PERMITEE

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Balance Calibration

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

This Standard Operating Procedure (SOP) provides a consistent methodology for routine operation and maintenance of the laboratory balances. This SOP applies to all laboratory balances that are used for the preparation of samples and standards and for the analysis of samples.

2.0 Definitions

2.1 No specific definitions are necessary to complete this procedure.

3.0 Interferences

3.1 No specific interferences are known for this procedure.

4.0 Health and Safety Considerations

4.1 No specific health and safety considerations are necessary other than the general procedures outlined in the Global HSE Manual.

5.0 Equipment and Supplies

5.1 Ohaus triple beam balance, Model 750-SW

5.2 Balance Calibration Log (Form 1004-1)

6.0 Reagents and Standards

6.1 Class F (or traceable OIML Class M2 or traceable ASTM E617 Class 6) weights: 100 g, 500 g, 1000 g, and 2000 g

7.0 Sample Collection, Preservation, Shipment and Storage

7.1 Sample collection, preservation, shipment and storage requirements are not applicable.

8.0 Quality Control

8.1 The balance is calibrated daily while in use.

8.2 Triple beam balances have an allowable deviation of ± 0.1 % from the recorded NIST certified weight.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

8.3 Compliance Engineers are trained in the requirements of this procedure through the Compliance Engineer training program. Training on SOP revisions will be documented through completion of Form 2009-1, as described in SOP 2009 (Compliance Engineer Training).

9.0 Calibration and Standardization

9.1 This SOP defines calibration procedures for the balance.

10.0 Procedure

10.1 Ensure that the weighing platform is clean. If the weighing platform is not clean, clean the pan with water. Dry the pan completely before proceeding with the calibration.

10.2 Calibration

10.2.1 Record the balance identification and weight identification when the Balance Calibration Log is initiated.

10.2.2 Record the analyst initials adjacent to the date the balance is calibrated.

10.2.3 Verify that the slide weights on zero (seated in the zero notch).

10.2.4 The beam should be level with the pointer. If this is not the case, “tare” the balance by adjusting the thumbscrew underneath the pan until the pointer rests at zero.

10.2.5 Place the 100 gram (g) weight on the weighing pan. Move the weights on the beam until the beam is level with the center of the arrow.

10.2.6 To find the mass of the object on the pan, simply add the numbers from the three beams. Record the mass in the Balance Calibration Log in the appropriate column.

10.2.7 Repeat steps 10.2.4 and 10.2.5 for the 500, 1000 and 2000 g weights.

10.2.8 If the mass exceeds the tolerance shown in Table 1 for the true weight (as provided by the Class F certification), recalibrate. If necessary, clean the balance pan. If the mass(s) is (are) outside the tolerance, notify the Quality Assurance Officer and/or Equipment Coordinator and make arrangements for the repair of the balance.

10.3 Operation

10.3.1 Never weigh anything without prior daily calibration.

10.3.2 Make sure the weighing platform is clean and that the balance is level horizontally.

10.3.3 Never weigh anything without using a container such as a beaker or retort cup.

10.3.4 Record the mass after the beam is stable.

10.4 Maintenance

10.4.1 Remove any material that has spilled.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

10.4.2 Record all maintenance on the Balance Calibration Log.

11.0 Calculations

11.1 No calculations are necessary for this procedure.

12.0 Data Assessment and Corrective Action

12.1 Fail the balance if the balance cannot be zeroed.

12.2 Fail the balance if the mass exceeds the tolerance shown in Table 1 for the true mass (as determined by the weight certification).

12.3 If the readings are not within range, notify the Quality Assurance Officer and/or Equipment Coordinator.

13.0 Pollution Prevention and Waste Management

13.1 Wastes are not generated with this procedure.

14.0 References

14.1 Ohaus manual

15.0 Documentation

15.1 All balance calibration and maintenance information is recorded on the Balance Calibration Log.

15.2 Acceptability of the calibration is documented in Section 4 of the Daily Activity Report.

15.3 Mark all unused fields with “N/A” and/or a line though the unused blank. Enter a comment in the comment column as to why the balance was not calibrated.

15.4 The Compliance Engineer maintains the Balance Calibration Log during a fluids drilling interval in the Drilling Interval Notebook.

15.5 Upon completion of the fluid drilling interval, original Balance Calibration Logs are provided to the permittee.

15.6 The District Office archives copies of the Balance Calibration Log in the District Office after completion of a fluids drilling interval.

15.7 Copies of the Class F weight certificates are stored in the Drilling Interval Notebook. The Equipment Coordinator stores the original weight certificates with the Equipment Log in the District Office.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Table 1

Acceptance Ranges for Balance Calibration

Weight (g)	Acceptance Range (g)
2000	± 2 or 0.1% of true
1000	± 1 or 0.1% of true
500	± 0.5 or 0.1% of true
100	± 0.1 or 0.1% of true

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Form 1004-1

Balance Calibration Log

Operator:		**OCS-G Number:**		**Month / Year:**	
Balance ID:		**F Class Weight ID:**		**Rig Name:**	
Area and Block (surface location):					
Compliance Engineer 1:				**Compliance Engineer 2:**	

Date	Analyst Initials	100 ± 0.1 g	500 ± 0.5 g	1000 ± 1 g	2000 ± 2 g	Acceptable? (Yes / No)	Comment	Analyst Signature
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
11								
12								
13								
14								
15								
16								
17								
18								
19								
20								
21								
22								
23								
24								
25								
26								
27								
28								
29								
30								
31								

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Laboratory Refrigerators

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

This Standard Operating Procedure (SOP) provides a consistent methodology for refrigerator monitoring. This SOP applies to all refrigerators in the laboratory that are used for storage of samples and standards.

2.0 Definitions

2.1 No specific definitions are necessary to complete this procedure.

3.0 Interferences

3.1 No specific interferences are known for this procedure.

4.0 Health and Safety Considerations

4.1 No specific health and safety considerations are necessary other than the general procedures outlined in the HSE Manual. Volatile or explosive materials may only be stored in refrigerators rated as explosion-proof.

5.0 Equipment and Supplies

5.1 NIST traceable thermometer, such as Control Company 61161-310 or equivalent

5.2 Refrigerator

6.0 Reagents and Standards

6.1 NIST certified thermometer, such as Control Company 61161-310 or equivalent

7.0 Sample Collection, Preservation, Shipment and Storage

7.1 Sample collection, preservation, shipment and storage requirements are not applicable.

8.0 Quality Control

8.1 The temperature of the refrigerator is verified daily.

8.2 Compliance Engineers are trained in the requirements of this procedure through the Compliance Engineer training program. Training on SOP revisions will be documented through completion of Form 2009-1, as described in SOP 2009 (Compliance Engineer Training).

© Copyright M-I L.L.C., 2004, All Rights Reserved.

9.0 Calibration and Standardization

9.1 The refrigerator thermometer is calibrated against an NIST certified thermometer every two years.

10.0 Procedure

10.1 Thermometer Calibration

10.1.1 Place the NIST thermometer and the refrigerator thermometers in an ice-water bath.

10.1.2 Record date checked, the temperature each thermometer reads, the adjustment required for the refrigerator thermometers to agree with the NIST thermometer, and the analyst initials in the Thermometer Calibration Log (Form 1005-1).

10.1.3 Label the thermometer with the date checked, the temperature, the adjustment required to be accurate, and the analyst initials.

10.2 Refrigerator Calibration:

10.2.1 Check refrigerator temperatures daily using the thermometer located inside the refrigerator.

10.2.2 Record the analyst initials and the current temperature from the thermometer taking the adjustment into account on the Refrigerator Calibration Log.

10.2.3 Adjust the refrigerator if the temperature is outside the quality control limits. Record the temperature after the adjustment.

10.2.4 Document any adjustments made in the Refrigerator Calibration Log (Form 1005-2).

10.2.5 Report any refrigerators that are not functioning properly to the permittee and request the permittee make arrangements for repairs or replacement.

10.3 Maintenance:

10.3.1 Promptly remove and discard samples and standards that are no longer being used.

11.0 Calculations

11.1 No calculations are necessary for this procedure.

12.0 Data Assessment and Corrective Action

12.1 Thermometers are calibrated every two years and the results recorded on the Certificate of Calibration issued by the manufacture.

12.2 Each thermometer certificate is marked with the correction factor.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

12.3 The refrigerator temperature must be between 2 and 6°C to be in compliance.

12.4 Document adjustments to the operation of the refrigerator on the Refrigerator Calibration Log (Form 1005-2).

12.5 Report any refrigerators that are not functioning properly to the permittee and request the permittee to make arrangements for repairs or replacement. Identify affected samples to the permittee. Note the request and affected samples on the Refrigerator Calibration Log.

13.0 Pollution Prevention and Waste Management

13.1 Wastes are not generated with this procedure.

14.0 References

14.1 References are not applicable to this procedure.

15.0 Documentation

15.1 Refrigerator temperatures and temperature adjustments are recorded in the Refrigerator Calibration Log.

15.2 Thermometer calibration information is recorded on the Thermometer Certificate of Calibration.

15.3 Mark all unused fields with “N/A” and/or a line though the unused blank. Enter a comment in the comment column as to why the refrigerator was not calibrated.

15.4 The Compliance Engineer maintains the Refrigerator Calibration Log during a fluids drilling interval in the Drilling Interval Notebook.

15.5 The Compliance Engineer maintains a copy of the certificate for the refrigerator thermometer in the Drilling Interval Notebook.

15.6 Upon completion of fluids drilling interval, original Refrigerator Calibration Logs are provided to the permittee.

15.7 The District Office archives copies of the Refrigerator Calibration Log after completion of a fluids drilling interval.

15.8 The Equipment Coordinator maintains the Thermometer Calibration Log in the Equipment Log at the District Office.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Form 1005-1

Thermometer Calibration Log

Date:		**Analyst**	
Thermometer Identification	**Actual Reading °C**	**Correction**	**Comment**
NIST Thermometer			

Not to be used in the field

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Form 1005-2
Refrigerator Calibration Log

Month and Year:		**Operator:**	
OCS-G Number:		**Rig Name:**	
Area and Block (surface location):			
Compliance Engineer 1:		**Compliance Engineer 2:**	

Date	Analyst Initials	4 ± 2 ° C	Comment	Analyst Signature	Date	Analyst Initials	4 ± 2 ° C	Comment	Analyst Signature
1					17				
2					18				
3					19				
4					20				
5					21				
6					22				
7					23				
8					24				
9					25				
10					26				
11					27				
12					28				
13					29				
14					30				
15					31				
16									

NIST Calibrated Thermometer Serial Number:	
Thermometer Correction Factor (from Certificate):	°C
Date of Last Calibration:	
Comments:	

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

This Standard Operating Procedure (SOP) provides a consistent methodology for the completion of field logs such as the field notebooks and Daily Activity Reports. The Field notebook is the only acceptable format for the handwritten initial collection of sampling information. The Daily Activity Reports are the primary format for organizing the documentation contained in the Drilling Interval Notebook and maybe handwritten or electronic.

2.0 Definitions

2.1 Day – Midnight (00:00) through 23:59, unless otherwise directed by the permittee.

2.2 Field Notebook – Waterproof, bound notebook used to record sample collection information.

2.3 Daily Activity Report – Form for summarizing sampling, calibration and analytical results.

3.0 Interferences

3.1 No specific interferences are known for this procedure.

4.0 Health and Safety Considerations

4.1 No specific health and safety considerations are necessary other than the general procedures outlined in the Global HSE Manual.

5.0 Equipment and Supplies

5.1 Indelible pens

5.2 Drilling Interval Notebook containing elements as described in Table 3-1 of the M-I SWACO Quality Manual

5.3 Field Notebook

6.0 Reagents and Standards

6.1 No reagents or standards are required for the completion of this procedure.

7.0 Sample Collection, Preservation, Shipment and Storage

7.1 This procedure documents the summary of sample collection, preservation, shipment and analysis activities that is maintained on the Daily Activity Reports and Field Notebooks.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

8.0 Quality Control

8.1 This is a quality control procedure designed to define the requirements for completing theField Notebooks and Daily Activity Reports.

8.2 Compliance Engineers are trained in the requirements of this procedure through the Compliance Engineer training program. Training on SOP revisions will be documented through completion of Form 2009-1, as described in SOP 2009 (Compliance Engineer Training).

9.0 Calibration and Standardization

9.1 This procedure describes the protocol for documenting acceptable calibration on the Daily Activity Reports.

10.0 Procedure

10.1 The sample identification is composed of the sample location, date, time and initials of the sampler. **For example, a sample collected from the centrifuge on January 31, 2002 at 20:35 by John Doe would be labeled as Cent/013102/20:35/JD**. This identifier is placed on the sample label, recorded in the Field Notebook and in appropriate sections of the Daily Activity Report. Field duplicates are identified by appending "-D" to the sample identification.

10.2 Field Notebook

10.2.1 When the Field Notebook is initiated, the first page of the notebook is labeled with the OCS-number, block number, permittee and well name. Printed names and signatures of each person entering data in the field notebook are also recorded on the first page.

10.2.2 The Compliance Engineer records sample collection data in the Field Notebook at the time samples are collected.

10.2.3 Each page should be dated, signed and numbered sequentially. There should be no skipped, blank pages.

10.2.4 The date, time, location and sampler signature are recorded for each sample taken in the Field Notebook.

10.2.5 The sample identification as described in Section 10.1 is assigned to each sample and recorded in the Field Notebook.

10.2.6 Other data relevant to the sample collection such as measured depth or density can also be recorded in the Field Notebook.

10.2.7 Other critical compliance activities, including communications from rig personnel, may also be recorded.

10.2.8 The format for recording sampling data in the field notebook is shown in Figure 1.

10.2.9 Recording initial handwritten information in other places is not authorized. No other personal records shall be maintained.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

10.3 Daily Activity Report

10.3.1 The Daily Activity Report (Form 1006-1) is completed **DAILY** during a drilling fluid interval.

10.3.2 More than one Daily Activity Report may be necessary to capture all the daily information. Use as many forms as necessary to accurately record all the daily information.

10.3.3 The **Date, Operator, Area, OCS-G, and Rig Name** are completed at the beginning of each day. The **Compliance Engineer** signs at the end of each day. This information is repeated if additional Daily Activity Reports are completed.

10.3.4 **Communications** from other personnel that are critical to compliance activities are recorded in this section.

10.3.5 **Observations** that may affect compliance, (e.g., weather, drilling fluid deliveries, etc.) are recorded. This is an appropriate block to record if no compliance activities are performed during the day. **Record the current depth and drilling activity daily in this section.**

10.3.6 Section 1 summarizes sampling and analytical activities for the retention on cuttings (ROC) procedure.

10.3.6.1 The sample identification (Section 10.1) is recorded in the column 1 of the Daily Activity Report.

10.3.6.2 The drilling interval depth as associated with this sample and as recorded in the APEX software is recorded in column 2.

10.3.6.3 Record the identification of the field sampling plan or the SOP that was followed to collect the sample in the Sampling Reference column (column 3).

10.3.6.4 The analytical result (%ROC) is recorded in column 4.

10.3.6.5 Record comments relevant to the test or sample in column 5 (such as interval # and footage represented by sample).

10.3.6.6 Record the Daily and Well ROC average at the bottom of section 1. The Well ROC average should be recorded every day.

10.3.7 Section 2 summarizes the sampling and analytical activities for the reverse-phase extraction (RPE) procedure, Static Sheen test, and other on-site compliance activities.

10.3.7.1 The sample identification (Section 10.1) is recorded in column 1 of the Daily Activity Reports.

10.3.7.2 Identify the location where the sample was taken from. (Column 2)

10.3.7.3 Sample preservation is recorded in column 3.

10.3.7.4 List the test method or SOP reference used to perform the testing procedure in column 4.

10.3.7.5 The test result (pass/fail) is recorded in column 5.

10.3.7.6 Record comments relevant to the test or sample in column 6.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

10.3.8 Section 3 is used for the collection of samples for contract laboratory analyses

10.3.8.1 If the samples are transferred to the permittee or another third party such as a laboratory, then chain-of-custody (C-O-C) documentation is required as described in M-I SWACO SOP 2001 (Chain-of-Custody Procedures).

10.3.8.2 The sample identification (Section 10.1) is recorded in column 1.

10.3.8.3 The analyses requested (i.e. toxicity, GC/MS, etc.) are recorded in column 2.

10.3.8.4 Sample preservation is recorded in column 3.

10.3.8.5 The C-O-C number is recorded in column 4.

10.3.8.6 The status (shipped or stored) of the sample is recorded in column 5 or 6.

10.3.8.7 Record comments relevant to the sample in column 7.

10.3.9 Section 4 is used to summarize daily equipment calibration procedures.

10.3.9.1 The equipment identification is the unique identifier assigned to the equipment by the Equipment Coordinator. The equipment identification is entered in column 1.

10.3.9.2 The calibration procedure is entered in column 2. The procedure may reference a SOP or the name of the procedure.

10.3.9.3 The analyst notes the acceptability of the calibration and/or inspection in column 3.

10.3.9.4 Comments (i.e., malfunctions, repairs, maintenance, etc.) are noted in column 4.

11.0 Calculations

11.1 No calculations are necessary for this procedure.

12.0 Data Assessment and Corrective Action

12.1 Corrective action is required if Field Notebooks or Daily Activity Reports are not correctly completed. Generally, the corrective action is additional Compliance Engineer training.

13.0 Pollution Prevention and Waste Management

13.1 Wastes are not generated with this procedure.

14.0 References

14.1 M-I SWACO SOP 2001 (Chain-of Custody Procedures)

14.2 Final NPDES General Permit for New and Existing Sources and New Dischargers in the Offshore Subcategory of the Oil and Gas Extraction Category for the Western Portion of the Outer Continental Shelf of the Gulf of Mexico (GMG290000)

© Copyright M-I L.L.C., 2004, All Rights Reserved.

14.3 Final NPDES General Permit for the Eastern Portion of the Outer Continental Shelf (OCS) of the Gulf of Mexico (GOM) (GMG280000); 63 FR 55745 (October 16, 1998); 66 FR 1498(March 14, 2001 Modification); 66 FR 18253 (April 6, 2001 Corrections); 65 FR 30886 (May15, 2000)

14.4 Operator and M-I SWACO Safe Work Plan

15.0 Documentation

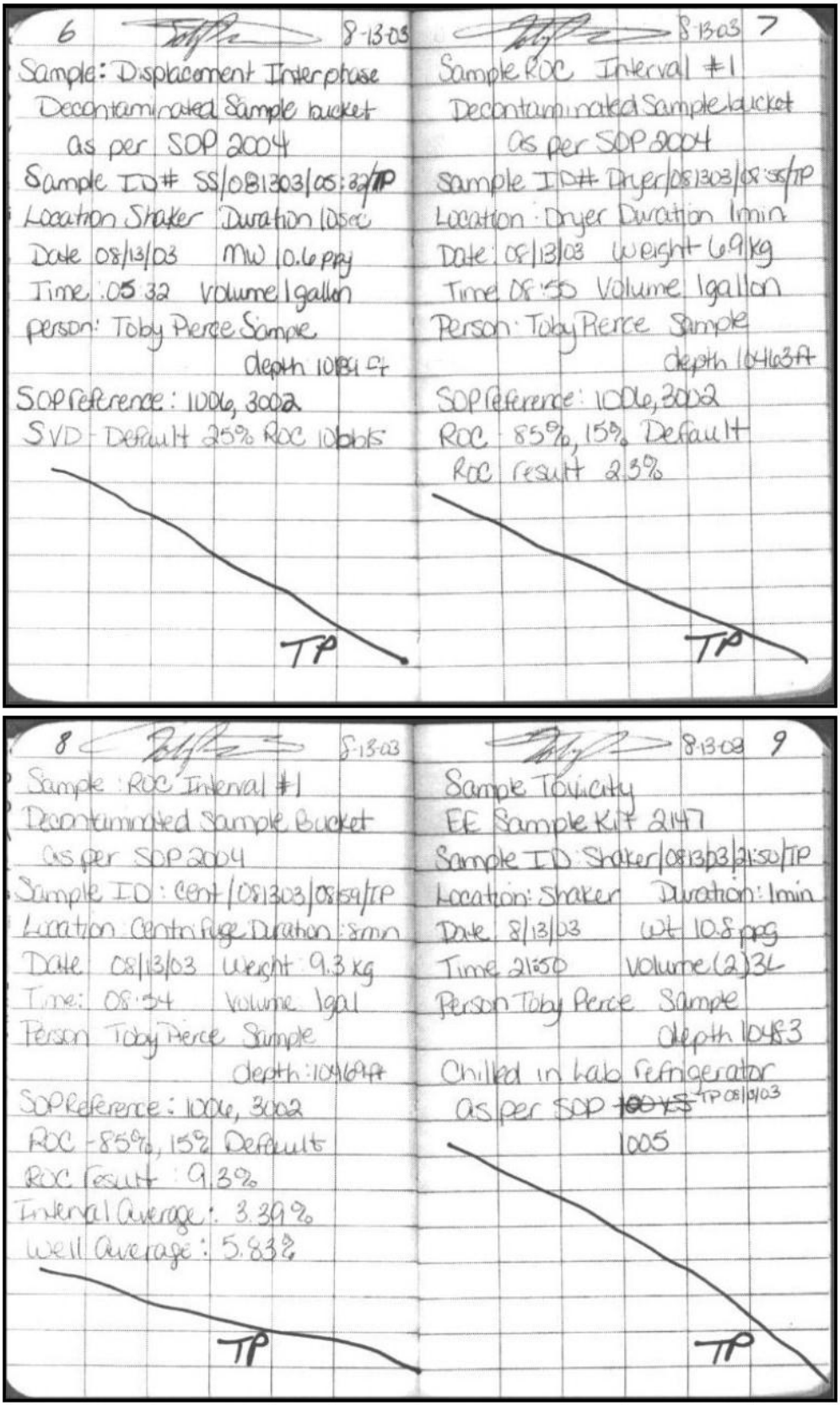
15.1 Daily Activity Reports are maintained in the Drilling Interval Notebook during the fluids drilling interval.

15.2 Upon completion of the drilling interval, original Daily Activity Reports are provided to the permittee and copies of the Daily Activity Reports are archived in the project files in the District Office.

15.3 Field notebooks are provided to the permittee at the completion of the fluids drilling interval and copies of the field notebooks are archived in the project files in the District Office.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Figure 1 -Example Field Notebook



6 8-13-03
Sample: Displacement Interphase
Decontaminated Sample bucket
as per SOP 2004
Sample ID# SS/081303/05:32/TP
Location Shaker Duration 10sec
Date 08/13/03 MW 10.6 ppg
Time: 05 32 Volume 1 gallon
person: Toby Pierce Sample
depth 10851 ft
SOP reference: 1006, 3002
SVD - Default 25% ROC 10bbls
TP

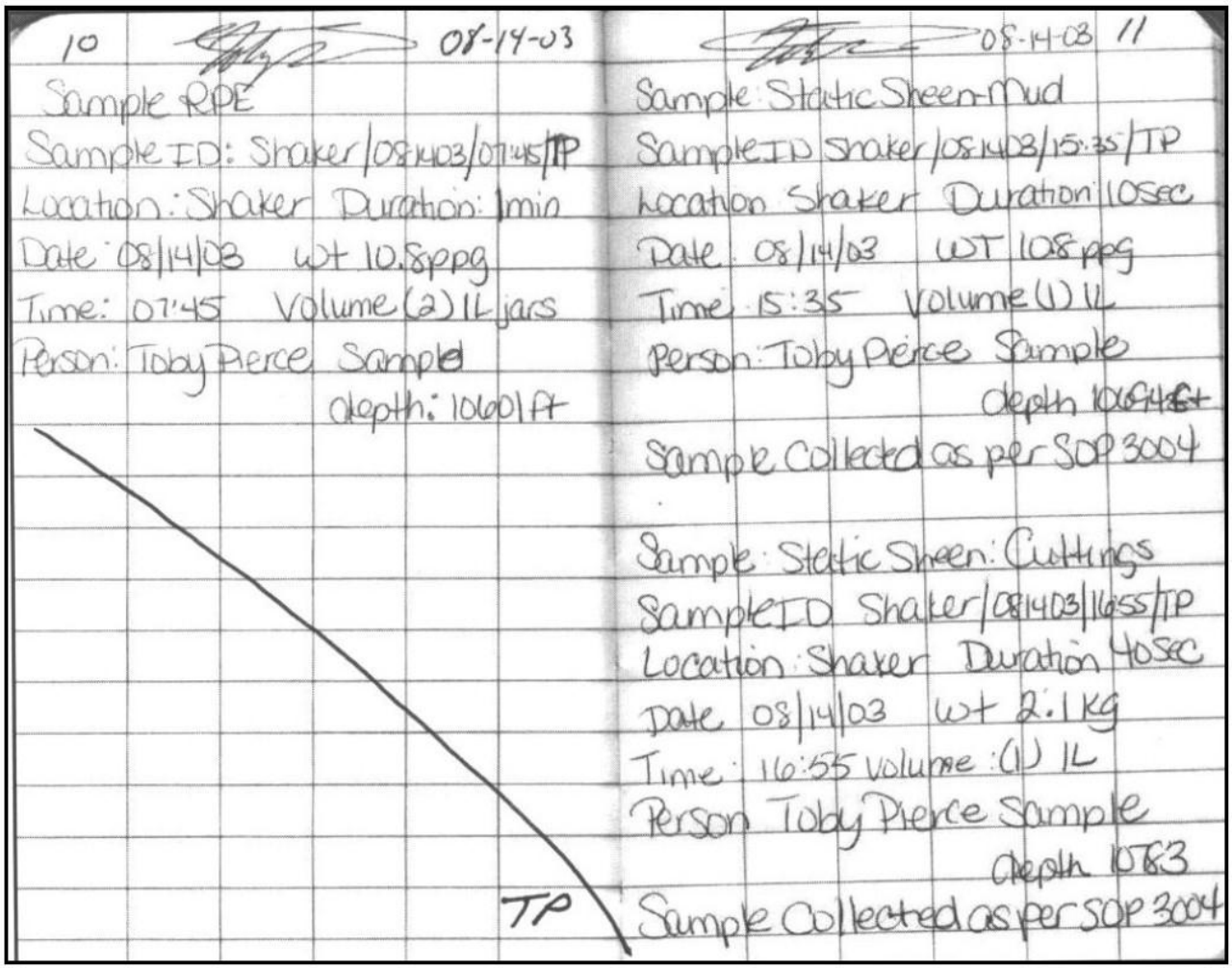
8-13-03 7
Sample ROC Interval #1
Decontaminated Sample bucket
as per SOP 2004
Sample ID# Dryer/081303/08:55/TP
Location: Dryer Duration 1min
Date: 08/13/03 Weight 6.9 kg
Time 08:50 Volume 1 gallon
Person: Toby Pierce Sample
depth 10463 ft
SOP reference: 1006, 3002
ROC 85%, 15% Default
ROC result 2.3%
TP

8 8-13-03
Sample: ROC Interval #1
Decontaminated Sample Bucket
as per SOP 2004
Sample ID: cent/081303/08:59/TP
Location: Centrifuge Duration: 8min
Date 08/13/03 Weight 9.3 kg
Time: 08:54 Volume 1gal
Person Toby Pierce Sample
depth: 10469 ft
SOP Reference: 1006, 3002
ROC - 85%, 15% Default
ROC Result 9.3%
Interval Average: 3.39%
Well Average: 5.83%
TP

8-13-03 9
Sample Toxicity
EE Sample Kit 2147
Sample ID: Shaker/081303/21:50/TP
Location: Shaker Duration: 1min
Date 8/13/03 wt 10.8 ppg
Time 21:50 Volume (2) 3L
Person Toby Pierce Sample
depth 10483
Chilled in Lab refrigerator
as per SOP ~~1005~~ TP 08/13/03
1005
TP

© Copyrig

Figure 1 – Example Field Notebook Page (continued)



10 08-14-03

Sample RPE
Sample ID: Shaker/081403/0745/TP
Location: Shaker Duration: 1min
Date: 08/14/03 wt 10.8ppg
Time: 07:45 Volume (2) 1L jars
Person: Toby Pierce Sample
depth: 10601 ft

TP

08-14-03 11

Sample: Static Sheen-Mud
Sample ID Shaker/081403/15:35/TP
Location Shaker Duration 10sec
Date: 08/14/03 WT 10.8 ppg
Time: 15:35 Volume (1) 1L
Person: Toby Pierce Sample
depth 10614ft
Sample Collected as per SOP 3004

Sample: Static Sheen: Cuttings
Sample ID Shaker/081403/1655/TP
Location: Shaker Duration 40sec
Date 08/14/03 wt 2.1 kg
Time: 16:55 volume: (1) 1L
Person Toby Pierce Sample
depth 10613
Sample Collected as per SOP 3004

© CopyrightM-1L.L.C., 2004, All Rights Reserved.

Daily Activity Report

Date:		**Compliance Engineer:**	
Operator:		**Surface Area and Block**	
OCS-G Number:		**Rig Name:**	
Rig Phone Number:		**Rig Fax Number:**	
Communications:			
Observations:			

Section 1 - ROC

Sample Identification (Location/Date/Time/Init)	Sample Depth (ft)	Sample Collection Reference	%ROC	Comments
		Daily ROC Percentage		
		Well ROC Percentage		

Section 2 - Other on-Site Samples

Sample ID (Loc/Dt/Time/Int)	Collection Site/Location	Preserv-ative	Test Method	Test Result	Comment

Section 3 - Offsite Samples

Sample ID (Loc/Dt/Time/Int)	Analysis Req.	Preserv-ative	C-O-C No.	Shipped?	Stored?	Comments

Section 4 - Equipment Calibration

Equipment Identification No.	SOP/Procedure	Calibration/Inspection Acceptable? (Yes/No)	Comments (Time of Malfunct; Repairs/Maint.)

Compliance Engineer Signature

Date

Demonstration of Capability

1.0 Scope and Application

This Standard Operating Procedure (SOP) provides a consistent methodology for analyst demonstration of capability. This SOP applies to all analysts that are performing environmental compliance analyses. This SOP describes the procedure for analyst demonstration of capability to perform analytical procedures described in the 3000 series SOPs.

2.0 Definitions

2.1 No specific definitions are necessary to complete this procedure.

3.0 Interferences

3.1 No specific interferences are known for this procedure.

4.0 Health and Safety Considerations

4.1 Health and safety considerations are described in the applicable analytical SOP.

5.0 Equipment and Supplies

5.1 See applicable analytical SOP.

6.0 Reagents and Standards

6.1 See applicable analytical SOP.

7.0 Sample Collection, Preservation, Shipment and Storage

7.1 Sample collection, preservation, shipment and storage requirements are not applicable.

8.0 Quality Control

8.1 Each analyst must demonstrate acceptable precision and accuracy as defined in the referenced EPA methods prior to analyzing compliance samples.

8.2 Compliance Engineers are trained in the requirements of this procedure through the Compliance Engineer training program. Training on SOP revisions will be documented through completion of Form 2009-1, as described in SOP 2009 (Compliance Engineer Training).

© Copyright M-I L.L.C., 2004, All Rights Reserved.

9.0 Calibration and Standardization

9.1 Calibration and standardization requirements are described in the applicable analytical SOP.

10.0 Procedure

10.1 ROC Test Procedure

10.1.1 The analytical procedure is M-I SWACO SOP 3002.

10.1.2 Obtain sufficient drill cuttings to perform the analytical procedure in quadruplicate. Cuttings should contain approximately 5 to 20 %ROC.

10.1.3 Thoroughly mix the cuttings and aliquot four replicates.

10.1.4 Analyze each replicate using the procedure in M-I SWACO SOP 3002.

10.1.5 Successful demonstration of analyst capability requires that the analyst coefficient of variation (CV) be less than 10%.

10.2 RPE Test Procedure

10.2.1 The analytical procedure is M-I SWACO SOP 3003.

10.2.2 Six quality control standards shall be prepared by spiking a Crude Oil F (or equivalent) into an internal olefin-based drilling fluid and a vegetable-ester based drilling fluid. The final concentrations of oil shall be 0.1%, 1%, and 2% in each drilling fluid. Sufficient volumes shall be prepared such that ten (10) aliquots of each standard are available for extraction and analysis.

10.2.3 A minimum of ten aliquots of each standard shall be prepared and analyzed according to the test method. Record the results on Form 3003-1 of M-I SWACO SOP 3003.

10.2.4 Successful demonstration of analyst capability will yield the results shown in Table 1 for the data set:

Table 1

Analyst Demonstration of Capability for RPE Procedure

Concentration	Acceptability
0.1 % Oil	Detected in less than 20% of the samples
1% Oil	Detected in greater than 75% of the samples
2% Oil	Detected in greater than 90% of the samples

© Copyright M-I L.L.C., 2004, All Rights Reserved.

10.3 Continued Proficiency

10.3.1 Continued proficiency for the ROC test is demonstrated by meeting the 95% mass balance requirement of M-I SWACO SOP 3002 and by acceptable field duplicate precision of less than 10 relative percent difference (RPD), **to be performed once per twenty sampling intervals** (to be tracked with the compliance engineer check sheet). Continued proficiency for the RPE test is demonstrated by correct interpretation of the positive and negative controls and spike samples.

11.0 Calculations

11.1 ROC Test Procedure

11.1.1 Precision of the replicate analyses is calculated with the following equations:

n = Total number of samples

X = Average of four replicate measurements (X) $\overline{X} = (X_1 + X_2 + X_3 + X_4)/n$

SD = Sample standard deviation $SD = \sqrt{\sum\left(\frac{(X-\overline{X})^2}{n-1}\right)}$

CV = Coefficient of variation $CV = \frac{SD}{\overline{X}} x100$

11.1.2 Accuracy of duplicate analyses is calculated with the following equation:

RPD = Relative Percent Difference $RPD = \frac{(A_1 - A_2)}{(A_1 + A_2)} x200$

Where A_1 and A_2 are the duplicate measurements

12.0 Data Assessment and Corrective Action

12.1 If the analyst does not successfully complete the Demonstration of Capability, the analyst is retrained and the Demonstration of Capability is repeated. The analyst will not perform a given compliance procedure until the Demonstration of Capability is successfully completed.

13.0 Pollution Prevention and Waste Management

13.1 Wastes generated with this procedure are managed as described in the applicable analytical SOP.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

14.0 References

14.1 M-I SWACO SOP 3001 (Retort Inspection and Calibration)

14.2 M-I SWACO SOP 3002 (Base Fluids Retained on Cuttings (ROC) Retort Test Procedure)

14.3 M-I SWACO SOP 3003 (Reverse Phase Extraction (RPE) Method for Detection of Oil Contamination in Non-Aqueous Drilling Fluids (NAF))

15.0 Documentation

15.1 The Certification Statement shown in Figure 1 is completed after the successful conclusion of a Demonstration of Capability.

15.2 Retain the raw data (applicable completed forms and instrument printouts) and the original certification in the District Office personnel qualifications files.

15.3 The Compliance Engineer maintains a copy of the Demonstration of Capability certification in the Compliance Engineer notebook.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Figure 1 Demonstration of Capability Certification Statement

Date:	
District Office Name:	
District Office Address:	
Analyst(s) Names:	
Matrix:	
Method number, SOP#, Rev#, and Analyte or Class of Analytes or Measured Parameters:	

We, the undersigned, CERTIFY that:

1. The analysts identified above, using the cited test method(s), which is in use at this District Office for the analyses of samples have met the Demonstration of Capability.

2. The analyst(s) identified on this certification performed the test method(s).

3. A copy of the test method(s) and the laboratory-specific SOPs are available for personnel on-site.

4. The data associated with the demonstration of capability are true, accurate, complete and self-explanatory.

5. Raw data (including the original of this certification form) necessary to reconstruct and validate these analyses have been retained at the District Office. A summary of the demonstration of capability is attached to the original certification form and maintained in the analyst's training records. The associated information is well-organized and available for review by authorized assessors or inspectors.

Senior Operations Manager	Signature	Date
Quality Assurance Officer's Name	Signature	Date

© Copyright M-I L.L.C., 2004, All Rights Reserved.

1.0 Scope and Application

This Standard Operating Procedure (SOP) describes the procedures for custody procedures for collection and submittal of permit compliance samples to mobile and fixed laboratories.

2.0 Definitions

2.1 Chain-of-custody is defined in "National Investigation Center Policies and Procedures Manual", EPA-330/9-78/001-R, Revised May 1986 as:

1. It is in your possession, or
2. It is in your view, after being in your possession, or
3. It was in your possession and then you locked it up to prevent tampering, or
4. It is in a designated secure area.

3.0 Interference

3.1 No specific interferences are known for this procedure.

4.0 Health and Safety Considerations

4.1 No specific health and safety considerations are necessary other than the general procedures outlined in the Global HSE Plan.

4.2 Consult Material Safety Data Sheets (MSDS) for drilling fluids used during drilling interval.

5.0 Equipment and Supplies

5.1 Chain-of-Custody (C-O-C) Form

5.2 Refrigerator that meets the criteria of M-I SWACO SOP 1005

5.3 Indelible Pen

6.0 Reagents and Standards

6.1 Reagents or standards are not applicable to this procedure.

7.0 Sample Collection, Preservation, Shipment and Storage

© Copyright M-I L.L.C., 2004, All Rights Reserved.

7.1 Sample collection, preservation, shipment and storage requirements are described in the sample and analysis SOPs.

8.0 Quality Control

8.1 This is a quality control procedure.

8.2 Compliance Engineers are trained in the requirements of this procedure through the Compliance Engineer training program. Training on SOP revisions will be documented through completion of Form 2009-1, as described in SOP 2009 (Compliance Engineer Training).

9.0 Calibration and Standardization

9.1 Calibration or standardization requirements are not applicable to this procedure.

10.0 Procedure

10.1 Mobile Laboratory Analyses

10.1.1 Label sample containers at sample collection as specified in M-I SWACO SOP 1006.

10.1.2 C-O-C forms are not required for mobile laboratory analyses.

10.1.3 Record sample collection information in the Field Notebook and on the Daily Activity Report as described in M-I SWACO SOP 1006.

10.1.4 Store samples for mobile laboratory analyses in a designated secure area under the proper conditions as specified in the sampling and analysis SOPs.

10.2 Fixed Laboratory Analyses

10.2.1 Label sample containers at sample collection as specified in M-I SWACO SOP 1006.

10.2.2 Complete the contract laboratory C-O-C as described below. If a contract laboratory C-O-C is not available or if the samples will be sent to the M-I SWACO laboratory, then complete the M-I SWACO C-O-C (Figure 1).

10.2.3 The sampler shall sign and date C-O-C in the area for “Sampler”.

10.2.4 Enter the Permittee Name and Location on the C-O-C form.

10.2.5 Enter the field sample identification, the analyses requested, the date and time of sample collection, preservation and number/type of containers in the appropriate spaces.

10.2.6 Repeat step 10.2.5 for each sample. Use additional C-O-C forms as needed.

10.2.7 Complete Section 3 of the Daily Activity Log as described in M-I SWACO SOP 1006.

10.3 Samples are stored under proper conditions until shipped or transferred to a third party.

10.4 When samples are provided to the drilling rig or shipped to a fixed laboratory, the Compliance Engineer shall sign and date the “Released by” block. The person receiving the

© Copyright M-I L.L.C., 2004, All Rights Reserved.

samples shall sign and date the "Received by". The Compliance Engineer retains a copy of the executed C-O-C and includes the original C-O-C with the samples.

10.5 The Compliance Engineer will ensure that the samples and original, executed C-O-C are sent to the contract laboratory or delivered to the appropriate personnel on the drilling rig.

10.6 Pack and ship the samples as specified in M-I SWACO SOP 2003.

11.0 Calculations

11.1 No calculations are necessary for this procedure.

12.0 Data Assessment and Corrective Action

12.1 Corrective action is required if C-O-C forms are not correctly completed. Generally, the corrective action is additional Compliance Engineer training.

13.0 Pollution Prevention and Waste Management

13.1 Wastes are not generated with this procedure.

14.0 References

14.1 "National Investigation Center Policies and Procedures Manual", EPA-330/9-78/001-R, Revised May 1986.

14.2 M-I SWACO SOP 1006

14.3 M-I SWACO SOP 2003

15.0 Documentation

15.1 Sample collection information is recorded as described in M-I SWACO SOP 1006.

15.2 Provide the receiving party with the original executed C-O-C when submitting the samples for analyses. Retain a copy of the executed C-O-C.

15.3 Archive the C-O-C copies in the Drilling Interval Logbook during the drilling interval.

15.4 Upon completion of the drilling interval, provide the permittee with a copy of the C-O-Cs retained after submittal of the samples. Archive a separate copy in the project files at the District Office.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Chain-of-Custody Procedures

Page 1 of

Chain-of-Custody Form

M-I Work Order #

Customer Information		Project Information		Parameter/Method Request for Analysis	
Purchase Order		Field:		A	Toxicity - 96 hour *Mysidopsis bahia*
Work Order		Block No.		B	Sediment Toxicity - 96 hour *Leptocheirus plumulosus*
Company Name		Well No:		C	Formation Oil by GC/MS
Send Report To:		OCS-G		D	PAH by HPLC/UV (1654A)
Address:		Drilling Rig		E	Biodegradation Rate
				F	Sediment Toxicity - 10 day
City/State/Zip		Comliance/Mud Enginner		G	Cadmium and Mercury
Phone		Division		H	
Fax		Drilling Foreman		I	

No.	Sample Description	Date	Time	Matrix	No. of Bottles	A	B	C	D	E	F	G	H	I
1														
2														
3														
4														
5														
6														
7														
8														
9														
10														
11														
12														
13														

Sampler(s): Please Print & Sign	Shipment Method:	Airbill No.:	Custody Seal No:	Results Due D

Relinquished by:	Date:	Time:	Received by:	Date:	Time:
Relinquished by:	Date:	Time:	Received by:	Date:	Time:
Relinquished by:	Date:	Time:	Received by:	Date:	Time:
Relinquished by:	Date:	Time:	Received by: (Laboratory)	Date:	Time:

Provide data to M-I representative at fax number:

Notes:

QC Package: (Check Box Below)

Analytical Results & QC Results ____

Results and backup data ____

Note: Any changes must be made in writing once samples and COC Form have been submitted by M-I, *L.L.C.*

COC

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Sample Collection for Suspended Particulate Phase (SPP) Toxicity Test

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

The purpose of the procedure is to provide a consistent method for the collection of drilling fluid samples for use in toxicity tests. These samples would be sent to a contract laboratory for 96-hour suspended particulate phase (SPP) toxicity testing using the method defined in 40 CFR 435, Appendix 2 to Subpart A.

2.0 Definitions

2.1 Base Fluid means the continuous phase or suspending medium of a drilling fluid formulation.

2.2 Drilling Fluid means the circulating fluid (mud) used in the rotary drilling of wells to clean and condition the hole and to counterbalance formation pressure.

3.0 Interferences

3.1 Sample interferences may be observed in the analytical results if sampling equipment is not properly decontaminated between samples or if contaminated gloves or sample containers are used.

4.0 Health and Safety Considerations

4.1 Fluids handled on the rig may cause skin irritation; wearing protective gloves (as described in the material safety data sheet [MSDS]) is recommended.

4.2 Fluid sample should be handled with the same precautions used in the fluid handling areas of the drilling rig.

4.3 Sampler must follow the Operator and Rig's safety procedures as well as the M-I SWACO safety procedures.

4.4 Consult the MSDS for specific health and safety information about the fluids being used in the treatment process.

4.5 Safety goggles must be worn during sample collection procedures.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

5.0 Equipment and Supplies

5.1 Nitrile gloves or other gloves suitable for handling fluid samples (as per MSDS). Change gloves before and between each sample.

5.2 Clean sample container (provided by the contract laboratory).

5.3 Chain-of-custody.

5.4 Sturdy ice chest with ice and packing materials for sample containers.

6.0 Reagents and Standards

6.1 There are no standards required for this procedure.

7.0 Sample Collection, Preservation, Shipment, and Storage

7.1 Each sample will be collected in a (1) 1-gal (4L) LDPE jar with plastic lid.

7.2 Sample will be maintained at 4±2 °C until analyzed.

7.3 Sample will be packaged and shipped in accordance with M-I SWACO SOP 2003 (Packaging and Shipment of Samples).

8.0 Quality Control

8.1 Samplers are trained in using this procedure by the Compliance Supervisor.

8.2 Samples must be maintained at 4±2 °C until tested.

8.3 No quality control samples are required.

9.0 Calibration and Standardization

9.1 No calibration required.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

10.0 Procedure

10.1 Drilling mud formulations to be tested shall be collected from active fluid systems. Obtain well-mixed grab sample from beneath the shale shaker after the mud has passed through the screens. Sample shall be stored in LDPE containers or in other appropriate uncontaminated vessels. This sample will be collected and analyzed weekly and at EOW.
The following sample containers will be provided by the laboratory. Sample containers may vary by laboratory; however, all sample containers and preservatives must comply with analytical method requirements.

Analyte	Method	Container	Preservative	Holding Time
SPP toxicity	40 CFR 435, Appendix 2 to Subpart A	(1) 1-gal (4L) LDPE jar	4±2°C	Initiate test within 90 days of sampling

10.2 Fill container with drilling fluid. Place the cap tightly on container after filling.

10.3 Label sample container with the sample identification number. The sample identification is composed of the sample location, date, time, and initials of the sampler. For example, a sample collected on January 31, 2012 at 1852 by John Doe would be labeled as SS/013112/18:52/JD. The label shall also contain the operator name, the block name and number, the OCS-G number, the analysis requested, the sample collection date and time, and sampler initials. Sample identification information will be recorded on the chain-of-custody.

10.4 Record sample location and identification information in the field notebook as per M-I SWACO SOP 1006 (Field Logs).

10.5 Mud samples shall be immediately chilled in a dedicated laboratory refrigerator to 4±2°C. One of the samples shall be shipped to the testing facility on wet ice or gel packs (do not use dry ice or blue ice) and continuously maintained at 4±2°C until the time of testing.

11.0 Calculations

11.1 There are no calculations with this procedure.

12.0 Data Assessment and Corrective Actions

12.1 If sample integrity has been compromised (e.g., container overfilled, sample not preserved, sample bottle cracked, etc.), it must be returned to the processing equipment for recycling and the used container must be placed in the appropriate waste container.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

13.0 Pollution Prevention and Waste Management

13.1 Return the purge volume to the treatment process.

13.2 Follow operator's requirements for disposal of used PPE and disposable sampling equipment.

14.0 References

14.1 Permit No: AKG 280000

14.2 40 CFR 435, Appendix 2 to Subpart A

14.3 M-I SWACO SOP 1006 (Field Logs)

14.4 M-I SWACO SOP 2001 (Chain-of-Custody Procedures)

14.5 M-I SWACO SOP 2003 (Packaging and Shipping of Samples)

14.6 M-I SWACO SOP 2004 (Decontamination of Equipment)

15.0 Documentation

15.1 Chain-of-custody, sample labels, field logbooks.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Packaging and Shipment of Samples

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

This Standard Operating Procedure (SOP) presents procedures for labeling samples, and packaging and shipping samples for transfer to an analytical laboratory.

2.0 Definitions

2.1 Environmental samples – samples whose toxic, flammable, corrosive, or otherwise hazardous constituents represent less than one percent by volume of the sample.

2.2 Hazardous samples – samples whose total concentration of toxic, flammable, corrosive or otherwise hazardous constituents are likely to be equal to or greater than one percent by volume of the sample.

3.0 Interferences

3.1 Use packaging material to fill the unused space in the cooler to prevent sample containers from breaking. Ensure that sample containers are tightly sealed. Improperly sealed or broken containers can result in cross-contamination.

3.2 Double-bag wet ice in resalable bag to prevent leaking, which can contribute to cross-contamination.

3.3 Maintain temperature at 4±2°C so that water samples do not freeze.

4.0 Health and Safety Considerations

4.1 Follow health and safety procedures outlined in the Global HSE Plan.

4.2 Consult Material Safety Data Sheets (MSDS) for drilling fluids used during drilling interval.

5.0 Equipment and Supplies

5.1 Use supplies provided by the laboratory. If not available, then obtain the following supplies:

5.1.1 Pre-cleaned sample containers

5.1.2 Sample labels

5.1.3 Sturdy cooler, in good repair

5.1.4 Bubble wrap or other packing material

5.2 Absorbent pads or packing material, such as vermiculite

5.3 Strapping tape

5.4 Ziploc® type bags (or equivalent), gallon and quart size

5.5 Ice (sufficient quantity to chill samples to 4°C)

5.6 Shipping labels and custody seals

5.7 Air bill and/or manifest

5.8 Indelible pen and/or marker

5.9 Field logbook

5.10 Chain-of-custody

5.11 Temperature blank

5.11 Trip blank (if required)

6.0 Reagents and Standards

6.1 No reagents or standards are required for this procedure.

7.0 Sample Collection, Preservation, Shipment and Storage

7.1 Samples will be collected in accordance with the applicable sampling SOP using the appropriate container and preservative required by the analytical method. These containers will be provided by the contract laboratory.

7.2 Samples will be stored in a dedicated laboratory refrigerator and maintained at 4±2°C until analyzed.

7.3 Samples will be shipped according to the procedures described in this SOP (Section 10.0).

8.0 Quality Control

8.1 This SOP is a quality control procedure.

8.2 Compliance Engineers are trained in the requirements of this procedure through the Compliance Engineer training program. Training on SOP revisions will be documented through completion of Form 2009-1, as described in SOP 2009 (Compliance Engineer Training).

9.0 Calibration and Standardization

9.1 Calibration and standardization procedures are not applicable.

10.0 Procedure

10.1 Samples should be collected in appropriate containers with sufficient volume and preservation as described in the sampling SOPs .

10.2 Sample Labeling

10.2.1 Samples shall be uniquely identified, labeled, and documented in the field at the time of collection.

10.2.2 Samples collected for laboratory analysis are identified by using standard sample labels that are affixed to the sample containers. The following information shall be included on the sample label at the time of collection using waterproof, non-erasable ink:

- Date - A six-digit number indicating the year, month and day of collection;
- Time - A four-digit number indicating the military time of collection;
- Sample Number – sample identification as described in M-I SWACO SOP 1006 (Field Logs) and applicable sampling SOPs;
- Preservative - (if any);
- Sampler - Signature of person collecting the sample; and
- Requested Analyses.

10.3 Follow chain-of-custody procedures throughout cooler packaging and shipment. Refer to M-I SWACO SOP 2001 (Chain-of-Custody Procedures).

10.4 Select the best method to transport the material based on quantity and hazard(s) of the sample. Qualified personnel will ship samples that are designated as hazardous materials.

10.5 Sample Packaging

10.5.1 This procedure only applies to those samples that M-I SWACO is packaging and shipping. Most samples will be transferred to the permittee and the permittee will be responsible for packing and shipping the sample.

10.5.2 Environmental samples should be packed prior to shipment using the following procedures:

- Allow sufficient headspace (approximately 10 percent of the volume of the container) in all bottles, except for volatile water samples. Samples collected in VOA vials for volatile analyses (TAH, SW8260B, etc.) should have no headspace.
- Ensure that the lids on all bottles are tight.
- Select a sturdy cooler in good repair. Secure and tape the drain plug with packaging tape.
- Place glass sample bottles into bubble wrap bags or wrap a layer of bubble wrap around glass containers.
- The samples are packed in a cooler using cushioning material such as bubble wrap, vermiculite, Styrofoam pellets, etc. Crushed ice or ice cubes shall not be used for packing material.
- Place noxious samples in paint cans with vermiculite before being placed in the cooler. The recipient of the samples shall be notified in advance so that proper precautions may be taken when opening the shipping container.
- Ensure that each cooler contains a temperature blank. Temperature blanks are plastic bottles containing water that are provided by the laboratory.
- If the cooler contains samples for volatile analyses (TAH, SW8260B, etc.), verify that the cooler contains a trip blank. A trip blank is a set of (3) sealed 40-mL VOA vials containing reagent grade water. These are provided by the contract laboratory.
- Fill the resalable plastic bags with ice. Double-bag the ice to minimize leaks. Place the bags on the sides of the cooler and double line the top of the samples.
- Complete the chain-of-custody (CoC) form in accordance with M-I SWACO SOP 2001 (Chain-of-Custody Procedures) and applicable sample SOPs. Sign and date the CoC before placing it in the cooler with the samples.
- The last page of the completed chain-of-custody form shall be kept with the field records. Place the original Coca in a resealable plastic bag and tape to the inside of the cooler lid.
- Add more packing material if needed.
- Sign and date custody seals. Place one on each end of the cooler, across the cooler lid. Use clear packaging tape across each custody seal. Seal the cooler with packaging tape.
- The cooler lid is labeled with the name, address, and phone number of the destination laboratory and the return address and phone number of the shipper. Air bills or manifests provided by the shipping company are also completed with the required information. The label on the cooler lid also shall identify the contents as environmental samples.
- The completed and labeled coolers shall be shipped as appropriate to minimize sample holding times and to maintain preservation.

10.5.3 Hazardous environmental samples are provided to the permittee to arrange for shipping.

- If M-I SWACO personnel must ship the samples, it will be necessary to determine the DOT classification of hazardous environmental samples prior to shipment before exact labeling and shipping procedures can be determined. A qualitative knowledge of the composition of the materials is necessary for classification. Consult with trained personnel who have knowledge of dangerous goods or hazardous materials regulations (see Section 13 - References) prior to packaging and shipping hazardous samples. Specific information for packaging and shipping hazardous samples is outside the scope of this SOP.

10.6 Sample Shipping

10.6.1 This procedure only applies to those samples that M-I SWACO is packing and shipping. Most samples will be transferred to the permittee and the permittee will be responsible for packing and shipping the sample.

10.6.2 Samples collected in the field shall be transported to the laboratory or field testing site as expeditiously as possible to avoid hold time exceedence and to ensure that samples remain properly preserved. If necessary, samples shall be kept chilled prior to shipping.

10.6.3 Sample coolers will be transported via helicopter to Barrow. An M-I SWACO representative will transfer the samples to Alaska Airlines Gold Streak for direct shipment to the appropriate laboratory for analysis.

10.6.3 Samples must be classified prior to shipment, as either environmental or hazardous materials samples. If there are questions, contact the Compliance Supervisor or appropriate permittee personnel.

10.7 Shipping addresses

Organic and Metals Analyses:
SGS Environmental Services, Inc.
200 W. Potter Drive
Anchorage, AK 99518
(907) 562-2343

Pace Analytical
940 So Harney
Seattle, WA 98108
(206) 767-5060

SPL, Inc.
500 Ambassador Coffer Parkway
Scott, LA 20583
(337) 237-4775

Stock barite analyses:
SGS Environmental Services, Inc.
200 W. Potter Drive
Anchorage, AK 99518
(907) 562-2343

TestAmerica Laboratories, Inc.
6310 Rothway Street
Houston, TX 77040
(713) 690-4444

Toxicity Analyses:
Bio-Aquatic Testing, Inc.
2501 Mayes Road, Suite 100
Carrollton, TX 75006
(972) 242-7750
(866) 822-7250

Environmental Enterprises USA, Inc.
58485 Pearl Acres Road, Suite D
Slidell, LA 70461
(985) 646-2787
(800) 966-2788

11.0 Calculations

11.1 No calculations are necessary for this procedure.

12.0 Data Assessment and Corrective Action

12.1 No corrective action is required by this procedure.

13.0 Pollution Prevention and Waste Management

13.1 Minimize the quantity of samples shipped to the amount needed for the analytical tests.

14.0 References

14.1 Regulations for transportation of hazardous materials in interstate, intrastate, and foreign commerce by rail car, aircraft, motor vehicle, and vessel are promulgated in 49 CFR Parts 171 through 181, Subchapter C- Hazardous Materials Regulations.

14.2 Regulations for packing, marking, labeling, and shipping of dangerous goods by air transport are promulgated by the International Air Transport Authority (IATA), which is equivalent to United Nations International Civil Aviation Organization (UN/ICAO). *Dangerous Goods Regulations*. International Air Transport Association (IATA).

14.3 Regulations for packing, marking, labeling, and shipping of dangerous goods by marine vessel are promulgated by the International Maritime Organization (IMO). *International Maritime Dangerous Goods Code*. International Maritime Organization (IMO), Amendment 29-98.

14.4 M-I SWACO SOP 1006 (Field Logs)

14.5 M-I SWACO SOP 2001 (Chain-of-Custody Procedures)

15.0 Documentation

15.1 Archive the air bill or manifest with the CoC in the Drilling Interval Logbook during the drilling interval.

15.2 Upon completion of the drilling interval, provide the permittee with the original air bill or manifest. Archive a copy of the air bill or manifest in the project files at the District Office.

Decontamination of Equipment

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

This Standard Operating Procedure (SOP) provides consistent methodology for decontamination of sampling equipment. Removing contaminants from equipment minimizes the likelihood of sample cross contamination, reduces or eliminates transfer of contaminants to clean areas, and prevents the mixing of incompatible substances.

2.0 Definitions

2.1 No specific definitions are necessary to complete this procedure.

3.0 Interferences

3.1 The use of an untreated potable water supply is not acceptable.

4.0 Health and Safety Considerations

4.1 No specific health and safety considerations are necessary other than the general procedures outlined in the Global HSE Plan.

4.2 Consult Material Safety Data Sheets (MSDS) for drilling fluids used during drilling interval.

5.0 Equipment and Supplies

5.1 Long and short handled brushes

5.2 Paper towels

5.3 Plastic or galvanized tubs, buckets or stainless steel sink

5.4 Drying rack

5.5 Appropriate personal protective equipment (PPE)

6.0 Reagents and Standards

6.1 Non-phosphate detergent such as Alconox®

6.2 Potable (treated tap) water

7.0 Sample Collection, Preservation, Shipment and Storage

7.1 Sample collection, preservation, shipment and storage requirements are not applicable.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

8.0 Quality Control

8.1 Efficacy of decontamination procedures can be determined by the collection and analysis of equipment blanks.

8.2 Compliance Engineers are trained in the requirements of this procedure through the Compliance Engineer training program. Training on SOP revisions will be documented through completion of Form 2009-1, as described in SOP 2009 (Compliance Engineer Training).

9.0 Calibration and Standardization

9.1 Calibration and standardization procedures are not applicable.

10.0 Procedure

10.1 Don appropriate PPE (minimum safety glasses with side shield and gloves).

10.2 Fill a sink, bucket or tub (large enough to contain equipment) with potable (treated tap) water and non-phosphate detergent.

10.3 Place the equipment in the soapy water and scrub the equipment.

10.4 Rinse the equipment with copious quantities of potable (treated tap) water.

10.5 Allow the equipment to air dry on a clean surface covered with paper towels or on a drying rack, if available.

10.6 Cover the sampling equipment or analytical glassware during storage.

11.0 Calculations

11.1 No calculations are necessary for this procedure.

12.0 Data Assessment and Corrective Action

12.1 If equipment blanks contain detectable concentration of target analytes, add extra cleaning steps to the procedure.

13.0 Pollution Prevention and Waste Management

13.1 Follow permittee's requirements for disposal of rinse water and soapy solutions.

14.0 References

14.1 No references are applicable.

15.0 Documentation

15.1 No documentation is necessary for this procedure.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Collection of Quality Control Samples

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

This Standard Operating Procedure (SOP) describes procedures to collect quality control samples. Requirements for collecting quality control samples are described in the appropriate sampling and analysis SOPs.

2.0 Definitions

2.1 Equipment Blank – provides a measure of the efficacy of decontamination procedures through the collection and analysis of a contaminant-free material that has been exposed to the sampling equipment.

2.2 Duplicate - a pair of field samples that are chemically identical at the time of containerization. Duplicates provide a measure of the precision in the sample collection and analysis procedures for a given sample matrix.

2.3 Matrix Spike/Matrix Spike Duplicate (MS/MSD) – prepared in the laboratory by spiking two aliquots of a single field sample with a known quantity of analyte. The MS/MSD samples are prepared and analyzed using the same conditions as the field sample. MS/MSD samples provide a measure of the precision and accuracy of the sample collection and analysis procedures for a given sample matrix.

3.0 Interferences

3.1 The quality control samples described in this procedure (duplicate and matrix spike) may provide information about sample interferences.

4.0 Health and Safety Considerations

4.1 No specific health and safety considerations are necessary other than the general procedures outlined in the Global HSE Plan.

4.2 Consult Material Safety Data Sheets (MSDS) for drilling fluids used during drilling interval.

5.0 Equipment and Supplies

5.1 Pre-cleaned sample containers (with preservatives, if required)

5.2 Stainless steel or plastic sampling bowl

5.3 Stainless steel or plastic sampling spoon

© Copyright M-I L.L.C., 2004, All Rights Reserved.

5.4 Other equipment as for collecting samples, as described in the applicable sampling SOPs.

6.0 Reagents and Standards

6.1 Analyte-free water

7.0 Sample Collection, Preservation, Shipment and Storage

7.1 Sample collection, preservation, shipment and storage requirements are described in the sampling and analysis SOPs.

8.0 Quality Control

8.1 This is a quality control procedure.

8.2 Compliance Engineers are trained in the requirements of this procedure through the Compliance Engineer training program. Training on SOP revisions will be documented through completion of Form 2009-1, as described in SOP 2009 (Compliance Engineer Training).

9.0 Calibration and Standardization

9.1 Calibration and standardization procedures are not applicable.

10.0 Procedure

10.1 Refer to M-I SWACO SOP 1006 (Field Logs) for sample identification requirements. Refer to M-I SWACO SOP 2001(Chain-of-Custody Procedures) for chain-of-custody procedures.

10.2 Equipment Blanks

10.2.1 Equipment blanks are not collected on disposable or dedicated equipment. If an equipment blank is required in the sampling and analysis SOPs or in the rig-specific sampling plan, then follow the procedures described below.

10.2.2 Properly decontaminate the sampling device as described in M-I SWACO SOP 2004 (Decontamination of Equipment).

10.2.3 Select the proper sample containers and an appropriate quantity of analyte-free water.

10.2.4 Slowly pour the analyte-free water through, over or into the sampling device until the sample bottle is filled to the appropriate level.

10.2.5 Securely tighten the cap on the bottle.

10.3 Duplicate Samples

10.3.1 If a field duplicate sample is required in the sampling and analysis SOPs, then follow the procedures described below.

10.3.2 Select the proper containers for a sample and a duplicate sample.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

10.3.3 Collect the sample in accordance with the appropriate sampling SOPs.

10.3.4 For cuttings samples, collect the sample material into a sample container and thoroughly homogenize the sample with a spoon. Take half the sample and place into another sample container, and homogenize both.

10.3.5 For mud samples, thoroughly homogenize the samples.

10.3.6 Fill the appropriate sample jars, placing equal portions of sample into the sample bottles.

10.3.7 Securely tighten the caps on the sample bottles.

10.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

10.4.1 Many laboratories can prepare the MS/MSD samples from the submitted sample volume. The sampler is only required to identify the sample for MS/MSD analysis on the chain of custody.

10.4.2 If the laboratory requires additional sample volume (as indicated in the sampling and analysis SOPs or in the rig-specific sampling plan), the samples should be collected as duplicate samples, filling three bottles with sample.

10.5 Prepare the sample bottle(s) for shipment in accordance with M-I SWACO SOP 2003 (Packaging and Shipment of Samples).

11.0 Calculations

11.1 No calculations are necessary for this procedure.

12.0 Data Assessment and Corrective Action

12.1 If the duplicate results consistently show poor precision, increase the time spent homogenizing the sample.

13.0 Pollution Prevention and Waste Management

13.1 Waste management procedures discussed in the applicable sampling and analysis SOPs apply to the equipment blank, field duplicate and matrix spike samples.

14.0 References

14.1 ““Handbook of Analytical Quality Control in Water and Wastewater Laboratories”. EPA-600/4-79-019, March 1979.

14.2 M-I SWACO SOP 1006 (Field Logs)

14.3 M-I SWACO SOP 2001 (Chain-of-Custody Procedures)

14.4 M-I SWACO SOP 2003 (Packaging and Shipment of Samples)

14.5 M-I SWACO SOP 2004 (Decontamination of Equipment)

© Copyright M-I L.L.C., 2004, All Rights Reserved.

15.0 Documentation

15.1 Collection of quality control samples is recorded in the field notebooks and on the Daily Activity Reports.

15.2 Daily Activity Reports are maintained in the Drilling Interval Notebook during the synthetic fluids drilling interval.

15.3 Upon completion of the drilling interval, original Daily Activity Reports are provided to the permittee and copies of the Daily Activity Reports are archived in the project files in the District Office.

15.4 Field notebooks are provided to the permittee at the completion of the synthetic fluids drilling interval and copies of the field notebooks are archived in the project files in the District Office.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Sample Collection for Oil and Grease Testing

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

This Standard Operating Procedure (SOP) describes processes to collect samples for oil and grease analyses. NPDES compliance samples must be analyzed by an on-shore contract laboratory using Environmental Protection Agency (EPA) Method 1664A (n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry). This SOP is designed to provide general guidelines for the types of equipment and sampling procedures required for the collection of representative samples from various sampling ports. **Specific procedures for sampling are described in the rig-specific Sampling and Analysis Plans.**

2.0 Definitions

2.1 Sample port – the sample locations, such as lines or taps, where the samples will be collected.

2.2 Equipment Blank – provides a measure of the efficacy of decontamination procedures through the collection and analysis of a contaminant-free material that has been exposed to the sampling equipment.

2.3 Field duplicate - A field duplicate sample is a second sample collected at the same location as the original sample. Duplicate samples are collected simultaneously or in immediate succession, using identical recovery techniques, and treated in an identical manner during storage, transportation, and analysis.

2.4 Matrix Spike - Matrix spikes are performed by spiking one of a pair of duplicate samples with a known quantity of analyte and extracting and analyzing both the spiked and the unspiked duplicate. In the absence of matrix interferences, the difference between the analytical results for these two duplicates will yield an acceptable recovery rate for the spike.

3.0 Interferences

3.1 Sample interferences may be observed in the analytical results if sampling equipment is not properly decontaminated between samples or if contaminated gloves or sample containers are used.

4.0 Health and Safety Considerations

4.1 Fluids handled on the rig may cause skin irritation; wearing protective gloves (as described in the material safety data sheet [MSDS]) is recommended.

©Copyright M-I L.L.C., 2004, All Rights Reserved.

4.2 Fluid sample should be handled with the same precautions used in the fluid handling areas of the drilling rig.

4.3 Sampler must follow the Operator and Rig's safety procedures as well as the M-I SWACO safety procedures.

4.4 Consult the MSDS for specific health and safety information about the fluids being used in the treatment process.

4.5 Sample containers may contain hydrochloric acid; gloves must be worn when handling sample containers.

4.6 Safety goggles must be worn during sample collection procedures.

4.7 Follow safety guidelines and precautions for use of PTFE bailers.

5.0 Equipment and Supplies

5.1 Nitrile gloves or other gloves suitable for handling fluid samples (as per MSDS) and containers with hydrochloric acid. Change gloves before and between each sample.

5.2 Chain-of-custody (C-O-C)

5.3 Disposable PTFE bailer, 2" by 36"

5.4 Uncontaminated Nylon rope or twine

5.5 Drip pan, metal

5.6 Purge bucket, such as 1-gallon metal bucket, for collecting purge volume of completion fluid

5.7 Sample bottles for EPA Method 1664A analyses: 1-liter pre-cleaned glass sample containers (with preservatives) and PTFE-lined screw cap

5.8 Sturdy ice chest with packing materials for sample containers.

6.0 Reagents and Standards

6.1 Hydrochloric (HCl) acid, 6N

7.0 Sample Collection, Preservation, Shipment and Storage

7.1 Samples should be preserved to < pH 2 using 6N HCl acid.

7.2 Samples should be maintained at 4°C ± 2 until tested.

7.3 Ship samples as described in M-I SWACO SOP 2003 (Packaging and Shipment of Samples).

8.0 Quality Control

©Copyright M-I L.L.C., 2004, All Rights Reserved.

8.1 Samplers are trained in using this procedure by the Compliance Supervisor.

8.2 If samples are collected with reusable equipment, collect field blanks as described in M-I SWACO SOP 2005 (Collection of Quality Control Samples).

8.3 Collect field duplicates every 10 samples.

8.4 Training records are maintained and are available from the M-I SWACO Compliance Supervisor upon request.

8.5 No plastic sampling containers or sampling devices of any kind shall be used.

8.6 No composite sampling shall be performed without permittee written permission.

9.0 Calibration and Standardization

9.1 Calibration and standardization procedures are not required.

10.0 Procedure for Collecting Oil and Grease Samples

10.1 The objective of this procedure is collecting a representative sample in a glass bottle.

10.2 **FIELD DOCUMENTATION:** All information for this sampling procedure is recorded in the field notebook as per M-I SWACO SOP 1006 (Field Logs).

10.3 Sampler must identify each sample and sample location. This is recorded in the field notebook as per M-I SWACO SOP 1006 (Field Logs).

10.4 It is preferential to use disposable sampling equipment. Reusable sampling tools must be decontaminated using the procedures in M-I SWACO SOP 2004 (Decontamination of Equipment) before collecting the samples. If reusable sampling equipment is used to collect samples, then field blanks must be collected as described in M-I SWACO SOP 2005 (Collection of Quality Control Samples).

10.5 The preferential sample point is a tap in the treatment system that can be isolated with a valve. This point will allow the collection of a grab sample directly into the sample bottle.

10.6 Collection from a Sampling Port

10.6.1 The sampler shall take the monthly Oil and Grease sample after the last point of filtration before the fluid is discharged. This sample shall be representative of the fluid after it has returned from the well bore and be representative of the fluid being discharged.

10.6.2 Calculate the amount of liquid present in the dead space between the line and the sample port.

10.6.3 Place a drip pan under the port and place the completion purge bucket in the drip pan. The completion purge bucket should be of sufficient size to hold the amount of liquid present in the dead space.

©Copyright M-I L.L.C., 2004, All Rights Reserved.

10.6.4 Slowly open the sample port and purge the volume of the liquid calculated above from the line and collect in the waste bucket. Purge the sample port for a minimum of 10 seconds. Return the liquid to the process for recycling.

10.6.5 After purging the line, collect the sample directly into the appropriate sample container. Do not pre-rinse the container. Do not overfill the container. If the container is overfilled the sample must be returned to the processing equipment for recycling and the used container must be placed in the appropriate waste container and a new sample collected into a new container.

10.6.6 Fill the sample bottle to approximately 1 inch of the top of the sample container.

10.6.7 If the sample container did not contain preservative, add 5 ml of 6N HCl to the 1-liter container. Use pH paper to verify a pH of less than 2. If pH is not less than 2, add 6N HCl to lower pH below 2.

10.6.8 Place the cap on the container and tighten. If the cap is cracked or has dropped on the grating, use a new cap.

10.6.9 Close the sample port valve after collection of the samples. Verify that the valve is closed.

10.7 Collection Using a PTFE Bailer

10.7.1 This procedure is designed to collect samples from a pit, tank, drum or other container that does not have liquid flow or a sample tap. In lieu of a tap, samples may be collected through the depth of the container using a PTFE bailer.

10.7.2 Follow M-I SWACO and Operator safety procedures for lockout/tagout of circulating and agitating equipment that may cause entanglement of sampling equipment.

10.7.3 Don the appropriate personal protective equipment. Use double pair of nitrile gloves.

10.7.4 Tie uncontaminated nylon rope or twine to the end of the PTFE bailer. Check the knot to ensure that PTFE bailer will not slip off the rope. Double check that the bailer will not slip off of the rope.

10.7.5 Lower the PTFE bailer into the container until approximately 1-foot below the surface of the liquid.

10.7.6 Remove the PTFE bailer and observe the liquid in the bailer for phase differences. If phase differences are observed, consult with the Operator before submitting the sample for analysis.

10.7.7 Empty the PTFE bailer into the sample container

10.7.8 If the PTFE bailer specified in this SOP is used for sample collection, there should be sufficient volume to fill a 1-liter glass container.

10.7.9 If the sample container did not contain preservative, add 5 ml of 6N HCl to the 1-liter container and 2 ml of 6N HCl to the 100-ml containers.

©Copyright M-I L.L.C., 2004, All Rights Reserved.

10.7.10 Place the cap on the container and tighten. If the cap is cracked or has dropped on the grating, use a new cap.

10.8 Quality Control Samples

10.8.1 If the sampler is required to collect MS/MSD samples, they should be collected as duplicate samples but with three sets of samples (one original sample, one matrix spike sample, and one matrix spike duplicate). Collect an additional one or two aliquots (1 L, additional smaller volume, or both) using the same sampling procedure for each set of twenty samples or less. These samples will be designated the matrix spike and, if collected, the matrix spike duplicate.

10.8.2 It is preferable to use disposable sampling equipment. M-I SWACO must obtain prior written permission from the Operator's Environmental Engineer prior to sampling with reusable sampling equipment. Reusable sampling tools must be decontaminated using the procedures in M-I SWACO SOP 2004 (Decontamination of Equipment) before collecting the samples. If reusable sampling equipment is used to collect samples, then field blanks must be collected as described in M-I SWACO SOP 2005 (Collection of Quality Control Samples).

10.8.3 Collect a field duplicate at a frequency of 1 in 10 samples using the same sampling procedure.

10.9 Sample Labeling and Shipment

10.9.1 Complete the sample labels as described in M-I SWACO SOP 2003 (Packaging and Shipment of Samples).

10.9.2 Prepare the samples for EPA 1664A analysis for shipment to the on-shore contract laboratory in accordance with M-I SWACO SOP 2003 (Packaging and Shipment of Samples).

11.0 Calculations

11.1 If applicable, calculate the dead volume (V) in the purge line using the following equation:

$$V \text{ (gallons)} = (7.48)(\pi)(r^2)(h)$$

Where $\pi = 3.14$

r = radius of sampling port (feet), and

h = length of port to be purged (feet).

12.0 Data Assessment and Corrective Action

12.1 If sample integrity has been compromised (e.g., container overfilled, sample not preserved, sample bottle cracker, etc.), it must be returned to the processing equipment for recycling and the used container must be placed in the appropriate waste container.

©Copyright M-I L.L.C., 2004, All Rights Reserved.

12.2 If the cap is cracked or has dropped on the grating, use a new cap.

13.0 Pollution Prevention and Waste Management

13.1 Return the purge volume to the treatment process

13.2 Follow operator's requirements for disposal of rinse water and soapy solutions that result from decontamination of the sampling equipment.

13.3 Follow operator's requirements for disposal of used PPE equipment.

13.4 Follow operator's requirements for disposal sampling equipment.

14.0 References

14.1 Final NPDES General Permit for New and Existing Sources and New Dischargers in the Offshore Subcategory of the Oil and Gas Extraction Category for the Western Portion of the Outer Continental Shelf of the Gulf of Mexico (GMG290000)

14.2 Final NPDES General Permit No. GMG 460000 for Offshore Oil and Gas Activities in the Eastern Gulf of Mexico

14.3 Operator and M-I SWACO Safe Work Plan

14.4 Method 1664, Revision A n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry, EPA-821-R-98-002 (PB99-121949), February 1999.

14.5 M-I SWACO SOP 1006 (Field Logs)

14.6 M-I SWACO SOP 2001 (Chain-of-Custody Procedures)

14.7 M-I SWACO SOP 2003 (Packaging and Shipping of Samples)

14.8 M-I SWACO SOP 2004 (Decontamination of Equipment)

14.9 M-I SWACO SOP 2005 (Collection of Quality Control Samples)

15.0 Documentation

15.1 Identify samples as described in M-I SWACO SOP 1006 (Field Logs).

15.2 For those samples shipped to fixed laboratories, field and quality control sample information is entered on the C-O-C as described in M-I SWACO SOP 2001 (Chain-of-Custody Procedures).

©Copyright M-I L.L.C., 2004, All Rights Reserved.

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

The purpose of this procedure is to provide a consistent method for the collection of drilling fluid samples for analysis for chromium VI, silver, and thallium. These samples will be sent to a contract laboratory for testing by method SW6020A (chromium, silver, and thallium). Chromium VI will be analyzed as total chromium.

2.0 Definitions

2.1 Base Fluid means the continuous phase or suspending medium of a drilling fluid formulation.

2.2 Drilling Fluid means the circulating fluid (mud) used in the rotary drilling of wells to clean and condition the hole and to counterbalance formation pressure.

2.3 Field duplicate - A field duplicate sample is a second sample collected at the same location as the original sample. Duplicate samples are collected simultaneously or in immediate succession, using identical recovery techniques, and treated in an identical manner during storage, transportation, and analysis.

2.4 Matrix Spike - Matrix spikes are performed by spiking one of a pair of duplicate samples with a known quantity of analyte and extracting and analyzing both the spiked and the unspiked duplicate. In the absence of matrix interferences, the difference between the analytical results for these two duplicates will yield an acceptable recovery rate for the spike.

3.0 Interferences

3.1 Sample interferences may be observed in the analytical results if sampling equipment is not properly decontaminated between samples or if contaminated gloves or sample containers are used.

4.0 Health and Safety Considerations

4.1 Fluids handled on the rig may cause skin irritation; wearing protective gloves (as described in the material safety data sheet [MSDS]) is recommended.

4.2 Fluid sample should be handled with the same precautions used in the fluid handling areas of the drilling rig.

4.3 Sampler must follow the Operator and Rig's safety procedures as well as the M-I SWACO safety procedures.

4.4 Consult the MSDS for specific health and safety information about the fluids being used in the treatment process.

4.5 Safety goggles must be worn during sample collection procedures.

5.0 Equipment and Supplies

5.1 Nitrile gloves or other gloves suitable for handling fluid samples (as per MSDS). Change gloves before and between each sample.

5.2 Clean sample container with preservative (provided by the contract laboratory).

5.3 Chain-of-custody.

5.4 Sturdy ice chest with ice and packing materials for sample containers.

6.0 Reagents and Standards

6.1 There are no standards required for this procedure.

7.0 Sample Collection, Preservation, Shipment, and Storage

7.1 Each sample will be collected in a 500-mL poly container preserved with HNO_3.

7.2 Samples will be maintained at 4±2 °C until analyzed.

7.3 Samples will be packaged and shipped in accordance with M-I SWACO SOP 2003 (Packaging and Shipment of Samples).

8.0 Quality Control

8.1 Samplers are trained in using this procedure by the Compliance Supervisor.

8.2 Samples must be maintained at 4±2 °C until tested.

8.2 Quality control samples will be collected at the following frequencies:

- Field duplicate samples (one per 10 or fewer samples)
- Matrix spike (MS) samples (one MS per 20 or fewer samples)

9.0 Calibration and Standardization

9.1 No calibration required.

10.0 Procedure

10.1 Sample must be collected when the drilling fluid is expected to have the highest concentrations of metals (e.g., after formulation and prior to use). This sample will be collected from the water phase of the drilling fluid with the purpose of obtaining partitioning of metals from drilling fluid to receiving water. The sample should be collected from the mud pits.

The following sample containers will be provided by the laboratory. Sample containers may vary by laboratory; however, all sample containers and preservatives must comply with analytical method requirements.

Analyte	Method	Container	Preservative	Holding Time
Total chromium Total silver Total thallium	SW6020A	1 x 500 mL poly	HNO_3, 4±2°C	180 days

10.2 Fill each container using care not to overflow or rinse out the preservative. Place the cap tightly on each container after filling.

10.3 Collect quality control samples. If required, collect a field duplicate sample using the same sampling procedure as the original sample. If the sampler is required to collect MS and MSD samples, two additional aliquots should be collected in the same manner as duplicate samples (one original sample, one matrix spike sample, and one matrix spike duplicate). These samples will be designated the matrix spike and, if collected, the matrix spike duplicate.

10.4 Label each sample container with the sample identification number. The sample identification is composed of the sample location, date, time, and initials of the sampler. For example, a sample collected on January 31, 2012 at 1852 by John Doe would be labeled as SS/013112/18:52/JD. The label shall also contain the operator name, the block name and number, the OCS-G number, the analysis requested, the sample collection date and time, and sampler initials. Sample identification information will be recorded on the chain-of-custody.

10.5 Record sample location and identification information in the field notebook as per M-I SWACO SOP 1006 (Field Logs).

10.6 Mud samples shall be immediately chilled in a dedicated laboratory refrigerator to 4±2°C. Samples shall be shipped to the testing facility on wet ice (do not use dry ice or blue ice) and continuously maintained at 4±2 °C until the time of testing.

11.0 Calculations

11.1 There are no calculations with this procedure.

12.0 Data Assessment and Corrective Actions

12.1 If sample integrity has been compromised (e.g., container overfilled, sample not preserved, sample bottle cracked, etc.), it must be returned to the processing equipment for recycling and the used container must be placed in the appropriate waste container.

13.0 Pollution Prevention and Waste Management

13.1 Return the purge volume to the treatment process.

13.2 Follow operator's requirements for disposal of used PPE and disposable sampling equipment.

14.0 References

14.1 Permit No: AKG 280000

14.2 SW-846 Method 6020A

14.3 M-I SWACO SOP 1006 (Field Logs)

14.4 M-I SWACO SOP 2001 (Chain-of-Custody Procedures)

14.5 M-I SWACO SOP 2003 (Packaging and Shipping of Samples)

14.6 M-I SWACO SOP 2004 (Decontamination of Equipment)

15.0 Documentation

15.1 Chain-of-custody, sample labels, field logbooks.

Sample Collection for TAH and TAqH Analyses

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

The purpose of this procedure is to provide a consistent method for the collection of drilling fluid samples for analysis for total aromatic hydrocarbons (TAH) and total aqueous hydrocarbons (TAqH). These samples will be sent to a contract laboratory for testing by methods SW8260B (TAH) and SW8270D SIM (TAqH).

2.0 Definitions

2.1 Base Fluid means the continuous phase or suspending medium of a drilling fluid formulation.

2.2 Drilling Fluid means the circulating fluid (mud) used in the rotary drilling of wells to clean and condition the hole and to counterbalance formation pressure.

2.3 Field duplicate - A field duplicate sample is a second sample collected at the same location as the original sample. Duplicate samples are collected simultaneously or in immediate succession, using identical recovery techniques, and treated in an identical manner during storage, transportation, and analysis.

2.4 Matrix Spike - Matrix spikes are performed by spiking one of a pair of duplicate samples with a known quantity of analyte and extracting and analyzing both the spiked and the unspiked duplicate. In the absence of matrix interferences, the difference between the analytical results for these two duplicates will yield an acceptable recovery rate for the spike.

3.0 Interferences

3.1 Sample interferences may be observed in the analytical results if sampling equipment is not properly decontaminated between samples or if contaminated gloves or sample containers are used.

4.0 Health and Safety Considerations

4.1 Drilling fluid samples should be handled with the same precautions used in the drilling fluid handling areas of the drilling rig.

4.1 Fluids handled on the rig may cause skin irritation; wearing protective gloves (as described in the material safety data sheet [MSDS]) is recommended.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

4.2 Fluid sample should be handled with the same precautions used in the fluid handling areas of the drilling rig.

4.3 Sampler must follow the Operator and Rig's safety procedures as well as the M-I SWACO safety procedures.

4.4 Consult the MSDS for specific health and safety information about the fluids being used in the treatment process.

4.5 Safety goggles must be worn during sample collection procedures.

5.0 Equipment and Supplies

5.1 Nitrile gloves or other gloves suitable for handling fluid samples (as per MSDS). Change gloves before and between each sample.

5.2 Clean sample container (provided by the contract laboratory).

5.3 Chain-of-custody.

5.4 Sturdy ice chest with ice and packing materials for sample containers.

6.0 Reagents and Standards

6.1 There are no standards required for this procedure.

7.0 Sample Collection, Preservation, Shipment, and Storage

7.1 Each sample will be collected in a 40 ml VOA vial or 1-L amber glass jar with Teflon®-lined cap.

7.2 Samples will be maintained at 4±2 °C until analyzed.

7.3 Samples will be packaged and shipped in accordance with M-I SWACO SOP 2003 (Packaging and Shipment of Samples).

8.0 Quality Control

8.1 Samples must be maintained at 4±2 °C until tested.

8.2 Quality control samples will be collected at the following frequencies:

- Field duplicate samples (one per 10 or fewer samples)
- Matrix spike (MS) and matrix spike duplicate (MSD) samples (one MS/MSD pair per 20 or fewer samples)
- Trip blank (supplied by the laboratory; one trip blank per cooler containing samples for volatile analysis).

© Copyright M-I L.L.C., 2012, All Rights Reserved.

9.0 Calibration and Standardization

9.1 No calibration required.

10.0 Procedure

10.1 Sample should be collected at the EOW (at same time as the SPP toxicity test). This sample will be collected once per well from water based drilling fluid. Drilling fluid formulations to be tested shall be collected from the active fluid systems. The following sample containers will be provided by the laboratory. Sample containers may vary by laboratory; however, all sample containers and preservatives must comply with analytical method requirements.

Analyte	Method	Container	Preservative	Holding Time
TAH	SW8260B	3 x 40 mL VOA vial	HCl, 4±2°C	14 days
TAqH	SW8270D SIM	2 x 1 L amber glass jar	4±2°C	7 days to extraction, 40 days to analysis

Obtain a grab sample from beneath the shale shaker after the mud has passed through the screens. Fill each container directly if possible. Collect samples in order of decreasing volatility (i.e., fill the VOA vials first, then the 1 L amber glass jars). Fill each VOA vial completely, leaving no headspace in the vial. Use care not to rinse out the preservative. Place the cap tightly on each container after filling.

10.3 Collect QC samples for each analytical method.

10.3.1 If required, collect a field duplicate sample using the same sampling procedure as the original sample.

10.3.2 If the sampler is required to collect MS and MSD samples, two additional aliquots should be collected in the same manner as duplicate samples (one original sample, one matrix spike sample, and one matrix spike duplicate). These samples will be designated the matrix spike and, if collected, the matrix spike duplicate.

10.4 Label each sample container with the sample identification number. The sample identification is composed of the sample location, date, time, and initials of the sampler. **For example, a sample collected from the shale shaker on January 31, 2012 at 1852 by John Doe would be labeled as SS/013112/18:52/JD**. The label shall also contain the operator name, the block name and number, the OCS-G number, the analysis requested, the sample collection date and time, and sampler initials. Sample identification information will be recorded on the chain-of-custody.

10.5 Samples shall be immediately chilled in a dedicated laboratory refrigerator to 4°C ±2. One of the samples shall be shipped to the testing facility on wet ice or gel packs (do not use dry ice or blue ice) and continuously maintained at 4±2 °C until the time of testing.

11.0 Calculations

11.1 There are no calculations with this procedure.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

12.0 Data Assessment and Corrective Actions

12.1 If sample integrity has been compromised (e.g., container overfilled, sample not preserved, sample bottle cracked, etc.), it must be returned to the processing equipment for recycling and the used container must be placed in the appropriate waste container.

13.0 Pollution Prevention and Waste Management

13.1 Return the purge volume to the treatment process.

13.2 Follow operator's requirements for disposal of used PPE and disposable sampling equipment.

14.0 References

14.1 Permit No: AKG 280000

14.2 SW-846 Methods 8260B and 8270D SIM

14.3 M-I SWACO SOP 1006 (Field Logs)

14.4 M-I SWACO SOP 2001 (Chain-of-Custody Procedures)

14.5 M-I SWACO SOP 2003 (Packaging and Shipping of Samples)

14.6 M-I SWACO SOP 2004 (Decontamination of Equipment)

15.0 Documentation

15.1 Chain-of-custody, sample labels, field logbooks.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

The purpose of the procedure is to provide a consistent method for the collection of wastewater samples for five-day biochemical oxygen demand (BOD) analysis. These samples would be sent to a contract laboratory for testing by Standard Method 5210B.

2.0 Definitions

2.8 Sanitary Waste - means human body waste discharged from toilets and urinals.

2.9 Domestic Waste - means material discharged from galleys, sinks, showers, safety showers, eye wash stations, hand washing stations, fish cleaning stations, and laundries.

3.0 Interferences

3.1 Sample interferences may be observed in the analytical results if sampling equipment is not properly decontaminated between samples or if contaminated gloves or sample containers are used.

4.0 Health and Safety Considerations

4.1 Fluids handled on the rig may cause skin irritation; wearing protective gloves (as described in the material safety data sheet [MSDS]) is recommended.

4.2 Fluid sample should be handled with the same precautions used in the fluid handling areas of the drilling rig.

4.3 Sampler must follow the Operator and Rig's safety procedures as well as the M-I SWACO safety procedures.

4.4 Consult the MSDS for specific health and safety information about the fluids being used in the treatment process.

4.5 Safety goggles must be worn during sample collection procedures.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

5.0 Equipment and Supplies

5.1 Nitrile gloves or other gloves suitable for handling fluid samples (as per MSDS). Change gloves before and between each sample.

5.2 Clean sample container (provided by the contract laboratory).

5.3 Chain-of-custody.

5.4 Sturdy ice chest with ice and packing materials for sample containers.

6.0 Reagents and Standards

6.1 There are no standards required for this procedure.

7.0 Sample Collection, Preservation, Shipment, and Storage

7.1 Each sample will be collected in (1) 1-L poly bottle.

7.2 Samples will be maintained at 4±2 °C until analyzed.

7.3 Samples will be packaged and shipped in accordance with M-I SWACO SOP 2003 (Packaging and Shipment of Samples).

8.0 Quality Control

8.1 Samplers are trained in using this procedure by the Compliance Supervisor.

8.2 Samples must be maintained at 4±2 °C until tested.

8.2 No quality control samples are required.

9.0 Calibration and Standardization

9.1 No calibration required.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

10.0 Procedure

10.1 Wastewater to be tested shall be collected from the locations specified in the rig-specific Sampling Plan for sanitary wastewater and domestic wastewater discharges. Samples will be collected weekly for BOD analysis.

The following sample containers will be provided by the laboratory. Sample containers may vary by laboratory; however, all sample containers and preservatives must comply with analytical method requirements.

Analyte	Method	Container	Preservative	Holding Time
BOD_5	SM20 5210B	(1) 1-L poly bottle	4±2°C	48 hours

10.2 Fill the container with wastewater. Place the cap tightly on each container after filling.

10.3 Label each sample container with the sample identification number. The sample identification is composed of the sample location, date, time, and initials of the sampler. For example, a sample collected on January 31, 2012 at 1852 by John Doe would be labeled as SS/013112/18:52/JD. The label shall also contain the operator name, the block name and number, the OCS-G number, the analysis requested, the sample collection date and time, and sampler initials. Sample identification information will be recorded on the chain-of-custody.

10.4 Record sample location and identification information in the field notebook as per M-I SWACO SOP 1006 (Field Logs).

10.5 Wastewater samples shall be immediately chilled in a dedicated laboratory refrigerator to 4±2°C. Samples shall be shipped to the testing facility on wet ice (do not use dry ice or blue ice) and continuously maintained at 4±2°C until the time of testing.

11.0 Calculations

11.1 There are no calculations with this procedure.

12.0 Data Assessment and Corrective Actions

12.1 If sample integrity has been compromised (e.g., container overfilled, sample not preserved, sample bottle cracked, etc.), it must be returned to the processing equipment for recycling and the used container must be placed in the appropriate waste container.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

13.0 Pollution Prevention and Waste Management

13.1 Return the purge volume to the treatment process.

13.2 Follow operator's requirements for disposal of used PPE and disposable sampling equipment.

14.0 References

14.1 Permit No: AKG 280000

14.2 Standard Method 9222D

14.3 M-I SWACO SOP 1006 (Field Logs)

14.4 M-I SWACO SOP 2001 (Chain-of-Custody Procedures)

14.5 M-I SWACO SOP 2003 (Packaging and Shipping of Samples)

14.6 M-I SWACO SOP 2004 (Decontamination of Equipment)

15.0 Documentation

15.1 Chain-of-custody, sample labels, field logbooks.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Sample Collection for Fecal Coliform Analysis

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

The purpose of the procedure is to provide a consistent method for the collection of wastewater samples for fecal coliform analysis. These samples will be sent to a contract laboratory for testing by Standard Method 9222D.

2.0 Definitions

2.8 Sanitary Waste - means human body waste discharged from toilets and urinals.

2.9 Domestic Waste - means material discharged from galleys, sinks, showers, safety showers, eye wash stations, hand washing stations, fish cleaning stations, and laundries.

3.0 Interferences

3.1 Sample interferences may be observed in the analytical results if sampling equipment is not properly decontaminated between samples or if contaminated gloves or sample containers are used.

4.0 Health and Safety Considerations

4.1 Fluids handled on the rig may cause skin irritation; wearing protective gloves (as described in the material safety data sheet [MSDS]) is recommended.

4.2 Fluid sample should be handled with the same precautions used in the fluid handling areas of the drilling rig.

4.3 Sampler must follow the Operator and Rig's safety procedures as well as the M-I SWACO safety procedures.

4.4 Consult the MSDS for specific health and safety information about the fluids being used in the treatment process.

4.5 Safety goggles must be worn during sample collection procedures.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

5.0 Equipment and Supplies

5.1 Nitrile gloves or other gloves suitable for handling fluid samples (as per MSDS). Change gloves before and between each sample.

5.2 Sterile sample container with preservative (provided by the contract laboratory).

5.3 Chain-of-custody.

5.4 Sturdy ice chest with ice and packing materials for sample containers.

6.0 Reagents and Standards

6.1 Sodium thiosulfate ($Na_2S_2O_3$) preservative.

7.0 Sample Collection, Preservation, Shipment, and Storage

7.1 Each sample will be collected in (1) 125-mL sterile poly container w/ Na2S2O3.

7.2 Samples will be maintained at 4±2 °C until analyzed.

7.3 Samples will be packaged and shipped in accordance with M-I SWACO SOP 2003 (Packaging and Shipment of Samples).

8.0 Quality Control

8.1 Samplers are trained in using this procedure by the Compliance Supervisor.

8.2 Samples must be maintained at 4±2 °C until tested.

8.2 No quality control samples are required.

9.0 Calibration and Standardization

9.1 No calibration required.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

10.0 Procedure

10.1 Wastewater to be tested shall be collected from the locations specified in the rig-specific Sampling Plan for sanitary wastewater and domestic wastewater discharges. Samples will be collected monthly for fecal coliform analysis.

The following sample containers will be provided by the laboratory. Sample containers may vary by laboratory; however, all sample containers and preservatives must comply with analytical method requirements.

Analyte	Method	Container	Preservative	Holding Time
Fecal coliform	SM20 9222D	(1) 125-mL sterile poly container w/ Na2S2O3	$Na_2S_2O_3$, 4±2°C	8 hours

10.2 Allow the line to clear for several minutes prior to sampling. Fill container directly and use care not to touch the inside of the container to avoid contamination of the sample. Use care not to overfill the container or rinse the preservative out of the container. Place the cap tightly on each container after filling.

10.3 Label each sample container with the sample identification number. The sample identification is composed of the sample location, date, time, and initials of the sampler. For example, a sample collected on January 31, 2012 at 1852 by John Doe would be labeled as SS/013112/18:52/JD. The label shall also contain the operator name, the block name and number, the OCS-G number, the analysis requested, the sample collection date and time, and sampler initials. Sample identification information will be recorded on the chain-of-custody.

10.4 Record sample location and identification information in the field notebook as per M-I SWACO SOP 1006 (Field Logs).

10.4 Wastewater samples shall be immediately chilled in a dedicated laboratory refrigerator to 4±2°C. Samples shall be shipped to the testing facility on wet ice (do not use dry ice or blue ice) and continuously maintained at 4±2°C until the time of testing.

11.0 Calculations

11.1 There are no calculations with this procedure.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

12.0 Data Assessment and Corrective Actions

12.1 If sample integrity has been compromised (e.g., container overfilled, sample not preserved, sample bottle cracked, etc.), it must be returned to the processing equipment for recycling and the used container must be placed in the appropriate waste container.

13.0 Pollution Prevention and Waste Management

13.1 Return the purge volume to the treatment process.

13.2 Follow operator's requirements for disposal of used PPE and disposable sampling equipment.

14.0 References

14.1 Permit No: AKG 280000

14.2 Standard Method 9222D

14.3 M-I SWACO SOP 1006 (Field Logs)

14.4 M-I SWACO SOP 2001 (Chain-of-Custody Procedures)

14.5 M-I SWACO SOP 2003 (Packaging and Shipping of Samples)

14.6 M-I SWACO SOP 2004 (Decontamination of Equipment)

15.0 Documentation

15.1 Chain-of-custody, sample labels, field logbooks.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Field Measurement of pH

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

The purpose of the procedure is to provide a consistent method for the field measurement of pH. This method uses a portable pH meter, such as the Hach HQ11d or equivalent, to measure pH in water based on USEPA Method 150.1.

2.0 Definitions

2.1 Sanitary Waste - means human body waste discharged from toilets and urinals.

2.2 Domestic Waste - means material discharged from galleys, sinks, showers, safety showers, eye wash stations, hand washing stations, fish cleaning stations, and laundries.

3.0 Interferences

3.1 Oil of any type in a water sample will coat the pH electrode. Temperature changes of the water during pH measurement will cause drift.

3.2 Refer to the manufacturer's instruction manual.

4.0 Health and Safety Considerations

4.1 Fluids handled on the rig may cause skin irritation; wearing protective gloves (as described in the material safety data sheet [MSDS]) is recommended.

4.2 Sampler must follow the Operator and Rig's safety procedures as well as the M-I SWACO safety procedures.

4.3 Safety goggles must be worn during sample collection procedures.

4.4 Consult MSDSs before handling reference materials or standards.

5.0 Equipment and Supplies

5.1 Nitrile gloves or other gloves suitable for handling fluid samples (as per MSDS). Change gloves before and between each sample.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

5.2 Daily activity report form and field logbook.

5.3 Portable pH meter and manufacturer's instruction manual.

6.0 Reagents and Standards

6.1 Buffer solution(s) for calibration.

7.0 Sample Collection, Preservation, Shipment, and Storage

7.1 Samples are collected at frequencies according to Region 10 Permit requirements as outlined in rig specific QAPP documentation from the locations specified in the rig-specific Sampling Plan.

7.2 Sample should be analyzed immediately following collection.

8.0 Quality Control

8.1 Compliance Engineers are trained in the requirements of this procedure through the Compliance Engineer training program. Training on SOP revisions will be documented through completion of Form 2009-1, as described in SOP 2009 (Compliance Engineer Training).

8.2 Refer to manufacturer's instruction manual for check standard procedures.

9.0 Calibration and Standardization

9.1 The portable pH meter will be calibrated according to the manufacturer's instruction manual.

10.0 Procedure

10.1 Samples to be tested shall be collected from the locations specified in the rig-specific Sampling Plan for discharges requiring pH testing. pH will be monitored according to Region 10 Permit requirements as outlined in rig specific QAPP documentation.

10.2 Collect water in one 100-mL plastic bottle with plastic cap.

10.3 Analyze the sample immediately. Follow the procedures in the manufacturer's instruction manual.

10.4 Record sample location and identification information in the field notebook as per M-I SWACO SOP 1006 (Field Logs).

10.5 Decontaminate pH probe or other reusable sampling equipment between samples.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

11.0 Calculations

11.1 There are no calculations with this procedure.

12.0 Data Assessment and Corrective Actions

12.1 There is no data assessment associated with this procedure.

13.0 Pollution Prevention and Waste Management

13.1 The wastewater samples will be placed into the sanitary or domestic wastewater systems.

13.2 Follow operator's requirements for disposal of used PPE and disposable sampling equipment.

14.0 References

14.1 Permit No: AKG 280000

14.2 Manufacturer’s instruction manual for portable pH meter

14.3 USEPA Method 150.1

14.4 M-I SWACO SOP 1006 (Field Logs)

14.5 M-I SWACO SOP 2004 (Decontamination of Equipment)

15.0 Documentation

15.1 Daily activity report and field logbook.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Field Measurement of Total Residual Chlorine

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

The purpose of the procedure is to provide a consistent method for the field measurement of total residual chlorine in sanitary wastewater discharges. This method uses the Hach Pocket Colorimeter™ II test kit, or equivalent, to measure total chlorine in wastewater using a method equivalent to Standard Method 4500-Cl F,G. Monitoring is not required if chlorine is not used as a disinfectant or for facilities serving fewer than 10 persons

2.0 Definitions

2.1 Sanitary Waste - means human body waste discharged from toilets and urinals.

3.0 Interferences

3.1 Cold water can cause condensation on the sample cells during color development that can interfere with instrument readings. Examine sample cells for condensation and wipe to remove excess liquid prior to reading.

3.2 Avoid collecting sample in a plastic container because plastics can react with and consume chlorine.

3.3 See manufacturer's instruction manual for more information about potential interferences.

4.0 Health and Safety Considerations

4.1 Fluids handled on the rig may cause skin irritation; wearing protective gloves (as described in the material safety data sheet [MSDS]) is recommended.

4.2 Sampler must follow the Operator and Rig's safety procedures as well as the M-I SWACO safety procedures.

4.3 Safety goggles must be worn during sample collection procedures.

4.4 Consult MSDSs before handling reference materials or standards.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

5.0 Equipment and Supplies

5.1 Nitrile gloves or other gloves suitable for handling fluid samples (as per MSDS). Change gloves before and between each sample.

5.2 Daily activity report form and field logbook.

5.3 Hach Pocket Colorimeter™ II or equivalent instrument Instruction Manual and test kit.

6.0 Reagents and Standards

6.1 N,N-diethyl-p-phenylenediamine (DPD) Total Chlorine Reagent Powder Pillows, or other method-specific reagent.

7.0 Sample Collection, Preservation, Shipment, and Storage

7.1 Samples of wastewater are collected weekly from the locations specified in the rig-specific Sampling Plan.

7.2 Sample should be analyzed within 15 minutes immediately following collection.

8.0 Quality Control

8.1 Compliance Engineers are trained in the requirements of this procedure through the Compliance Engineer training program. Training on SOP revisions will be documented through completion of Form 2009-1, as described in SOP 2009 (Compliance Engineer Training).

8.2 Accuracy check procedures are included in the manufacturer's instruction manual.

9.0 Calibration and Standardization

9.1 Instrument will be calibrated according to the manufacturer's instruction manual.

10.0 Procedure

10.1 Wastewater to be tested shall be collected from the locations specified in the rig-specific Sampling Plan for sanitary wastewater discharges. Samples will be collected weekly for total residual chlorine analysis.

10.2 Collect the sample in 100-mL plastic bottle with plastic cap.

10.3 Analyze the sample within 15 minutes. Follow the procedures in the manufacturer's instruction manual.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

10.4 Record results on the Daily Activity Report (Form 1006-1) and the field logbook.

11.0 Calculations

11.1 There are no calculations with this procedure.

12.0 Data Assessment and Corrective Actions

12.1 There is no data assessment associated with this procedure.

13.0 Pollution Prevention and Waste Management

13.1 The wastewater samples are placed into the sanitary wastewater systems.

14.0 References

14.1 Permit No: AKG 280000

14.2 Manufacturer's instruction manual

15.0 Documentation

15.1 Daily activity report and field logbooks.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Sample Collection for Total Suspended Solids (TSS) Analysis

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

The purpose of the procedure is to provide a consistent method for the collection of wastewater samples for total suspended solids (TSS) analysis. These samples would be sent to a contract laboratory for testing by Standard Method 2540D.

2.0 Definitions

2.8 Sanitary Waste - means human body waste discharged from toilets and urinals.

3.0 Interferences

3.1 Sample interferences may be observed in the analytical results if sampling equipment is not properly decontaminated between samples or if contaminated gloves or sample containers are used.

4.0 Health and Safety Considerations

4.1 Fluids handled on the rig may cause skin irritation; wearing protective gloves (as described in the material safety data sheet [MSDS]) is recommended.

4.2 Fluid sample should be handled with the same precautions used in the fluid handling areas of the drilling rig.

4.3 Sampler must follow the Operator and Rig's safety procedures as well as the M-I SWACO safety procedures.

4.4 Consult the MSDS for specific health and safety information about the fluids being used in the treatment process.

4.5 Safety goggles must be worn during sample collection procedures.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

5.0 Equipment and Supplies

5.1 Nitrile gloves or other gloves suitable for handling fluid samples (as per MSDS). Change gloves before and between each sample.

5.2 Clean sample container (provided by the contract laboratory).

5.3 Chain-of-custody.

5.4 Sturdy ice chest with ice and packing materials for sample containers.

6.0 Reagents and Standards

6.1 There are no standards required for this procedure.

7.0 Sample Collection, Preservation, Shipment, and Storage

7.1 Each sample will be collected in (1) 1-L poly bottle.

7.2 Samples will be maintained at 4±2 °C until analyzed.

7.3 Samples will be packaged and shipped in accordance with M-I SWACO SOP 2003 (Packaging and Shipment of Samples).

8.0 Quality Control

8.1 Samples must be maintained at 4±2 °C until tested.

8.2 No quality control samples are required.

9.0 Calibration and Standardization

9.1 No calibration required.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

10.0 Procedure

10.1 Wastewater to be tested shall be collected from the locations specified in the rig-specific Sampling Plan for sanitary wastewater discharges. Samples will be collected weekly for TSS analysis.

The following sample containers will be provided by the laboratory. Sample containers may vary by laboratory; however, all sample containers and preservatives must comply with analytical method requirements.

Analyte	Method	Container	Preservative	Holding Time
TSS	SM20 2540D	(1) 1-L poly bottle	4±2°C	7 days

10.2 Fill the container with wastewater. Place the cap tightly on each container after filling.

10.3 Label each sample container with the sample identification number. The sample identification is composed of the sample location, date, time, and initials of the sampler. For example, a sample collected on January 31, 2012 at 1852 by John Doe would be labeled as SS/013112/18:52/JD. The label shall also contain the operator name, the block name and number, the OCS-G number, the analysis requested, the sample collection date and time, and sampler initials. Sample identification information will be recorded on the chain-of-custody.

10.4 Record sample location and identification information in the field notebook as per M-I SWACO SOP 1006 (Field Logs).

10.5 Wastewater samples shall be immediately chilled in a dedicated laboratory refrigerator to 4±2°C. Samples shall be shipped to the testing facility on wet ice or gel packs (do not use dry ice or blue ice) and continuously maintained at 4±2°C until the time of testing.

11.0 Calculations

11.1 There are no calculations with this procedure.

12.0 Data Assessment and Corrective Actions

12.1 If sample integrity has been compromised (e.g., container overfilled, sample not preserved, sample bottle cracked, etc.), it must be returned to the processing equipment for recycling and the used container must be placed in the appropriate waste container.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

13.0 Pollution Prevention and Waste Management

13.1 Return the purge volume to the treatment process.

13.2 Follow operator's requirements for disposal of used PPE and disposable sampling equipment

14.0 References

14.1 Permit No: AKG280000

14.2 Standard Method 2540D

14.3 M-I SWACO SOP 1006 (Field Logs)

14.4 M-I SWACO SOP 2001 (Chain-of-Custody Procedures)

14.5 M-I SWACO SOP 2003 (Packaging and Shipping of Samples)

14.6 M-I SWACO SOP 2004 (Decontamination of Equipment)

15.0 Documentation

15.1 Chain-of-custody, sample labels, field logbooks.

© Copyright M-I L.L.C., 2012, All Rights Reserved.

Retort Inspection and Calibration

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

The modified API Recommended Practice 13B-2 is designed to measure the amount of non-aqueous drilling fluid (NAF) contained on cuttings generated during a drilling operation. The procedure is a retort test that measures oil material (NAF base fluid) and water released from a cuttings sample when heated in a calibrated and properly operating "retort" instrument. The inspection and calibration requirements described in this standard operating procedure (SOP) will demonstrate that the retort is properly calibrated and operating prior to performing the API Recommended Practice 13B-2 (M-I SWACO SOP 3002).

2.0 Definitions

2.1 Base Fluid - the continuous phase or suspending medium of a drilling fluid formulation.

2.2 NAF – non-aqueous drilling fluids, i.e., with a base fluid that is a water-immiscible fluid.

3.0 Interferences

3.1 No interferences are known for this procedure.

4.0 Health and Safety Considerations

4.1 Follow health and safety procedures outlined in the Global HSE Plan.

4.2 Consult Material Safety Data Sheets (MSDS) for drilling fluids used during drilling interval.

4.3 Drilling fluid samples should be handled with the same precautions used in the drilling fluid handling areas of the drilling rig.

4.4 The NAF retention on cuttings involves separating liquids from approximately 50 ml of cuttings by distillation at high temperature in a 50 ml mud retort apparatus. Two retorts may be running simultaneously and continuously for several hours at a time. This procedure generates heat and a small amount of water and organic vapor.

4.5 If the condenser or cup hole is plugged, the retort may explode. The condition of the equipment should be checked daily during use.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

4.6 The temperature of the retort will be at 950ºF during testing, so it is a potential thermal hazard.

5.0 Equipment and Supplies

5.1 Digital thermometer, range –50 to 150°C, ± 1°C between –20 and 100°C (VWR 61161-310 or equivalent)

5.2 Triple-beam balance, range 2000 g, precision ± 0.1g

5.3 10 ml Disposable Syringe, (Becton, Dickinson and Company) No.309603, or equivalent.

5.4 Teflon® syringe filter, 25-mm, 0.45 μm pore size, Whatman or equivalent.

5.5 Retort Assembly, retort body, cup and lid: 303 stainless steel or equivalent.

5.5.1 Retort cup with lid, volume 50 ml

5.5.2 Condenser – capable of cooling the oil and water vapors below their liquification temperature

5.5.3 Heating jacket – nominal 350 watts

5.5.4 Temperature control – capable of limiting temperature of retort to at least 930°F (500°C) and enough to boil off all NAFs.

5.5.5 JP-Tube (Liquid Receiver) – 10 ml cylindrical Pyrex® or equivalent glassware with rounded bottom, funnel-shaped top, and 0.1 ml graduations; precision ± 0.05 ml; outside diameter 10-mm; wall thickness 1.5 ± 0.1 mm; calibration to contain “TC” @ 20°C; accompanied by Certificate of Verification.

5.5.6 JP-Tube (Liquid Receiver) – 20 ml cylindrical Pyrex® or equivalent glassware with rounded bottom, funnel-shaped top, and 0.1 ml graduations; precision ± 0.05 ml; outside diameter 13-mm; wall thickness 1.2 ± 0.1 mm; calibration to contain “TC” @ 20°C; accompanied by Certificate of Verification.

5.5.7 JP-Tube (Liquid Receiver) – 50 ml cylindrical Pyrex® or equivalent glassware with rounded bottom, funnel-shaped top, and 0.25 ml graduations (or 0 – 100% graduations); precision ± 0.05 ml; outside diameter 10-mm; wall thickness 1.5 ± 0.1 mm; calibration to contain “TC” @ 20°C; accompanied by Certificate of Verification or Certificate of Conformity.

5.6 Fine steel wool (No. 000 or 0000)

5.7 Drill bit or stiff wire

© Copyright M-I L.L.C., 2004, All Rights Reserved.

5.8 Thread sealant lubricant – high temperature lubricant; Never-Seez® or equivalent

5.9 Paper towels

5.10 Miscellaneous cleaning aids – pipe cleaners, brush, retort spatula and cork screw.

6.0 Reagents and Standards

6.1 Solids free NAF

7.0 Sample Collection, Preservation, Shipment and Storage

7.1 A sample of solids-free NAF is collected from the batch of NAF as sent by the supplier, prior to circulating down hole, according to the procedures described in the appropriate sampling SOP.

8.0 Quality Control

8.1 Compliance Engineers are trained in the requirements of this procedure through the Compliance Engineer training program. Training on SOP revisions will be documented through completion of Form 2009-1, as described in SOP 2009 (Compliance Engineer Training).

8.2 The inspection procedures described in Sections 10.3, 10.4, and 10.5 are performed at the following frequency:

8.2.1 Inspect when new, prior to placing in service.

8.2.2 Inspect at the beginning of service at a new location (or well).

8.2.3 Inspect daily.

8.2.4 Inspect when returned from location to the Compliance Supervisor.

8.2.5 Inspect prior to performing the verification procedures listed in Sections 10.7 and 10.8.

8.3 The procedure described in Section 10.7 is performed at the following frequency:

8.3.1 Verify prior to placing in service.

8.3.2 Verify monthly while in service.

8.4 The procedure described in Section 10.8 is performed at the following frequency:

8.4.1 Verify prior to placing in service through documentation of a Certificate of Verification or Certificate of Conformity.

8.4.2 Verify at a minimum every two years.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

9.0 Verification and Standardization

9.1 This SOP defines verification procedures for the retort.

9.2 Calibrate the balance as described in M-I SWACO SOP 1004 (Balance Calibration).

9.3 Calibrate the thermometers as described in M-I SWACO SOP 1005 (Laboratory Refrigerators).

10.0 Procedure

10.1 Prior to running all tests, inspect the retort cup lid hole and the retort cell-condenser tube to verify both are fully open and free of any solids accumulation. Clean these passages with a pipe-cleaner and “rod” with a drill bit or stiff wire before all tests.

10.2 Perform the visual inspection daily (See 10.3, 10.4 and 10.5).

10.3 Visually inspect retort cup, cup lid and retort cell top for the following:

10.3.1 General cell damage (i.e., cracks, splits, dents, wear, warping, etc.).

10.3.2 Condition of threads (clean and sharp).

10.3.3 Interior and exterior metal surface damage (pitting, wall thinning, etc.).

10.3.4 Cup lid hole should be fully open and free of any solids accumulation.

10.3.5 Retort cell-condenser tube should be checked with the drill bit or “T”-handled drill bit to insure that the connection is fully open, and free of any solids accumulation.

10.3.6 Complete appropriate items on the Daily Inspection Retort Form (Form 3001-1).

10.4 Visually inspect retort case and external heating jacket for:

10.4.1 General damage (i.e., split case, evidence of electrical arcing, heat damage, cracks, splits, wear or warping of heating chamber, etc.).

10.4.2 Electrical cord for damage or evidence of arcing or shorting.

10.4.3 If external visual inspection indicates a potential problem, disconnect the power cord, remove front cover and inspect thermal blocks, electrical connections, free operation of thermostat, etc.

10.4.4 Smooth operation of switches and control.

10.4.5 On/off operation of indicator lights.

10.4.6 Complete the appropriate items on the Daily Inspection Retort Form (Form 3001-1).

10.5 Visually inspect the JP-tube for:

© Copyright M-I L.L.C., 2004, All Rights Reserved.

10.5.1 Permanent identification marking legibility.

10.5.2 Scale on volume division legibility.

10.5.3 Chips or cracks in glass.

10.5.4 Debris or solids that cannot be removed.

10.6 If the retort fails any of the inspections in Sections 10.3 through 10.5, mark as "Out of Service". Clean or repair if possible; alternatively return to manufacturer for repair/inspection or discard and replace. After cleaning or repairs, re-inspect the retort.

10.7 Volumetric NAF Recovery Performance Test

10.7.1 Allow the retort heating chamber to cool below 150°F prior to beginning any new retort test.

10.7.2 Clean and dry the retort assembly and condenser.

10.7.3 Pack the retort body (upper chamber) with steel wool.

10.7.4 Apply lubricant/sealant to threads of retort cup and retort stem (high-temperature grease, i.e. Never-Seez®).

10.7.5 Prior to performing the Volumetric NAF Recovery Performance Test, filter the NAF test material. Pour the NAF into a 10 ml plastic syringe fitted with a disposable 0.45 μm filter. Expel the NAF into a clean 50 ml JP-tube. Repeat as necessary to fill the JP-tube.

10.7.6 Pour the solids-free NAF from the 50 ml JP-tube into the retort sample cup.

10.7.7 Place the lid on retort sample cup and rotate to obtain a proper fit, allowing excess NAF base fluid to escape so that final volume is exactly 50 ml. Wipe excess NAF base fluid from lid, outside of cup and threads; avoid wicking out NAF base fluid from the retort cup lid hole.

10.7.8 Screw the retort sample cup into the retort body (upper chamber). Keep assembly upright so that NAF does not escape or flow into the drain/condenser tube. (Although there are no solids to be trapped by the steel wool, using the steel wool will assure the NAF does not escape or flow into the drain or condenser tube).

10.7.9 Attach the condenser to the retort assembly, seating firmly. Keep assembly upright so that NAF does not escape or flow into the drain/condenser tube.

10.7.10 Attach or position the calibrated 50 ml JP-tube used in 10.7.5 so that it will collect all of the condensed NAF liquid.

10.7.11 Turn on the retort and allow it to run at least one hour.

10.7.12 When no more NAF condensed liquid is recovered, remove the JP-tube and allow the condensate to cool to room temperature.

10.7.13 Read and record the total volume of NAF fluid collected on the Periodic Retort Verification Data Sheet (Form 3001-2). If the amount of condensed NAF liquid is less than 48.5 ml, repeat the procedures in Section 10.7.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Retort Inspection and Calibration

10.8 JP-Tube (Liquid Receiver) Volume Specification Verification: 10 ml, precision ± 0.05 ml or 20 ml, precision ± 0.05 ml:

10.8.1 Allow JP-tube and distilled water to reach ambient temperature. Measure water temperature with digital thermometer. Record the temperature and record density of water at nearest temperature (Table 1) on the Periodic Retort Verification Data Sheet (Form 3001-2).

10.8.2 Place the clean, empty JP-tube on the balance and record the empty weight (W_1, grams).

10.8.3 Use the pipette to fill JP-tube to the first gradation (2 ml) with distilled water.

10.8.4 Place JP-tube on the balance. Record the weight of the JP-tube (W_2, grams) on the Periodic Retort Verification Data Sheet (Form 3001-2).

10.8.5 Add an increment of water to the next gradation (4 ml) with the distilled water.

10.8.6 Place JP-tube on the balance. Record the weight of the JP-tube (W_3, grams) on the Periodic Retort Verification Data Sheet (Form 3001-2).

10.8.7 Add an increment of water to the next gradation (6 ml) with the distilled water.

10.8.8 Place JP-tube on the balance. Record the weight of the JP-tube (W_4, grams) on the Periodic Retort Verification Data Sheet (Form 3001-2).

10.8.9 Add an increment of water to the next gradation (8 ml) with the distilled water.

10.8.10 Place JP-tube on the balance. Record the weight of the JP-tube (W_5, grams) on the Periodic Retort Verification Data Sheet (Form 3001-2).

10.8.11 Add an increment of water to the next gradation (10 ml) with the distilled water.

10.8.12 Place JP-tube on the balance. Record the weight of the JP-tube (W_6, grams) on the Periodic Retort Verification Data Sheet (Form 3001-2).

10.8.13 Calculate JP-tube volumes, V_{Mark}, as shown in Equation 1. Use the density of water at the measured temperature. Record the V_{Mark} on the Periodic Retort Verification Data Sheet (Form 3001-2).

$$V_{Mark} = \frac{W_b - W_a \text{ (g)}}{\text{Density of water (g/ ml}} \qquad \text{Equation 1}$$

where

a – weight of JP-tube and water prior to adding increment
b – weight of JP-tube and water with increment added

10.9 If the retort fails any of the calibration verifications in Sections 10.7 or 10.8, mark as “Out of Service”. Clean or repair if possible; return to manufacturer for repair/inspection or discard and replace. After cleaning or repairs, re-inspect, and recalibrate the retort.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

11.0 Calculations

11.1 The JP-tube volume, V_{MARK}, is calculated as shown in Equation 1 in Section 10.7.

12.0 Data Assessment and Corrective Actions

12.1 If any of the questions on the Daily Inspection Retort Form (Form 3001-1) are answered "Yes", the retort must be removed from service until cleaning, repairs and/or maintenance are complete.

12.2 The retort may be returned to service after successful completion ("No") of the Daily Inspection Retort Form (Form 3001-1).

12.3 If the retort fails any of the calibrations on the Periodic Retort Verification Data Sheet (Form 3001-2), mark as "Out of Service". Clean or repair if possible; return to manufacturer for repair/inspection or discard and replace. After cleaning or repairs, reinspect, and recalibrate the retort.

12.4 The retort may be returned to service after successful completion of the calibrations on the Periodic Retort Verification Data Sheet (Form 3001-2).

12.5 Repairs and/or maintenance and other corrective actions are noted on the Daily Inspection Retort Form (Form 3001-1) or the Periodic Retort Verification Data Sheet (Form 3001-2).

13.0 Pollution Prevention and Waste Management

13.1 The only waste material generated by this procedure is the NAF. The waste is returned to the mud system upon completion of the tests.

14.0 References

14.1 Appendix 7 to Subpart A of Part 435 and API Recommended Practice 13B-2.

14.2 M-I SWACO SOP 1004 (Balance Calibration)

14.3 M-I SWACO SOP 1005 (Laboratory Refrigerators)

14.4 M-I SWACO SOP 3002 (Base Fluid Retained on Cuttings Retort Test Procedure)

15.0 Documentation

15.1 Complete the Daily Retort Inspection Sheet (Form 3001-3) daily during a drilling interval.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Retort Inspection and Calibration

15.1.1 The Compliance Engineer maintains the Daily Retort Inspection Sheet during a synthetic fluids drilling interval in the Drilling Interval notebook.

15.1.2 Upon completion of the synthetic fluid drilling interval, original Daily Retort Inspection Sheet are provided to the permittee. The District Office archives copies of the Daily Inspection Retort Form after completion of a synthetic fluids drilling interval.

15.1.3 The Daily Retort Inspection Sheet must be restarted if a retort is changed out during the month.

15.1.4 Mark all unused fields with "N/A" and/or a line though the unused blank. Enter a comment in the comment column as to why the retort was not calibrated.

15.1.5 The Daily Retort Inspection Form (Figure 1) may be used to calibrate retorts on a single day basis such as in preparation for a periodic verification.

15.2 Complete the Periodic Retort Verification Data Sheet (Form 3001-2) at the frequencies specified in Section 8.3.

15.2.1 If the Compliance Engineer calibrates the retort during a synthetic fluids drilling interval, the form is maintained in the Drilling Interval notebook and archived in the project files upon completion of a drilling interval.

15.2.2 If the equipment coordinator calibrates the retort, the original form is maintained in the Equipment Log and a copy accompanies the retort in the Equipment records.

Figure 1: Water Density Table

VOLUME OF ONE GRAM OF WATER

The following table, which is designed for gravimetric calibration of volumetric apparatus, gives the specific volume of water at standard atmospheric pressure as a function of temperature.

REFERENCE

Marsh, K. N., Editor, *Recommended Reference Materials for the Realization of Physicochemical Properties*, pp. 25-27, Blackwell Scientific Publications, Oxford, 1987.

t/°C	Volume of 1 g H_2O in cm^3	t/°C	Volume of 1 g H_2O in cm^3	t/°C	Volume of 1 g H_2O in cm^3
10	1.0002980	17	1.0012246	24	1.0027079
11	1.0003928	18	1.0014044	25	1.0029607
12	1.0005007	19	1.0015952	26	1.0032234
13	1.0006212	20	1.0017969	27	1.0034956
14	1.0007542	21	1.0020092	28	1.0037771
15	1.0008992	22	1.0022320	29	1.0040679
16	1.0010561	23	1.0024649	30	1.0043679

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Retort Inspection and Calibration

Form 3001-1: Daily Retort Inspection Form

Operator:		Location:	(Surface Location)
OCS-G Number:		Rig Name:	
Date and Time:		Analyst:	
Retort Model:		Retort ID:	

Visual Condition Inspection (10.3,10.4, 10.5)	Yes	No	Comment
Retort cell damaged (10.3)?			
Retort threads damaged (10.3)?			
Retort metal surfaces damaged (10.3)?			
Retort cup lid hole plugged (10.3)?			
Retort cell-condenser plugged (10.3)?			
Retort case damaged (10.4)?			
Electrical cord damaged (10.4)?			
Thermal blocks, electrical connections, operation of			
Switches and controls stick (10.4)?			
Indicator lights do not operate (10.4)?			
Permanent ID of JP-tubes illegible (10.5)?			
Volume scales illegible (10.5)?			
Chips or cracks in glass (10.5)?			
Debris or solids in JP-tubes (10.5)?			

Retort Model:		Retort ID:	

Visual Condition Inspection (10.3,10.4, 10.5)	Yes	No	Comment
Retort cell damaged (10.3)?			
Retort threads damaged (10.3)?			
Retort metal surfaces damaged (10.3)?			
Retort cup lid hole plugged (10.3)?			
Retort cell-condenser plugged (10.3)?			
Retort case damaged (10.4)?			
Electrical cord damaged (10.4)?			
Thermal blocks, electrical connections, operation of			
Switches and controls stick (10.4)?			
Indicator lights do not operate (10.4)?			
Permanent ID of JP-tube illegible (10.5)?			
Volume scale illegible (10.5)?			
Chips or cracks in glass (10.5)?			
Debris or solids in JP-tube (10.5)?			

If any response is “Yes”, then clean and repair or remove from service.

Analyst Signature:		Date:	

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Retort Inspection and Calibration

Form 3001-2 Periodic Retort Verification Data Sheet

Date:		Analyst:	
Operator:		OCS-G Number:	
Area and Block:	(Surface Location)	Rig:	
Balance ID:		JP Tube ID:	

Performance Test of NAF Fluid Recovery (10.7) (Monthly)

Retort ID:		JP Tube ID:	
Start Time (time of day):		Stop Time (time of day):	
Total Volume NAF recovered (ml) at end of test:			

Performance Test of NAF Fluid Recovery (10.7) (Monthly)

Retort ID:		JP Tube ID:	
Start Time (time of day):		Stop Time (time of day):	
Total Volume NAF recovered (ml) at end of test:			

Performance Test of NAF Fluid Recovery (10.7) (Monthly)

Retort ID:		JP Tube ID:	
Start Time (time of day):		Stop Time (time of day):	
Total Volume NAF recovered (ml) at end of test:			

JP-Tube Volume Procedure (10.8) (Every 2 years)

	Weight (gram)	Water Density (grams)	Calculated Volume (ml)	Volume Scale Reading (ml)	Pass/Fail (Within 0.05mL)
W1					
W2					
W3					
W4					
W5					
W6					

Procedure Results	Yes	No	Comments
NAF Recovery < 48.5 ml (10.7)?			
JP-tube volume exceeds ± 0.05 ml (10.8)?			

If any response is "Yes" then clean and repair or remove from service.

Analyst Signature:		**Date:**	

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Retort Inspection and Calibration

Form 3001-3 Daily Retort Inspection Sheet

Operator:		Month and Year:		OCS-G-Number:		Area and Block:	(Surface Location)
Retort Model Number:		Retort Serial Number:		Comment	Retort Serial Number:		Comment

Day	Time	Initial	Retort cell damaged (10.3)? (Y/N)	Retort threads damaged (10.3)? (Y/N)	Retort metal surfaces damaged (10.3)? (Y/N)	Retort cup lid hole plugged (10.3)? (Y/N)	Retort cell-condenser plugged (10.3)? (Y/N)	Retort case damaged (10.4)? (Y/N)	Electrical cord damaged (10.4)? (Y/N)	Thermal blocks, electrical connections, operation of thermostat damaged (10.4)? Y/N)	Switches and controls stick (10.4)? (Y/N)	Indicator lights do not operate (10.4)? (Y/N)	Permanent ID of JP-tubes illegible 10.5)?(Y/N)	Volume scales illegible (10.5)? (Y/N)	Chips or cracks in glass (10.5)? (Y/N)	Debris or solids in JP-tubes (10.5)? (Y/N)	If any response is "Yes", then clean and repair or remove from service.	Retort cell damaged (10.3)? (Y/N)	Retort threads damaged (10.3)? (Y/N)	Retort metal surfaces damaged (10.3)? (Y/N)	Retort cup lid hole plugged (10.3)? (Y/N)	Retort cell-condenser plugged (10.3)? (Y/N)	Retort case damaged (10.4)? (Y/N)	Electrical cord damaged (10.4)? (Y/N)	Thermal blocks, electrical connections, operation of thermostat damaged (10.4)? Y/N)	Switches and controls stick (10.4)? (Y/N)	Indicator lights do not operate (10.4)? (Y/N)	Permanent ID of JP-tubes illegible (10.5)(Y/N)	Volume scales illegible (10.5)? (Y/N)	Chips or cracks in glass (10.5)? (Y/N)	Debris or solids in JP-tubes (10.5)? (Y/N)	If any response is "Yes", then clean and repair or remove from service.
1																															
2																															
3																															
4																															
5																															
6																															
7																															
8																															
9																															
10																															
11																															
12																															
13																															
14																															
15																															

Analyst 1 Print Name	Analyst 1 Signature	Analyst 2 Print Name	Analyst 2 Signature

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Retort Inspection and Calibration

Form 3001-3 Daily Retort Inspection Sheet

Operator:		Month and Year:		OCS-G-Number:		Area and Block:	(Surface Location)
Retort Model Number:		Retort Serial Number:		Comment	Retort Serial Number:		Comment

Day	Time	Initial	Retort cell damaged (10.3)? (Y/N)	Retort threads damaged (10.3)? (Y/N)	Retort metal surfaces damaged (10.3)? (Y/N)	Retort cup lid hole plugged (10.3)? (Y/N)	Retort cell-condenser plugged (10.3)? (Y/N)	Retort case damaged (10.4)? (Y/N)	Electrical cord damaged (10.4)? (Y/N)	Thermal blocks, electrical connections, operation of thermostat damaged (10.4)? Y/N)	Switches and controls stick (10.4)? (Y/N)	Indicator lights do not operate (10.4)? (Y/N)	Permanent ID of JP-tubes illegible 10.5)?(Y/N)	Volume scales illegible (10.5)? (Y/N)	Chips or cracks in glass (10.5)? (Y/N)	Debris or solids in JP-tubes (10.5)? (Y/N)	If any response is "Yes", then clean and repair or remove from service.	Retort cell damaged (10.3)? (Y/N)	Retort threads damaged (10.3)? (Y/N)	Retort metal surfaces damaged (10.3)? (Y/N)	Retort cup lid hole plugged (10.3)? (Y/N)	Retort cell-condenser plugged (10.3)? (Y/N)	Retort case damaged (10.4)? (Y/N)	Electrical cord damaged (10.4)? (Y/N)	Thermal blocks, electrical connections, operation of thermostat damaged (10.4)? Y/N)	Switches and controls stick (10.4)? (Y/N)	Indicator lights do not operate (10.4)? (Y/N)	Permanent ID of JP-tubes illegible (10.5)(Y/N)	Volume scales illegible (10.5)? (Y/N)	Chips or cracks in glass (10.5)? (Y/N)	Debris or solids in JP-tubes (10.5)? (Y/N)	If any response is "Yes", then clean and repair or remove from service.
16																																
17																																
18																																
19																																
20																																
21																																
22																																
23																																
24																																
25																																
26																																
27																																
28																																
29																																
30																																
31																																

Analyst 1 (Print Name)	Analyst 1 (Signature)	Analyst 2 (Print Name)	Analyst 2 (Signature)

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Base Fluids Retained on Cuttings Retort Test Procedure

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

The modified API Recommended Practice 13B-2 is designed to measure the amount of non-aqueous drilling fluid (NAF) contained in cuttings generated during a drilling operation. The procedure is a retort test that measures NAF base fluid and water released from a cuttings sample when heated in a calibrated and properly operating "retort" instrument. This Standard Operating Procedure (SOP) provides a consistent methodology for completing the retort test. A sample of cuttings is heated in the retort, which distills out the liquid associated with the sample. The liquid is condensed and collected in a receiver and separated into two liquid phases, the NAF base fluid and water.

2.0 Definitions

2.1 Base Fluid - the continuous phase or suspending medium of a drilling fluid formulation.

2.2 NAF – non-aqueous drilling fluid, i.e. with a base fluid that is a water-immiscible fluid.

3.0 Interferences

3.1 No interferences are known for this procedure.

4.0 Health and Safety Considerations

4.1 Follow health and safety procedures outlined in the Global HSE Plan.

4.2 Consult Material Safety Data Sheets (MSDS) for drilling fluids used during drilling interval.

4.3 Drilling fluid samples should be handled with the same precautions used in the drilling fluid handling areas of the drilling rig.

4.4 The NAF retention on cuttings involves separating liquids from approximately 50 ml of cuttings by distillation at high temperature in a 50 ml mud retort apparatus. Two retorts may be running simultaneously and continuously for several hours at a time. This procedure generates heat and a small amount of water and organic vapor.

4.5 If the condenser or cup hole is plugged, the retort may explode. The condition of the equipment should be checked daily during use.

4.6 The temperature of the retort will be at 950ºF during testing, so it is a potential thermal hazard.

5.0 Equipment and Supplies

© Copyright M-I L.L.C., 2004, All Rights Reserved.

5.1 Triple-beam balance, range 2000 g, precision ± 0.1g

5.2 Retort Assembly, retort body, cup and lid: 303 stainless steel or equivalent.

5.2.1 Retort cup with lid, volume 50 ml

5.2.2 Condenser – capable of cooling the oil and water vapors below their liquification temperature

5.2.3 Heating jacket – nominal 350 watts

5.2.4 Temperature control – capable of limiting temperature of retort to at least 930°F (500°C) and enough to boil off all NAFs.

5.2.5 JP-Tube (Liquid Receiver) – 10 ml cylindrical Pyrex® or equivalent glassware with rounded bottom, funnel-shaped top, and 0.1 ml graduations; precision ± 0.05 ml; outside diameter 10-mm; wall thickness 1.5 ± 0.1 mm; calibration to contain "TC" @ 20°C; accompanied by Certificate of Verification.

5.2.6 JP-Tube (Liquid Receiver) – 20 ml cylindrical Pyrex® or equivalent glassware with rounded bottom, funnel-shaped top, and 0.1 ml graduations; precision ± 0.05 ml; outside diameter 13-mm; wall thickness 1.2 ± 0.1 mm; calibration to contain "TC" @ 20°C; accompanied by Certificate of Verification.

5.3 Fine steel wool (No. 000 or 0000)

5.4 Drill bit or stiff wire

5.5 Thread sealant lubricant – high temperature lubricant; Never-Seez® or equivalent

5.6 Paper towels

5.7 Miscellaneous cleaning aids – pipe cleaners, brush, retort spatula and cork screw.

5.8 Permittee-approved software for ROC calculations

5.9 Retort Input Data Form 3002-1

5.10 Daily Activity Report Form 1006-1

6.0 Reagents and Standards

6.1 There are no reagents or standards associated with this method.

7.0 Sample Collection, Preservation, Shipment and Storage

7.1 Sampling will be performed with sampling equipment decontaminated as per M-I SWACO SOP 2004 (Decontamination of Sampling Equipment) or with dedicated sampling equipment. Samples will be collected as described in the applicable sampling SOPs.

7.2 A representative sample is collected from each discharge stream at a point following the last treatment equipment. Sample locations are described in the rig-specific sampling plan.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

7.3 Samples within each interval must be collected within one hour of each other. Testing should be started within two hours of individual sample collection.

8.0 Quality Control

8.1 Compliance Engineers are trained in the requirements of this procedure through the Compliance Engineer training program. Training on SOP revisions will be documented through completion of Form 2009-1, as described in SOP 2009 (Compliance Engineer Training).

8.2 Demonstration of Capability: Each analyst that performs this procedure shall have successfully completed a Demonstration of Capability as defined in M-I SWACO SOP 1008 (Demonstration of Capability).

8.3 Once per 20 sampling intervals, analyze two duplicate samples (two aliquots of the same sample after careful homogenization) which are expected to have a ROC between 5% and 20%. Calculate the relative percent difference (RPD) between the two results. The RPD should be less than 10%. (track duplicate sampling intervals using compliance engineer check sheet)

8.4 The mass balance for each sample is calculated using the permittee-approved software. For each sample, the mass balance must be within ± 5% of the mass of the wet sample.

9.0 Calibration and Standardization

9.1 M-I SWACO SOP 1004 (Balance Calibration) describes the calibration and standardization for the balance used in this procedure.

9.2 M-I SWACO SOP 3001 (Retort Inspection and Calibration) describes the calibration and standardization for the retort used in this procedure.

10.0 Field Procedure for Testing ROC Using the 50 ml Compliance Retort

10.1 Prior to running all tests, perform the Daily Inspection described in M-I SWACO SOP 3001 (Retort Inspection and Calibration) and complete the Daily Inspection Equipment Form.

10.2 All testing data is recorded on the Daily Activity Report as specified in M-I SWACO SOP 1006 (Field Logs). Sample data are recorded on the ROC Data Input Sheet (Figure 1).

10.3 Analytical procedure

10.3.1 Pack the retort body (upper chamber) with steel wool.

10.3.2 Apply lubricant/sealant to threads of retort cup and retort stem (high-temperature grease, i.e. Never-Seez®).

10.3.3 Weigh and record the mass of the clean empty retort cup, lid and body to 0.1 g. This is mass A.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

10.3.4 Gently mix the cuttings to obtain a homogeneous sample. Partially fill the retort sample cup with the sample. Remove any sample that is on the threads with a paper towel.

10.3.5 Place the lid on the retort sample cup and rotate to obtain a proper fit.

10.3.6 Screw the retort sample cup into the retort body (upper chamber). Keep the assembly upright. Weigh and record the mass to 0.1 g; this is mass B.

10.3.7 Attach the condenser to the retort assembly, seating firmly. Keep the assembly upright and place the retort assembly into the retort oven and close the lid.

10.3.8 Weigh and record the mass of the clean, empty 10 ml or 20 ml JP-tube to 0.1 g. This is mass C.

10.3.9 Attach or position the weighed 10 or 20 ml JP-tube so that it will collect all of the condensed NAF liquid and water. Secure the JP-tube at the proper height with the rubber washer provided in the retort kit so all the condensed fluids will be collected.

10.3.10 Turn the retort on and run for a minimum of 1 hour. The thermostat shall be set at 950°F.

10.3.11 After all the NAF has boiled off, turn off the retort. Remove the JP-tube and allow it to cool. Observe the JP-tube; if solids have boiled into the JP-tube, the test is void and you must repeat the test. Record the volume of water; this is V in mls. If an emulsion interface is present, carefully heat the JP-tube. Wearing the thermal protection gloves provided in the retort kit, remove the retort from the heating jacket while grasping the condenser. Carefully heat the emulsion band by rolling the JP-tube against the retort cell. This is done over short time intervals as to avoid boiling the liquids. After the emulsion is broken, allow the JP-tube to cool and read and record the water volume (lowest point of the meniscus). This is your V in mls.

10.3.12 Weigh and record the mass of the JP-tube and its contents (oil and water). This is mass D in grams.

10.3.13 Remove the assembly and condenser from the heating jacket and allow them to cool without water quenching.

10.3.14 Weigh and record the mass of the cooled retort cell body and lid. This is mass E in grams.

10.3.15 Clean the retort assembly, condenser and JP-tube immediately after finishing each test. Scrape the solids from the retort assembly and condenser. Wipe clean with a paper towel. Immerse in water if necessary to remove the solids. Clean the receiver as described in M-I SWACO SOP 2004 (Decontamination of Equipment).

10.3.16 Gently place the metal heat sink in the heating jacket to absorb the heat. This will accelerate the cooling time between retort runs.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

11.0 Calculations

11.1 Calculate the RPD as follows:

$$RPD = \frac{(R1 - R2) * 200}{(R1 + R2)}$$

where R1 = the higher ROC result

R2 = the lower ROC result

11.2 The permittee-approved software calculates the mass balance using the following equation:

$$\text{Mass Balance} = \frac{(MD + MBF + V)}{Mw}$$

where MD = Mass of dry retort cuttings (Mass E – Mass A)

MBF = Mass of NAF base fluid (Mass D – Mass C – Volume V)

V = Volume of water recovered (assumes 1 ml = 1 g)

Mw = Mass of wet cuttings (Mass B – Mass A)

11.3 The permittee-approved software performs the required calculations.

12.0 Data Assessment and Corrective Actions

12.1 The permittee-approved software assesses the data. The software provides the mass balance result or a warning if the mass balance criteria are not met.

12.2 The procedure shall be repeated for any sample that fails the mass balance ratio. Homogenize the sample thoroughly and repeat the procedure if the sample is still within the holding time. If the sample has exceeded the holding time and drilling is still inside the interval, collect another sample, thoroughly homogenize the new sample and repeat the procedure. If the sample has exceeded the holding time and drilling has commenced in the next interval, thoroughly homogenize the original sample and repeat the procedure.

12.3 The procedure shall be repeated using a smaller sample size for any sample where solids boiled over into the JP-tube. Homogenize the sample thoroughly and repeat the procedure if the sample is still within the holding time. If the sample has exceeded the holding time and drilling is still inside the interval, collect another sample, thoroughly homogenize the new sample and repeat the procedure. If the sample has exceeded the holding time and drilling has commenced in the next interval, thoroughly homogenize the original sample and repeat the procedure.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

12.4 If the holding time is exceeded and drilling is still inside the interval, collect another set of samples and repeat the procedure. If the holding time is exceeded and drilling has commenced on the next interval, use the data from the original sample.

13.0 Pollution Prevention and Waste Management

13.1 Samples are retained until the holding time has expired or until the Compliance Engineer has verified the acceptability of the test results, whichever comes first.

13.2 The waste material generated by this procedure is NAF and water that is returned to the mud system. The fluid is returned to the active mud system upon completion of the tests. Cuttings (excess sample) are returned to the mud system.

14.0 References

14.1 Appendix 7 to Subpart A of Part 435 and API Recommended Practice 13B-2.

14.2 M-I SWACO SOP 1004 (Balance Calibration)

14.3 M-I SWACO SOP 1006 (Field Logs)

14.4 M-I SWACO SOP 1008 (Demonstration of Capability)

14.5 M-I SWACO SOP 2004 (Decontamination of Equipment)

14.6 M-I SWACO SOP 3001 (Retort Inspection and Calibration)

15.0 Documentation

15.1 Sample collection information is recorded in the Field Notebook.

15.2 Calculations are documented in the permittee-approved software and recorded in the Daily Activity Report (Form 1006-1)

15.3 Mark all unused fields with “N/A” and/or a line though the unused blank.

15.4 The Compliance Engineer maintains the Retort Input Data Forms (Form 3002-1) and software outputs in the Drilling Interval Notebook. A copy of the Retort Input Data Forms (Form 3002-1) is provided to the permittee daily.

15.5 Upon completion of the drilling interval, provide the permittee with the Retort Input Data Forms (Form 3002-1) and software outputs. Archive a copy of the Retort Input Data Forms (Form 3002-1) and software outputs in the project files at the District Office.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Form 3002-1 Retort Input Data

Certificate of Analysis

Operator:		**Rig:**				**Date:**	
Area & Block: (Surface Location)		**OCS-G Number:**				**Interval #:**	
Method Reference:	**40 CFR 435, Appendix 7 to Subpart A – API Recommended Practice 13B-2**					**Permit Number:**	
Sample Collection Point:						**Sample Time:**	
Start Depth:		**End Depth:**		**Sample Depth:**		**Sample Vol.:**	
Retort Start Time:		**Retort End Time:**		**Retort S/N:**		**Cell #:**	

RETORT CELL WITH STEEL WOOL (A):		**Grams**
CELL + WET CUTTING WEIGHT (B):		**Grams**
EMPTY JP TUBE WEIGHT (C):		**Grams**
LIQUID + JP TUBE WEIGHT (D):		**Grams**
CELL + DRY CUTTING WEIGHT (E):		**Grams**
WATER VOLUME IN JP TUBE (V):		**mL**
Mass Balance:		**1 ± 0.05**
ROC RESULT FROM SOFTWARE:		**%BF**
Comments:		

Sample Collection Point:						**Sample Time:**	
Start Depth:		**End Depth:**		**Sample Depth:**		**Sample Vol.:**	
Retort Start Time:		**Retort End Time:**		**Retort S/N:**		**Cell #:**	

RETORT CELL WITH STEEL WOOL (A):		**Grams**
CELL + WET CUTTING WEIGHT (B):		**Grams**
EMPTY JP TUBE WEIGHT (C):		**Grams**
LIQUID + JP TUBE WEIGHT (D):		**Grams**
CELL + DRY CUTTING WEIGHT (E):		**Grams**
WATER VOLUME IN JP TUBE (V):		**mL**
Mass Balance:		**1 ± 0.05**
ROC RESULT FROM SOFTWARE:		**%BF**
Comments:		

Software Used: (Name and Version)		**Interval Average % BF:**		**Well Average % BF:**	
Analyst Signature:				**Date:**	

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Reverse Phase Extraction (RPE) Method for Detection of Oil Contamination in Non-Aqueous Drilling Fluids (NAF)

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

This Standard Operating Procedure (SOP) is used for the determination of crude oil, formation oil or other petroleum contamination in non-aqueous drilling fluids (NAFs). This method is a qualitative (positive/negative) test to determine the presence of oil in NAF prior to discharging drill cuttings from offshore production platforms.

This method has been designed to show positive contamination for 5% of representative crude oils at a concentration of 0.1% in drilling fluid (vol./vol.), 50% of representative crude oils at a concentration of 0.5%, and 95% of representative crude oils at a concentration of 1%.

An aliquot of drilling fluid is extracted with isopropyl alcohol. The mixture is allowed to settle and the solvent layer is filtered to remove residual solids. An aliquot of the filtered extract is placed on a reverse phase extraction (RPE) cartridge. The cartridge is eluted with isopropyl alcohol. Oil contaminants are retained on the cartridge and their presence (or absence) is detected based on observed fluorescence using a black light.

2.0 Definitions

2.1 NAF – Non-aqueous drilling fluids with a continuous phase that is a water-immiscible fluid (natural or synthetic). Also referred to as base fluid.

3.0 Interferences

3.1 Solvent, reagents, glassware and other sample-processing hardware may yield artifacts that affect results.

3.2 Fluorescent materials, other than oil contamination, will bias the results positively.

4.0 Health and Safety Considerations

4.1 Isopropyl alcohol (isopropanol) is flammable and should be used in a well-ventilated area. Consult the applicable Material Safety Data Sheet (MSDS) for other health and safety considerations.

4.2 Unknown samples may contain high concentrations of toxic compounds. Sample containers should be handled with nitrile gloves to prevent exposure. Sample preparation should be

© Copyright M-I L.L.C., 2004. All Rights Reserved.

conducted in a well-ventilated area to limit exposure to harmful contaminants. Drilling fluid samples should be handled with the same precautions used in the drilling fluid handling areas of the drilling rig.

5.0 Equipment and Supplies

5.1 Sampling Equipment

	Specification	OFI/M-I SWACO Equivalent
5.1.1	Sample Collection bottle/jars, new with lot certified to be free of artifacts.	Two one-liter plastic bottles with Teflon ® lined screw cap.
5.1.2	Refrigerator, capable of maintaining sample temperature at 4 ± 2°C	Supplied by Permitee
5.1.3	Marker	Black, writes on glass
5.1.4	Nitrile Gloves	For handling hazardous samples

5.2 Glassware Cleaning Equipment

	Specification	OFI/M-I SWACO Equivalent
5.2.1	Laboratory sink	Supplied by Permitee.

5.3 Sample Extraction Equipment

	Specification	OFI/M-I SWACO Equivalent
5.3.1	Vials, glass, 20 mL	
5.3.2	Beakers, 100 mL	
5.3.3	Glass syringe, 10 mL – Use for IPA only	BD 10 mL glass syringe No. 06-2142
5.3.4	Plastic syringe, 5 mL	BD 5 mL plastic syringe No. 309603
5.3.5	Plastic syringe, 1 mL	BD 1 mL plastic syringe No. 309602
5.3.6	Pipette, 20 mL	20 mL glass pipette used in Static Sheen test
5.3.7	Glass stirring rod	
5.3.8	Disposable syringes, plastic	B-D Disposable Syringe 1 mL No.309602 B-D Disposable Syringe 5 mL No.309603
5.3.9	Teflon® syringe filter, 25-mm, 0.45 μm pore size	PTFE 0.45 μm disposable syringe filter

© Copyright M-I L.L.C., 2004. All Rights Reserved.

5.3.10 Reverse phase extraction C_{18} cartridge	Waters Sep-Pac Plus C-18, No. W1166L1

5.4 Fluorescence Detection Equipment

Specification	OFI/M-I SWACO Equivalent
5.4.1 Black light	UVP Compact 4 watt Ultraviolet Lamp, Model UGV-11
5.4.2 Black box for viewing	UVP Chromato-VUE Cabinet
5.4.3 Viewing platform for cartridges	

6.0 Reagents and Standards

Specification	OFI/M-I SWACO Equivalent
6.1 Isopropyl alcohol (IPA), 99%	
6.1.1 NAF	Unweighted base fluid or uncirculated mud
6.1.2 Reference crude oil	Crude Oil "F" or equivalent supplied by M-I SWACO HSE Department
6.1.3 Standard crude oil	NIST SRM 1582 petroleum crude oil
6.1.4 Positive Control Sample	Standard crude oil spiked into cartridge supplied by OFI, maintained in a closed brown bottle and kept moist with IPA by co-storing a small piece of paper soaked in IPA

7.0 Sample Collection, Preservation, Shipment and Storage

7.1 **Collection of Drilling Fluid Samples from the active mud system**: Collect a one-liter bottle of drilling fluid from the active mud system. The bottle should be submerged in the drilling fluid directly and no intermediate sampling devices should be used. The outside of the bottle should be wiped clean of mud and labeled as described in M-I SWACO SOP 1006 (Sample Location/Date/Time/Initials). The sample label shall also contain the sample type (NAF A). The sample should be collected after the mud passes through the shale shaker and before it passes through other solids control equipment, i.e. the same location that toxicity samples are collected.

7.2 A sample of NAF is collected from the batch of NAF as sent by the supplier, prior to circulating downhole. Collect (2) one-liter bottles of unused drilling fluid. The bottles should be submerged in the drilling fluid directly and no intermediate sampling devices should be used. The outside of the bottles should be wiped clean of mud and labeled as described in

© Copyright M-I L.L.C., 2004. All Rights Reserved.

M-I SWACO SOP 1006 (Sample Location/Date/Time/Initials). The sample label shall also contain the sample type (NAF B).

7.3 Sample containers should also be labeled with the date and time of sample collection, preservative, sampler's name, and type of analysis.

7.4 The sample identification, sample location, sample equipment, preservation technique as well as the name of the sample collector should be recorded on Section 2 of the Daily Activity Report .

7.5 If testing is not performed immediately, all samples must be refrigerated at 4 ± 2°C from time of collection until time of analysis.

7.6 All samples must be analyzed within 28 days of the date and time of sample collection.

8.0 Quality Control

8.1 Demonstration of Capability: Each analyst that performs this procedure shall have successfully completed a Demonstration of Capability as defined in M-I SWACO SOP 1008.

8.2 Sample Duplicates:

8.2.1 Each sample from a sampling site or discharge shall be prepared and analyzed in duplicate using the procedures described in Section 10.0.

8.2.2 Duplicate results are acceptable if each of the results give the same response (positive/negative). If the results are different, the samples may not be homogeneous. Prepare the samples again, mixing the sample well prior to extraction. Analyze the remixed samples again.

8.2.3 If different results are obtained a second time, the analytical system is out of control and the problem shall be identified and corrected.

8.3 Spiked Duplicates:

8.3.1 Spike a field sample that is expected to contain less than 0.5% crude oil with 1% (by volume) of standard crude oil as described in Section 10.3.

8.3.2 Prepare and analyze as field samples as described in Section 10.0.

8.3.3 If no low-level drilling fluid is available, the unused NAF B can be used as the drilling fluid sample.

8.3.4 Spike, prepare and analyze spiked duplicate samples with each set of field samples.

8.4 Laboratory Reagent Blank:

© Copyright M-I L.L.C., 2004. All Rights Reserved.

8.4.1 Prepare a reagent blank using the procedures described in Section 10.2.

8.4.2 If no fluorescence is observed, then the IPA, filter and cartridge are clean.

8.4.3 If fluorescence is observed in the reagent blank cartridge, the system is out of control and sample analyses are halted until the source of contamination is eliminated. Sample analyses may resume after a prepared reagent blank shows no fluorescence under the black light.

8.4.4 All samples shall be associated with an uncontaminated reagent blank before the results may be reported for regulatory compliance.

8.5 NAF Reference Blank:

8.5.1 Prepare a NAF reference blank from the NAFs collected as described in Section 7.2. This quality control sample is used as a reference when viewing the test samples.

8.5.2 The NAF reference blanks is prepared as described in Section 10.0

8.5.3 The fluorescence or absence of fluorescence in the compliance samples is determined relative to the NAF reference cartridge.

8.6 Positive Control Sample:

8.6.1 A positive control cartridge is supplied with the field kits.

8.6.2 The acceptability of the positive control cartridge is confirmed prior to extraction and analysis of samples.

8.6.3 The positive control cartridge is acceptable if the paper in the storage bottle is still moistened with IPA and the sample fluoresces.

8.6.4 After each use, a fresh IPA-moistened paper is placed in the storage bottle and the older paper is disposed of.

8.6.5 Positive control samples are prepared by dissolving 87 mg of standard crude oil into 10.00 mL of methylene chloride. Mix 40 µl of this solution into 10 mL of IPA. Transfer 0.5 mL of this solution into a preconditioned C_{18} cartridge. Rinse the cartridge with 2 mL of IPA. Record the preparation of the positive control in the standards notebook as described in M-I SWACO SOP 1002 (Traceability of Reagents, Standards and Reference Materials).

9.0 Calibration and Standardization

9.1 Calibration and standardization procedures are not employed for this procedure.

9.2 Acceptable performance of the black light is indicated by negative results in the laboratory reagent blank and positive results in the positive control sample.

10.0 Procedure

© Copyright M-I L.L.C., 2004. All Rights Reserved.

10.1 Collect the following samples as described in Section 7.0.

10.1.1 A one-liter bottle of drilling fluid from the active system **(NAF A)**.

10.1.2 (2) one-liter bottles of unused drilling fluid **(NAF B).**

10.2 Confirm the acceptability of the Positive Control Sample.

10.3 Prepare a reagent blank:

10.3.1 Pour IPA to the 50 mL mark in a 100 mL beaker and label the beaker as **Unfiltered IPA**.

10.3.2 Draw 4 mL of Unfiltered IPA into the 10 mL syringe. Attach the syringe filter to the end of the 10 mL glass syringe and slowly filter the IPA into a 20 mL glass vial. Label the vial as Reagent Blank Filtrate **(RB).** Dispose of the syringe filter.

10.3.3 Label a new Sep Pak™ C_{18} cartridge as **RB**. Draw 10 mL of Unfiltered IPA into the 10 mL syringe. Attach the syringe to the C_{18} cartridge and pass the 10 mL of **Unfiltered IPA** through the cartridge at 1–2 drops per second into an empty 100 mL beaker labeled as "**Waste**". When the cartridge is well conditioned it will be transparent, not opalescent. **Do not force air through the cartridge**. Detach the syringe from the cartridge.

10.3.4 Place a 5 mL plastic syringe with the plunger removed on the cartridge. Use a new 1 mL plastic syringe to draw up 0.5 mL from the RB filtrate vial. Place the RB filtrate into the 5 mL syringe. Using the 10 mL glass syringe, add 3.0 mL of IPA to the 5 mL plastic syringe. Replace the plunger and slowly depress the syringe at 1--2 drops per second. Stop the plunger when no filtrate remains in the syringe barrel. **Do not force air through the cartridge**. Detach the syringe from the cartridge. Remove the plunger. Reattach the syringe to the cartridge.

10.3.5 Draw 2 mL of unfiltered IPA into the 10 mL syringe. Place the IPA into the 5 mL plastic syringe. Replace the plunger and depress the plastic syringe slowly at 1-2 drops per second. Stop the plunger when no filtrate remains in the syringe barrel. **Do not force air through the cartridge**. Detach the syringe from the cartridge.

10.3.6 Place the sample cartridge in the black box. Illuminate the cartridges with black light at 365-nm and look for fluorescence.

10.3.7 Record results in the RPE Analytical Report (Figure 1). If the reagent blank cartridge does not fluoresce, then proceed with the preparation of NAF reference blanks, samples and spiked duplicate samples. If the reagent blank cartridge fluoresces, halt the analysis of samples until the problem is corrected and a reagent blank provides acceptable results.

10.4 Prepare spiked duplicate samples:

© Copyright M-I L.L.C., 2004. All Rights Reserved.

10.4.1 Label a vial **NAFS1**. Using a 20 mL pipette or syringe, remove exactly 20 mL of **NAF A** mud and inject it into the 20 mL vial. Using a 1 mL disposable syringe, add 0.2 mL of reference F crude oil to the vial. Close the vial and shake it vigorously.

10.4.2 Label a second vial **NAFS2**. Prepare vial as described in Step 10.4.1.

10.4.3 The resulting samples (NAFS1 and NAFS2) are extracted and prepared using the procedures described in 10.5.

10.5 Sample Extraction:

10.5.1 Bring the NAF A and NAF B samples to room temperature. Shake the containers for 1 minute.

10.5.2 Prepare the NAFS1 and NAFS2 samples as described in Section 10.4.

10.5.3 Pour about 50 mL of IPA into a 100 mL glass beaker labeled "**Unfiltered IPA**".

10.5.4 Label five 20 mL vials as NAFA1X, NAFA2X, NAFBX, NAFS1X and NAFS2X (X for extract). Add 10 mL of IPA to each "X" vial with the 10 mL glass syringe. For each sample, transfer 0.2 mL of mud with a disposable 1.0 mL syringe by first drawing in 0.8 mL of sample and then expelling 0.2 mL into the 20 mL vial. Add a second 10 mL aliquot of IPA to each "X' vial with the 10 mL glass syringe. Cap and shake each vial for at least 2 minutes. **Let the extracts settle for at least 15 minutes**.

10.5.5 Remove 10 mL of IPA from the **Unfiltered IPA** beaker with the 10 mL glass syringe. Attach the syringe to the Sep Pak™ C_{18} cartridge and pass the 10 mL of **Unfiltered IPA** through the cartridge at 1-2 drops per second into a beaker labeled "**Waste**". When the cartridge is well conditioned it will be transparent, not opalescent. Do not force air through the cartridge. Detach the syringe from the cartridge. Repeat for the next four cartridges.

10.5.6 Label five vials as NAFA1F, NAFA2F, NAFBF, NAFS1F and NAFS2F (F for filtrate). Remove 4 mL of extract from the "X" vials using a 5 mL plastic syringe. Use a new syringe for each extract. Attach a Teflon® syringe filter disc onto the 5 mL syringe. Filter the solution into the corresponding "F" vial. Dispose of the filter.

10.5.7 Label five preconditioned C_{18} cartridges as NAFA1, NAFA2, NAFB, NAFS1 and NAFS2. Attach a new 5 mL plastic syringe with the plunger removed to the cartridge. Use a new 1 mL plastic syringe to draw up 0.5 mL of the filtrate from the "F" vials. Place the 0.5 of filtrate into the 5 mL plastic syringe. Add 3 mL of IPA (using the 10 mL glass syringe) to the 5 mL plastic syringe. Slowly depress the syringe at 1-2 drops per second. Stop the plunger when no filtrate remains in the syringe barrel. Collect the excess IPA in a beaker labeled "**Waste**". **Do not force air through the cartridge**. Detach the syringe from the cartridge. Remove the plunger.

10.5.8 Reattach the 5 mL plastic syringe to the cartridge. Add 2 mL of IPA to the syringe (using the 10 mL glass syringe). Rinse each cartridge with 2 mL of IPA using the 5 mL plastic syringe.

© Copyright M-I L.L.C., 2004. All Rights Reserved.

Slowly depress the syringe at 1-2 drops per second. Stop the plunger when no fluid remains in the syringe barrel. Collect the excess IPA in a beaker labeled "**Waste**". Do not force air through the cartridge. Detach the syringe from the cartridge.

10.6 Sample fluorescence testing:

10.6.1 Turn on the black light.

10.6.2 View set "1" of the quality control samples. Place sample **NAFB** to the left of the positive control sample in the viewing box. Confirm that the **NAFB** sample passes (i.e., fluoresces less) than positive control sample. If the unused mud sample does not provide the expected results, follow the corrective action in Section 12.0. Record results in the RPE Analytical Report (Figure 1).

10.6.3 View replicate "1" of the active mud system samples. Place sample **NAFB** to the left of sample **NAFA1** and place the positive control sample to the right of sample **NAFA1** in the viewing box. Determine if the **NAFA1** sample passes (i.e., fluoresces less) or fails (i.e., fluoresces equal to or greater than) compared to the positive control sample. Record results in the RPE Analytical Report (Figure 1).

10.6.4 View replicate "2" of the active mud system samples. Place sample **NAFB** to the left of sample **NAFA2** and place the positive control sample to the right of sample **NAFA2** in the viewing box. Determine if the **NAFA2** sample passes (i.e., fluoresces less) or fails (i.e., fluoresces equal to or greater than) compared to the positive control sample. Record results in the RPE Analytical Report (Figure 1).

10.6.5 View set "1" of the quality control samples. Place sample **NAFB** to the left of the positive control sample and place **NAFS1** to the right of the positive control sample in the viewing box. Confirm that the **NAFS1** sample fails (i.e., fluoresces equal to or greater than) compared to the positive control sample. Record results in the RPE Analytical Report (Figure 1).

10.7 View set "2" of the quality control samples. Place sample **NAFB** to the left of the positive control sample and place **NAFS2** to the right of the positive control sample in the viewing box. Confirm that the **NAFS2** sample fails (i.e., fluoresces equal to or greater than) compared to the positive control sample. Record results in the RPE Analytical Report (Figure 1).

10.8 If the sample results for **NAFA1** and **NAFA2** match, the analysis is complete. If samples **NAFA1** and **NAFA2** provide different results, record the results and invalidate the test and follow the corrective action in Section 12.0. Record the results in the Daily Activity Report, Section 2.

11.0 Calculations

© Copyright M-I L.L.C., 2004. All Rights Reserved.

11.1 No calculations are required for this procedure.

12.0 Data Assessment and Corrective Actions

12.1 If the reagent blank cartridge fluoresces, halt the analysis of samples until the problem is corrected and a reagent blank provides acceptable results. Potential problems include contamination of the IPA, filter discs or cartridges. Repeat the procedure with fresh filter discs or cartridges.

12.2 If the positive control does not fluoresce, prepare or obtain a new positive control.

12.3 If the 1% spiked samples do not fluoresce equal to or greater than the positive control, reprepare both the spiked and unspiked samples.

12.4 Duplicate sample (NAFA) results are acceptable if each of the results give the same response (positive/negative). If the results are different, the samples may not be homogeneous. Prepare the samples again, mixing the sample well prior to extraction. Analyze the remixed samples again.

12.5 If the samples (NAFA) are positive, notify the permittee.

13.0 Pollution Prevention and Waste Management

13.1 Waste IPA remains with the permittee for appropriate disposal.

13.2 Authentic samples (drilling fluids) failing the fluorescence test, shall be considered contaminated samples. These samples remain with the permittee for appropriate disposal.

14.0 References

14.1 Appendix 6 to Subpart A of 40 CFR Part 435.

14.2 M-I SWACO SOP 1006: Field Log

15.0 Documentation

15.1 The Compliance Engineer completes Figure 1 (RPE Analytical Report) and maintains in the Drilling Interval Notebook until completion of the synthetic fluids drilling interval. The original RPE Analytical Report is transferred to the permittee upon completion of the synthetic fluids drilling interval. A copy of the RPE Analytical Report is returned to the Records Custodian.

15.2 Mark all unused fields with “N/A” and/or a line though the unused blank.

15.3 Complete Daily Activity Report Section 2 and maintain in the Drilling Interval Notebook.

© Copyright M-I L.L.C., 2004. All Rights Reserved.

15.4 After completion of the synthetic fluids drilling interval, the Field Logs are archived by the Records Custodian at the District Office. A copy of the RPE Analytical Report is archived by the Records Custodian at the District Office.

© Copyright M-I L.L.C., 2004. All Rights Reserved.

Figure 1

RPE Analytical Report **Certificate of Analysis**			
Operator:		Area and Block:	(Surface Location)
OCS-G Number:		Rig Name:	
Collection Date:		Collection Time:	
Analysis Date:		Analysis Time:	
Analyst:		Permit Number:	

Method Reference: Appendix 6 to Subpart A of Part 435

Sample ID	Sample Results	Yes	No	Result (Pass/Fail)
	NAFA1 fluoresces equal to or greater than the positive control?			
	NAFA2 fluoresces equal to or greater than the positive control?			
	Does NAFA1 result agree with NAFA2 result?			
	NAFA1 fluoresces equal to or greater than the positive control?			
	NAFA2 fluoresces equal to or greater than the positive control?			
	Does NAFA1 result agree with NAFA2 result?			

Results above are acceptable if NAFA fluoresces less than positive control, and NAFA1 agrees with NAFA2.

	Quality Control Results	Yes	No	Acceptable? (Yes/No)
	Reagent Blank (RB) does not fluoresce?			
	NAFB fluoresces less than positive control?			
	NAFS1 fluoresces equal to or greater than the positive control?			
	NAFS2 fluoresces equal to or greater than the positive control?			

Quality control results are acceptable if all answers are "Yes".

Comments:

Analyst Signature:		Date:	

© Copyright M-I L.L.C., 2004. All Rights Reserved.

Free Oil by Static Sheen Method

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

This Standard Operating Procedure (SOP) provides consistent methodology for the qualitative (pass/fail) analysis of drilling fluid or drill cuttings for static sheen. Static sheen is a compliance test for the "No discharge of free oil" requirement for discharge of drilling fluids and drill cuttings from offshore production platforms.

2.0 Definitions

2.1 Free oil – any oil contained in a waste stream that, when discharged, will cause a film or sheen upon or a discoloration of the surface of the receiving water.

2.2 Sheen – a silvery or metallic reflection or gloss; increased reflectivity, visual color, iridescence or an oil slick on the water surface.

3.0 Interferences

3.1 This test requires that the sample be introduced below the water surface. Any introduction of the sample to the water surface (e.g., from outside the syringe when immersing and removing it from the water) interferes with the test observation.

3.2 Residual free oil on improperly washed equipment is a primary source of contamination. All reusable equipment must be thoroughly cleaned using the procedures in M-I SWACO SOP 2004 (Decontamination of Equipment).

4.0 Health and Safety Considerations

4.1 No specific health and safety considerations are necessary other than the general procedures outlined in the Global HSE Plan.

4.2 Consult Material Safety Data Sheets (MSDS) for drilling fluids used during drilling interval.

5.0 Equipment and Supplies

5.1 Equipment and supplies are to be provided by the permittee. If they are not available, obtain the items listed below.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

5.2 2 Rubbermaid® dishpans, No. 2951 or 11.5 quart or equivalent. (Container must have an internal cross-section parallel to its opening has an area of 1000 $cm^2 \pm 50$ cm^2 and a depth of 13 to 30 cm).

5.3 20- or 30-gallon black plastic trash bags.

5.4 20-mL or 25-mL disposable plastic syringes.

5.5 Disposable plastic weigh boats.

5.6 Sample collection containers: 32-oz wide-mouth glass jar with Teflon®-lined cap or equivalent; cleaned as specified in M-I SWACO SOP 2004 (Decontamination of Equipment).

5.7 Stainless steel spatula.

5.8 Triple beam balance.

5.9 5-gallon bucket for seawater.

5.10 Ambient seawater.

5.11 Test area with fluorescent lighting.

5.12 Daily activity report (M-I SWACO SOP 1006 – Field Logs).

5.13 Static Sheen Test Report Form 3004-1.

6.0 Reagents and Standards

6.1 There are no standards associated with this method.

7.0 Sample Collection, Preservation, Shipment, and Storage

7.1 Samples of drilling fluids are collected daily from beneath the shale shaker after cuttings have been removed. The sample volume should range from 200 to 500 mL and be collected in a glass jar.

7.2 Samples of drill cuttings are collected daily from the shale shaker screen with a clean spatula or similar instrument and placed in a sample container. The sample volume should range from 200 to 500 g.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

7.3 Samples must be tested no later than one hour after collection. Samples must be stored in a dedicated laboratory refrigerator and maintained at 4±2°C until tested.

8.0 Quality Control

8.1 Compliance Engineers are trained in the requirements of this procedure through the Compliance Engineer training program. Training on SOP revisions will be documented through completion of Form 2009-1, as described in SOP 2009 (Compliance Engineer Training).

9.0 Calibration and Standardization

9.1 Calibrate the balance as described in M-I SWACO SOP 1004 (Balance Calibration).

10.0 Procedure

10.1 Cut a new plastic garbage bag in half and place the liners in each dishpan.

10.2 Collect five gallons of seawater.

10.3 Pour the seawater into the plastic bag-lined dishpans to within ½ inch of the top.

10.4 Mud Samples

10.4.1 Homogenize the mud sample thoroughly.

10.4.2 Fill and empty the disposable syringe with the homogenized mud three times. Fill the syringe with 20 mL of mud. Inject 15 mL of mud into the seawater 1 cm below the surface.

10.4.3 Stir the seawater with a syringe to distribute the test material homogenously.

10.5 Cuttings Samples

10.5.1 Mix the cuttings thoroughly with a clean spatula.

10.5.2 Using the stainless steel spatula, weigh 15 grams of cuttings onto a disposable plastic weigh boat.

10.5.3 In the second dishpan, immerse the weigh boat into the water and use the spatula to scrape the cuttings into the bottom of the container. Stir the cuttings with the spatula to evenly distribute the solids on the bottom of the dishpan.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

10.6 Observations

10.6.1 Make all observations within one hour of transferring the sample into the container. Observations should be made every 10 minutes with the final observation being 60 minutes from the start of the test.

10.6.2 Look for a silvery or metallic sheen, or gloss, increased reflectivity, visual color, iridescence or an oil slick. Look from at least three directions at angles 30 to 60 degrees from horizontal.

10.6.3 If the free oil covers more than 10% of the surface area, the film may be too thick to see color or sheen, so look for an oil slick.

10.6.4 If a sheen is observed on less than ½ of the surface area continue to make observations for a total of one hour. If the sheen still covers less than ½ of the surface area at the end of one hour, the sample passes the static sheen test and the discharge can continue.

10.6.5 If the sample causes a sheen to occur on more than ½ of the surface area within one hour of starting the test, the sample does not pass the static sheen test. Notify the permittee.

10.6.6 Record observations on the Static Sheen Test Report Form 3004-1.

10.6.7 Record results on the Daily Activity Report (Form 1006-1).

11.0 Calculations

11.1 There are no calculations with this procedure.

12.0 Data Assessment and Corrective Actions

12.1 If a test for a sample is not begun within one hour of sample collection or if a negative result is not confirmed by continued observation for up to one hour, the test is invalid. Collect another sample and repeat the test.

12.2 If a sample does not pass the sheen test, notify the permittee.

13.0 Pollution Prevention and Waste Management

13.1 Samples are retained until the holding time has expired or until the Compliance Engineer has verified the acceptability of the test results, whichever comes first.

13.2 Plastic trash bag liners are placed in the trash.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

13.3 The seawater/mud and seawater/cuttings slurries are placed into the mud system.

14.0 References

14.1 Appendix 1 to Subpart A of Part 435.

14.2 M-I SWACO SOP 1004 (Balance Calibration)

14.3 M-I SWACO SOP 1006 (Field Logs)

14.4 M-I SWACO SOP 2004 (Decontamination of Equipment)

15.0 Documentation

15.1 Sample collection information is recorded in the Field Notebook and the Daily Activity Report.

15.2 The results of the static sheen tests are recorded on the Static Sheen Test Report Form (Form 3004-1) and on the Daily Activity Report (Form 1006-1).

15.3 Mark all unused fields with “N/A” and/or a line though the unused blank. Enter a comment in the comment column as to why the empty column was not used.

15.4 The Compliance Engineer maintains the Static Sheen Report Forms in the Drilling Interval Notebook.

15.5 Upon completion of the drilling interval, provide the permittee with the original Static Sheen Test Report Forms. Archive a copy of the Static Sheen Test Report Forms in the project files at the District Office.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Form 3004-1 – Static Sheen Test Report Form

Certificate of Analysis

Operator:		**OCS-G Number:**	
Rig Name:		**Area and Block:**	(Surface Location)
Permit Number:		**Method Reference:**	**40 CFR Subpart A, Appendix 1 to Subpart A**

Sample ID Number				
Date of Sampling and Analysis				
Type of Sample				
Time of Sampling				
Location of Sample				
Sample Collector				
Test Location				
Analyst				
Time Test Initiated				
Observations	Time	Pass / Fail	Time	Pass / Fail
1				
2				
3				
4				
5				
6				
Results of Analysis	Pass / Fail		Pass / Fail	
Comments:				
Analyst Signature:		Date:		

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Visual Sheen Test

Quality Assurance Officer	Date
Compliance Supervisor	Date

1.0 Scope and Application

The purpose of the procedure is to provide a consistent method for performing a visual sheen test of waste streams discharging into the marine environment around a drilling platform.

2.0 Definitions

2.1 **Sheen** – means a silvery or metallic sheen, gloss, or increased reflectivity, visual color or iridescence on the water surface.

2.2 **Free oil** – any oil contained in a waste stream that, when discharged, will cause a film or sheen upon or a discoloration of the surface of the receiving water.

2.3 **Drilling Fluid** - means the circulating fluid (mud) used in the rotary drilling of wells to clean and condition the hole and to counterbalance formation pressure. Classes of drilling fluids are:

2.4 **TCW fluids** - means Treatment Completion Workover fluids. These are defined as salt solutions, weighted brines, polymers and various additives used to prevent damage to the well bore during operations which prepare the drilled well for hydrocarbon production or alter the formation in some way to increase production; or biocides, corrosion inhibitors, or other chemicals which are used to treat seawater or freshwater to prevent corrosion or fouling of piping or equipment.

2.5 **Deck Drainage** - means any waste resulting from deck washings, spillage, rainwater, and runoff from gutters and drains including drip pans and work areas within facilities subject to this permit.

2.6 **Miscellaneous Discharge** – means the discharge of:

- Desalination Unit Discharge
- Blowout Preventer Fluid
- Uncontaminated Bilge Water
- Uncontaminated Freshwater
- Boiler Blowdown
- Excess Cement Slurry
- Diatomaceous Earth Filter Media
- Uncontaminated Ballast Water
- Mud, Cuttings, and Cement at the Seafloor
- Uncontaminated Seawater
- Source Water and Sand

2.7 **Produced Water** - means the water (brine) brought up from the hydrocarbon-bearing strata during the extraction of oil and gas, and can include formation water, injection water, and any chemicals added downhole or during the oil/water separation process.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

2.8 **Sanitary Waste** - means human body waste discharged from toilets and urinals.

2.9 **Domestic Waste** - means material discharged from galleys, sinks, showers, safety showers, eye wash stations, hand washing stations, fish cleaning stations, and laundries.

3.0 Interferences

3.1 This test can not be performed when atmospheric or surface conditions prohibit the observer from detecting a sheen (e.g., overcast skies, rough seas, ect.).

4.0 Health and Safety Considerations

4.1 No specific health and safety considerations are necessary other than the general procedures outlined in the Global HSE Plan.

5.0 Equipment and Supplies

5.1 Daily observation worksheet.

6.0 Reagents and Standards

6.1 Reagents or standards are not applicable to this procedure.

7.0 Sample Collection, Preservation, Shipment and Storage

7.1 There is no sample collection for this procedure.

8.0 Quality Control

8.1 Compliance Engineers are trained in the requirements of this procedure through the Compliance Engineer training program. Training on SOP revisions will be documented through completion of Form 2009-1, as described in SOP 2009 (Compliance Engineer Training).

9.0 Calibration and Standardization

9.1 No calibration required.

10.0 Procedure

10.1 The observer must be positioned on the rig or platform, relative to both the discharge point and current flow at the time of discharge, such that the observer can detect a sheen should it surface down current from the discharge. For any discharges that have been occurring for at least 15 minutes previously, observations can be made any time thereafter. For discharges of less than 15 minutes duration, observations must be made during both discharge and 5 minutes after discharge has ceased.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

10.2 Obtain and record wind speed, wind direction, and current direction from appropriate personnel on site (e.g., marine department, barge engineer, ect.).

10.3 If an observation cannot be made, record this in the Daily Observation Worksheet along with a comment as to why the observation cannot be made (e.g., overcast skies, rough seas, ect.).

11.0 Calculations

11.1 There are no calculations with this procedure.

12.0 Data Assessment and Corrective Actions

12.1 There is no data assessment associated with this procedure.

13.0 Pollution Prevention and Waste Management

13.1 There are no wastes that are generated with this procedure.

14.0 References

14.1 Final NPDES General Permit for New and Existing Sources and New Discharges in the Offshore Subcategory of the Oil and Gas Extraction Category for the Western Portion of the Outer Continental Shelf of the Gulf of Mexico (GMG290000)

14.2 Final NPDES General Permit No. GMG 460000 for Offshore Oil and Gas Activities in the Eastern Gulf of Mexico

15.0 Documentation

15.1 Daily Observation Worksheet

15.2 Archive the Daily observation worksheet in the Drilling Interval Logbook during the drilling interval.

15.3 Mark all unused fields with “N/A” and/or a line though the unused blank.

15.4 Upon completion of the drilling interval, provide the permittee with a copy of the Daily Observation Worksheet. Archive a separate copy in the project files at the District Office.

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Visual Sheen Test

Daily Observation Worksheet

Operator:
OCS-G-
Surface A&B:
Rig:

Draw Location of Sheen, Solids, or Foam Relative to Rig

N

Date:
Time:
Observer:

Observations

Visual Sheen	Yes	No	N/A	Comments
Drilling Fluid				
Drill Cuttings				
TCW Fluid				
Deck Drainage				
Miscellaneous				
Produced Water				
Sanitary Waste				
Domestic Waste				
Floating Solids	Yes	No	N/A	
Sanitary Waste				
Domestic Waste				
Foam	Yes	No	N/A	
Domestic Waste				

N
Direction of Current

Seas:
- Calm
- 0-4 Feet
- 4-8 Feet
- 8-12 Feet
- 12+ Feet

Wind Knots

N
Direction of Wind

Draw Location of Sheen, Solids, or Foam Relative to Rig

N

Date:
Time:
Observer:

Observations

Visual Sheen	Yes	No	N/A	Comments
Drilling Fluid				
Drill Cuttings				
TCW Fluid				
Deck Drainage				
Miscellaneous				
Produced Water				
Sanitary Waste				
Domestic Waste				
Floating Solids	Yes	No	N/A	
Sanitary Waste				
Domestic Waste				
Foam	Yes	No	N/A	
Domestic Waste				

N
Direction of Current

Seas:
- Calm
- 0-4 Feet
- 4-8 Feet
- 8-12 Feet
- 12+ Feet

Wind Knots

N
Direction of Wind

Draw Location of Sheen, Solids, or Foam Relative to Rig

N

Date:
Time:
Observer:

Observations

Visual Sheen	Yes	No	N/A	Comments
Drilling Fluid				
Drill Cuttings				
TCW Fluid				
Deck Drainage				
Miscellaneous				
Produced Water				
Sanitary Waste				
Domestic Waste				
Floating Solids	Yes	No	N/A	
Sanitary Waste				
Domestic Waste				
Foam	Yes	No	N/A	
Domestic Waste				

N
Direction of Current

Seas:
- Calm
- 0-4 Feet
- 4-8 Feet
- 8-12 Feet
- 12+ Feet

Wind Knots

N
Direction of Wind

Observer Signature: **Date:**

© Copyright M-I L.L.C., 2004, All Rights Reserved Revision 4 Mar-04

© Copyright M-I L.L.C., 2004, All Rights Reserved.

Local Work Instructions:

Continuous Temperature Monitoring of Non-Contact Cooling Water SHELL LWI-001

Approved By:	Peter Nelson	**Written By:**	Buddy Brooks
Scope:	Shell operations	**Reviewed/Revised By:**	Jeremy Chadwell
Issue Date:	2/11/2013	**Revision/Review Date:**	2/25/2013
Revision level:	Original	**Next Review Date:**	2/26/2015

SCOPE

This document offers work level instructions for the proper completion of continuous temperature monitoring of non-contact cooling water at Alaska SHELL operations.

RESPONSIBILITY

The M-I SWACO Compliance Supervisor is responsible to ensure that this LWI has been provided to each person prior to conducting this task.
Each M-I SWACO Compliance Specialist is responsible for reviewing the below procedure, and referenced documents prior to beginning the work outlined within and for adhering to the below document while performing the task.

1.0 References:

1.0 NPDES Permit

2.0 General Requirements:

2.0 M-I SWACO Compliance trained personnel will oversee all monitoring and documentation.

3.0 Safety Guidelines:

3.0 Standard PPE for the area that the temperature will be taken must be worn. This will include hard hat, FRC coveralls, eye protection, hearing protection and hard toed work boots. Note that other PPE may be required depending on the discharge point location.

4.0 Instructions:

4.0 Temperature sensors installed at each non-contact cooling water discharge point will continuously measure and record the temperature of the effluent fluid. The data will be logged and reviewed daily so the high and low temperatures can be recorded. Temperatures are sampled from each discharge point once per minute; with the value logged as the results are displayed in real time on the computer screen. The Compliance Specialist will be able to monitor each systems cooling water temperatures while in the compliance lab.

4.1 Every 24 hours the temperature readings will be reviewed by the Compliance Specialist and the daily high and low temperatures will be recorded.

4.2 The high and low temperatures for each cooling water discharge will be logged on the NPDES spreadsheet.

5.0 Contingency:

5.0 Process for sampling and recording temperatures in the event of a single sensor failure

5.0.1 Proper PPE for the area that the samples will be collected must be donned prior to entering those areas.

5.0.2 In the event that a single temperature sensor fails, temperatures will be taken manually at the discharge point with a certified traceable thermometer.

5.0.3 Samples will be collected every hour and temperature measured immediately. Values will be logged and the maximum and minimum temps recorded on the NPDES spreadsheet.

5.1 Process for sampling and recording temperatures in the event of multiple censor failures or complete system failure.

5.1.0 In the event of multiple censor failures or a complete system failure, the Compliance Specialist will manually sample temperatures of non-contact cooling waters every six hours.

PAPER COPIES ARE UNCONTROLLED. THIS COPY VALID ONLY AT THE TIME OF PRINTING. THE CONTROLLED VERSION OF THIS DOCUMENT CAN BE FOUND ON THE ALASKA E-COLLABORATION SITE.

5.1.1 Systems which tend to have the greatest variance in temperatures, along with high volume discharges, will be prioritized above other discharge systems.

5.1.2 Samples will be collected and the temperatures immediately measured using a certified traceable thermometer.

5.1.3 Every 24 hours, the Compliance Specialist will record the maximum and minimum temperatures for each non-contact cooling water discharge on the NPDES spreadsheet.

Revision Log

Date:	Document History:	Revised/reviewed by:	Location:
2/22/13	Original Created	Buddy Brooks	Alaska Shell Operations
2/25/13	Approved for distribution	Peter Nelson	Alaska Shell Operations
2/25/13	Reviewed	Jeremy Chadwell	Alaska Shell Operations

PAPER COPIES ARE UNCONTROLLED. THIS COPY VALID ONLY AT THE TIME OF PRINTING. THE CONTROLLED VERSION OF THIS DOCUMENT CAN BE FOUND ON THE ALASKA E-COLLABORATION SITE.

1.0 SCOPE

This protocol describes the procedure for effluent sampling for Biological Testing.

2.0 SUMMARY OF PROCEDURE

Effluent samples for toxicity analysis will be collected by grab samples of the effluent discharges. The effluent samples will be collected from the discharge pipe after the last on board treatment process and before the effluent is discharged into the receiving waters. In addition, each individual outfall will be sampled even if multiple outfalls of the same discharge type are occurring simultaneously. Effluent samples for toxicity analysis will be collected using pre-cleaned LDPE cubitainers and kept on ice in coolers under proper chain-of-custody procedures. All sampling will occur using clean sampling techniques. The holding time for WET samples is established at 36 hours and samples must not exceed a holding time of 72 hours.

All toxicity testing will be conducted at the ENVIRON Port Gamble Environmental Laboratory located in Port Gamble Washington.

3.0 DEFINITIONS

LDPE cubitainers: Soft-sided low density polyethylene (LDPE) container.

Chain-of-Custody (CoC): Chain-of-custody (CoC) procedures include inventorying and documentation during sample collection, shipment, and laboratory processing. A sample is considered to be in an individual's custody if the sample is (1) in the physical possession or view of the responsible party, (2) secured to prevent tampering, or (3) placed in a restricted area by the responsible party.

PROPRIETARY AND CONFIDENTIAL INFORMATION FOR REVIEW PURPOSES ONLY, DO NOT DUPLICATE OR DISTRIBUTE

4.0 EQUIPMENT

- LDPE cubitainers
- Gloves
- Eye protection
- Indelible marker
- CoC Form
- Cooler(s)
- Water quality probe (e.g. Orion Star Model A329 pH/ISE/Conductivity/ DO Meter)
- Thermometer
- Appropriate clothing and safety gear

5.0 PROCEDURE

An adequate volume for each effluent sample will be collected to conduct the rapid screening test and WET testing, if triggered. This includes 2L for the rapid screen test and 45L for three WET chronic assays (collected as one-45L sample or three-15L samples collected every-other-day). Samples will be collected using clean sampling techniques. Samples will be shipped in coolers to ENVIRON Port Gamble Environmental Laboratory. CoC procedures will be followed for each sample.

5.1 Clean Sampling Techniques

All materials used for collection will be approved for use and will either be pre-cleaned materials from a reputable supplier or cleaned on-site following standardized EPA cleaning methodologies. Clean sampling techniques will be used for collection of sample and include:

- Gloved hands to protect person sampling and integrity of sample.
- When cap is removed, place in a location face down that it will not become contaminated.
- Collect sample directly into sample container (if feasible) or use a suitable, clean, transfer vessel to collect and place in sample container. The sample port should not touch the inside or lip of the sample container.
- If the sample port is at a dead end when liquid can collect in the line and remain stagnant, the port will be purged of this stagnant material (and discarded appropriately) prior to collecting a sample that is representative of the waste stream.
- Sample port will be clean and free of corrosion or other foreign debris.
- Sample container will be completely filled. If any air remains, this will be squeezed out prior to sealing with screw cap closure.

PROPRIETARY AND CONFIDENTIAL INFORMATION FOR REVIEW PURPOSES ONLY, DO NOT DUPLICATE OR DISTRIBUTE

- Label sample appropriately. This can be achieved by writing with an indelible marker (i.e. Sharpie™) on the lid or container or a tag tied to the lid may also be used if it is secure.
- Samples must be maintained at 0 - 6 °C and not allowed to freeze.
- Samples will be stored in an igloo™ type cooler with wet or blue ice or stored in a designated cold-room refrigerated unit. Samples will be maintained away from potential contaminants and human food.
- Samples will be shipped inside igloo™ style coolers with sufficient wet and blue ice to maintain temps for up to 48-hour transit. Wet ice will be bagged such that any melt water will not leak out of the cooler.

5.2 Chain-of-Custody

Samples are to be accompanied by a chain-of-custody sheet during transfer. When the possession of samples is transferred (for example, from the site supervisor to a courier) the individual relinquishing the samples signs and records the date and time on the chain-of-custody document. The individual receiving the samples repeats the procedure. This record represents the official documentation for all transference of the sample custody until the samples have arrived at the laboratory. The chain-of-custody procedures include:

- Date and time of completion of sample collection must be documented on the Chain-of-Custody in order to determine sample holding times. Sampler's name must also be recorded on the Chain-of-Custody.
- Headspace in the cubitainers will be minimized by filling them completely, or pushing out the air before closing them.
- Composite samples will be cooled to 4°C as they are collected. Grab samples should be cooled to 4°C before being shipped, if possible. Both types must be shipped/transported on ice or blue ice, even if they are being delivered immediately after collection.
- Those samples being shipped overnight will be accepted if the temperature is between 0 and 6°C. If the sample is greater than 6°C, or if the holding time has been exceeded, the client will be notified. The laboratory may proceed with testing with client approval and the data will be qualified by including a discussion of any protocol deviations the analysis report. If deemed feasible, the client may elect to provide a replacement sample for the out-of-compliance sample and the initial sample rejected for further testing.
- Custody seals on the outside of the cooler are recommended to assess whether the sample may have been tampered with during the shipping process. A custody seal consists of a signed adhesive sticker than is placed across the lid and body of a

PROPRIETARY AND CONFIDENTIAL INFORMATION FOR REVIEW PURPOSES ONLY, DO NOT DUPLICATE OR DISTRIBUTE

cooler during the sealing process and is designed to show evidence of ripping, shredding, or cutting that may occur during unauthorized opening of the cooler.

- A phone call or email to ENVIRON Port Gamble Environmental Laboratory with carrier and tracking information is recommended, especially if the sample is to be received on the weekend. Tracking information may be emailed to the lab director at bhester@environcorp.com. Additional contact information is provided in Table 1.
- Signatory of release/acceptance through transport

Samples must be received in a timely manner that facilitates initiation of the biological tests within 36 hours of samples collection. Project specific guidance for this program allows an extension of this holding time of no greater than 72 hours from the time of collection.

Table 1. ENVIRON Contact List

Brian Hester	360-297-6045	BHester@environcorp.com
Meg Pinza	360-297-6066	MPinza@environcorp.com
Jay Word	360-297-6048	JDWord@environcorp.com

5.3 Sample Receipt

For laboratory test scheduling purposes, at least 5 days' notice is required for the receipt of a sample. Tests are conducted with organisms at a specific age range that are obtained from an organism supplier. If organisms are unavailable, the sampling may be requested to be done at a different time.

Upon receipt, effluent samples are assessed for acceptability. Shipments are initially evaluated for the structural integrity of the shipping container (insulated cooler or box), the appropriateness of the sample container (correct type and volume), the presence of blue or wet ice, and the inclusion of the proper COC documentation. Effluent samples are then logged and water quality parameters are measured. These parameters include dissolved oxygen, temperature, pH, and salinity/conductivity. Additional parameters such as and ammonia and chlorine may be measure if requested or suspected to be a contaminant of concern in the sample.

6.0 SAFETY

The standard safety considerations for sampling - caution deploying and retrieving equipment, utilizing proper clothing and safety gear, and stepping in the bight of lines or cables - apply to the field crew during sampling. The designated safety officer on the vessel or field team shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an accident or emergency. Particular care should be given to fingers and hands when working with any sampling device.

7.0 PERSONNEL

The boat captain and/or field team leader shall be the primary persons responsible for ensuring the safety of personnel and following procedural guidelines. The field crew will be informed of boat rules and shall follow the captain's and field team leader's guidelines.

PROPRIETARY AND CONFIDENTIAL INFORMATION FOR REVIEW PURPOSES ONLY, DO NOT DUPLICATE OR DISTRIBUTE

1.0 SCOPE

To estimate the chronic toxicity of effluents and receiving waters to topsmelt, *Atherinops affinis*, during a seven-day, static-renewal exposure. Procedures are based on **EPA/600/R-95/136** and **WDOE WQ-R-95-80**.

2.0 SUMMARY OF TEST

2.1 Approach

Number of replicates per concentration	5
Volume of test chamber	600 mL (minimum)
Volume of test samples and controls	200 mL (minimum)
Number of test organisms per chamber	5
Test substance renewals	Daily
Type of biological observations	Survival and growth (dry weight and biomass)
Definition of death for this test	Lack of movement after a pulse of water has been applied from a disposable pipette
Times of biological observations	Survival - daily; growth at end of test
Type of physical observations	Bath and chamber temperature and light
Times of physical observations	Bath temperature continuous; chamber temperature and light daily
Types of water quality analyses	DO, temperature, salinity, and pH in one replicate per concentration, daily

2.2 Physical Requirements

DO	≥ 4.0 mg/L
Temperature	20 ± 1ºC
Salinity	5-34 ppt (± 2 ppt of selected test salinity for California); 30 (or 34) ± 2 ppt for Washington
pH	7.8 - 8.2 (dilution water), 6-9 (test sample)
Lighting	16 hours light, 8 hours dark (± 15 min.) at 50-100 foot-candles (550-1050 lux)

2.3 Biological Requirements

Feeding	Test organisms will be fed 40 newly-hatched (less than 24-hour old) *Artemia* nauplii per larva twice a day from day 0 through day 6. Organisms are not fed on day 7.
Life stage	Larvae (9-15 days post-hatch) will be used
Dilution water	Filtered (0.45µm) Hood Canal seawater diluted with reagent grade deionized water to test salinity or reconstituted seawater made with bioassay grade salts (i.e. Crystal Sea Marine Mix or equivalent)

2.4 Interferences

Toxic substances may be introduced by contaminants in dilution water, glassware, sample hardware, and testing equipment.

Improper effluent sampling and handling may adversely affect test results.

Pathogenic and/or predatory organisms in the dilution water and effluent may affect test organism survival and confound test results.

Food added during the test may sequester metals and other toxic substances and confound test results.

3.0 TEST ORGANISM

The test organism will be *Atherinops affinis* (Topsmelt). This organism is to be used in effluent and receiving water testing.

3.1 Test Organism Specifications

Species:	*Atherinops affinis* Topsmelt)
Source:	Aquatic BioSystems, Fort Collins, CO
Age:	Larvae (9 - 15 days post hatch) will be used

3.2 Test Organism Care

Records of the stock shipments will be kept, including the original source, feeding regime, and holding water characteristics.

Stock cultures of *A. affinis* will be fed newly-hatched (< 24 hours old) *Artemia* daily. Food identification, source, preparation, and quality will be tracked.

If the organisms' survival rate in any replicate on any day falls below 50%, the volume of *Artemia* will be reduced by one-half for the remainder of the test.

4.0 TEST SUBSTANCE

The test substance will be labeled, properly stored, and tracked by internal chain-of-custody procedures throughout its tenure at the laboatory. The test substance will not be heated, filtered, distilled, frozen, or otherwise altered without prior written consent by the Client. The test substance is stored at 0 - 6ºC in a secure and distinct storage area. The test substance will be used within 36 hours of collection.

5.0 EQUIPMENT

5.1 Instrumentation

Light meter
DO meter and probe
pH meter and probe
Conductivity meter and probe
Thermistor
Nitex® mesh sieves (0.5 mm)
Drying oven
Desiccator

5.2 Apparatus

5.2.1 Test Area

The test area consists of a water bath, temperature controlled room, or incubator capable of maintaining constant temperature and appropriate illumination. The facility will be well ventilated and free of fumes.

5.2.2 Lighting

Overhead lighting will be at 50-100 foot-candles (550-1050 Lux), with a photoperiod of 16 hours light and 8 hours dark (± 15 min.).

5.2.3 Test Chambers

600-mL glass beakers or equivalent

6.0 PROCEDURE

Nine (9) to 15-day old larvae are exposed in a static-renewal system to different concentrations of effluent or to receiving water for a period of seven days. Test results are

based on the survival and growth (change in dry weight) of the larvae as compared to the control.

6.1 Preparation

6.1.1 Labware Preparation

Labware is described as any plastic or glass material used in the laboratory that will come into contact with any of the test substances or organisms in this evaluation. Labware must be cleaned prior to use. Labware will first be soaked in deionized water then scrubbed with a brush on all surfaces using non-phosphate detergent in deionized water. Alconox® is a widely used established brand of detergent used in laboratory applications. The clean materials will then be rinsed three times with running deionized water. Labware will then be allowed to soak in a 10% hydrochloric acid bath and afterwards rinsed three times with deionized water. Glass labware with also receive a solvent rinse with reagent grade acetone, and finally rinsed three times with deionized water. Some plastic labware is not resistant to solvents and may be damaged by acetone. Plastic labware such as Teflon can receive a solvent rinse, but all other plastics should be investigated prior to solvent rinsing.

6.1.2 Dilution Water Preparation

Dilution water will be made from filtered natural or reconstituted seawater diluted to the appropriate test salinity (5 to 34 ± 2 ppt) with deionized water as needed.

6.1.3 Test Organism Acclimation

During the holding period, the organisms are acclimated to the temperature and salinity at which the test will be conducted, unless already at the correct values. The water quality conditions will be changed no more than 3ºC or 3ppt per 24 hours to minimize stress. During the holding period, just enough newly-hatched *Artemia* nauplii will be fed twice daily so that some food is constantly present.

6.1.4 Test Organism Addition

Nine (9) to 15-day old larvae are active and difficult to capture and are subject to handling mortality; care must be taken when handling. The fish culture is concentrated by transferring animals from the short term culture to a nested sieve (0.5 mm) submerged in dilution water. The fish are concentrated by slightly lifting the nested sieve so that the water volume is reduced but the animals are still within water. Animals are then scooped with a small cup (intermediate holding vessel) and decanted into sets of five animals each. Transferring animals with a wide-bore pipette should be avoided, but may be used to remove unwanted fish. Within a short time from transfer the intermediate holding vessels are immediately checked by a different technician for organism health and the desired number of animals is correct. The larvae are then transfered into test chambers. Test organisms will be transferred to test chambers in a manner to avoid systematic bias

(randomly). Any organisms remaining (stranded) in the intermediate holding vessel after the transfer will be discarded and replaced. Test chambers will be arranged randomly in the water bath.

6.2 Primary Task

6.2.1 Test Dilution Preparation

Test dilutions will be prepared using labware cleaned according to Section 6.1.1 or using pre-cleaned labware of a disposable nature. Dilution water will be the only water used in making up all stock and final dilutions. Each test chamber will be labeled with the test ID number, dilution, and replicate. The position of the test chambers will be randomized. This position will be maintained throughout the test.

6.2.2 Test Measurements

Data will be recorded on data sheets.

Water Quality. All probes will be cleaned thoroughly before initial use. The probes will be rinsed with deionized water between each concentration. Readings will be taken on the "old" test solution as well as the renewal solutions. Data collection will start in the controls and proceed from the lowest test concentration to the highest. If 100% mortality occurs in any test chamber readings will be taken on that day, but no subsequent readings will be taken from that test chamber.

Biological. The number of live and dead larvae in each test chamber is recorded daily, and the dead larvae are discarded. At the end of the test, the numbers of surviving larvae in each test chamber are counted and placed in weigh boats.

Immediately before drying, the larvae are rinsed in deionized water. The rinsed larvae are transferred by forceps to a tared weighing boat and dried at 60ºC for 24 hours or at 100ºC for a minimum of 6 hours. Immediately upon removal from the drying oven, the weighing boats are placed in a desiccator to cool and to prevent the adsorption of moisture from the air until weighed. All weighing boats containing the dried larvae are weighed to 0.01 mg; the tare weight is subtracted; and the measurement is recorded.

6.2.3 Daily Cleaning of Test Chambers

Before the daily renewal of test dilutions, uneaten and dead *Artemia* and other debris are removed from the bottom of the test chambers with a pipette. Remaining dilution water will be decanted or removed using a siphon, leaving approximately 10-15% of total volume. If handling mortality occurs, the number and chamber position of the dead larvae will be recorded.

6.2.4 Test Solution Renewal

The test solutions are renewed daily, immediately after cleaning the test chambers. The water level in each chamber is lowered to a depth of 7-10 mm, leaving 10-15% of the test solution. New test solution is added slowly by refilling each chamber with the appropriate amount of test solution without excessively disturbing the larvae.

6.3 Post-task

6.3.1 Data Analysis

The end points of this chronic toxicity test using *Atherinops* are based on the adverse effects on survival and growth. Calculate the effects on growth using the original number of test organisms, and calculate the mean weights of the controls (used to evaluate if weights met test acceptability criteria) using the surviving number of test organisms.

Results Needed:

- Percent mortality in controls
- Percent mortality in test concentrations
- LC_{50} value and 95% confidence limits
- EC_{50} value and 95% confidence limits (effects on growth)
- Tables showing biological, chemical, and physical data

6.3.2 Method

LC_{50} values and 95% confidence limits will be determined using a computer approach published by Norberg-King (1988) of the U.S. EPA and a commercial statistic software program. The Inhibition Concentration percentage, or ICp, approach to calculating point estimates of toxicity (i.e., LC_{50}) is based upon a monotonic smoothing technique of biological response versus concentration. Bootstrapped estimates of mean response at each concentration allow for distribution-free estimates of standard error and confidence intervals. The result is a non-parametric statistical test that requires no assumptions of normality or homogeneous variance and is robust enough to accommodate a wide variety of biological responses.

6.3.3 Waste Management

Upon completion of analysis, any remaining sample material is stored until the holding time has expired. At that point, samples are either returned to the clients at their request or disposed. Date of disposal is recorded in the sample receipt log. Samples are disposed of by putting them down the drain.

6.3.4 Pollution Prevention

For glassware cleaning, acid baths are used to minimize quantities of acid that reach the drain. Known quantities of reference toxicant (copper sulfate) are collected for hazardous waste disposal.

6.4 Reference Toxicant Test

A positive control test (reference toxicant test) must be tested concurrently with any chronic toxicity effluent test performed with *Atherinops affinis*. This test is used to assess the health of a particular batch of test organisms or organisms from a specific source (i.e. field collected or a specific supplier). Five concentrations (20, 40, 80, 160, 320 ppb) of a reference substance (copper sulfate) may be used in a 7-day exposure to assess the health of the test organisms. (Concentrations may be adjusted in cases of changes in organism sensitivity.) Five replicate test chambers per reference substance concentration will be used. The LC_{50} values will be compared with historical data from definitive bioassays. The results of mortality and growth with the reference substance will be reported and used in combination with control responses to characterize the health of the test organisms.

It should be noted that currently there is currently only a single supplier for topsmelt (Aquatic BioSystems, Fort Collins CO.).

7.0 HEALTH AND SAFETY CONSIDERATIONS

Laboratory personnel will practice good personal sanitation and health practices, consistent with the objectives of this protocol.

Any health-related problem or other condition of laboratory personnel that may be considered to affect the study adversely will be reported to the Client.

Any injury to laboratory personnel obtained during this study, which may be considered related to the test material, will be reported to the Client.

Every reasonable precaution will be taken to minimize exposure of personnel, the laboratory, and the environment to the test substance.

8.0 PERSONNEL

Any laboratory personnel demonstrating competence with this method may perform the procedure.

9.0 QUALITY ASSURANCE REQUIREMENTS (ACCEPTANCE CRITERIA)

This study will be conducted according to the Standard Operating Procedures in effect during the time the study is being performed. In the case where there is a conflict between the other SOPs and this protocol, the protocol will be the definitive procedure.

9.1 Test Acceptability

Test acceptability criteria are:

- 80% or greater survival in controls
- If the test starts with 9-day-old larvae, the mean weight per larva must exceed 0.85 mg in the reference and brine controls; the mean weight of preserved larvae must exceed 0.72 mg.
- The LC_{50} for survival must be within two standard deviations of the control chart mean for the laboratory. The LC_{50} for survival with copper must be <205 µg/L.
- The minimum significant difference (%MSD) of <25% relative to the control for survival for the reference toxicant test. The (%MSD) of <50% relative to the control for growth for the reference toxicant test.

9.2 Corrective Action / Contingencies for Out-of-Control Data

Equipment malfunctions, failure of internal QA/QC checks, failure of follow-up on audit findings, noncompliance with QA requirements, or other problems may result in an out-of-control event and the need for corrective action. Please refer to the QA Manual (Section 13) for criteria used for determination of an out-of-control event, appropriate corrective action, contingencies for handling out-of-control data, and responsible parties.

10.0 REFERENCE DOCUMENTS

Chapman, G.A., D.L. Denton, and J.M. Lazarchak (Eds.). 1995. Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms. U.S. EPA Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, EPA/600/R-95/136.

Norberg-King, T.J. 1988. An interpolation estimate for chronic toxicity: The ICp approach. Technical Report 05-88, National Effluent Toxicity Assessment Center, Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, Minnesota.

Washington State Department of Ecology. 2008 Revision. Laboratory Guidance and Whole Effluent Toxicity Test Review Criteria. Water Quality Program. Publication No. WQ-R-95-80.

1.0 SCOPE

To determine the chronic toxicity to *Menidia beryllina* (inland silverside) when exposed to a test substance for 7 days. Procedures are based on the **Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine Organisms. 3th Ed. (EPA 2002)** (**EPA-821-R-02-014).** The implementation of this method is further defined in the Washington Department of Ecology document **Laboratory Guidance and Whole Effluent Toxicity Test Review Criteria (WQ-R-95-80)** for regulatory use on samples originating in Washington State**.**

2.0 SUMMARY OF TEST

2.1 Approach

Table 1. General Test Conditions for Performing Chronic Toxicity Testing on *M. beryllina*

Test type	Static Renewal
Test duration	7 Days
Test temperature	25±1 ºC
Test Salinity	30± 2 ppt (recommended); Range = 5 – 32 ppt
Lighting	Ambient laboratory, 16 hours light, 8 hours dark (± 15 min.) at 50-100 foot-candles (550-1050 lux)
Test chamber size	600 – 1000 mL (recommended)
Test solution volume	500 – 750 mL (recommended)
Renewal of test solution	Daily
No. of organisms per chamber	10
No. of replicates per treatment	4
Feeding	1000 *Artemia* nauplii Days 0 -2 1500 *Artemia* nauplii Days 3 – 6 None on Day 7
Test solution aeration	None unless DO levels fall below 4.0 mg/L
Type of biological observations	Death, growth (dry weight)
Definition of death for this test	Lack of movement after a pulse of water has been applied from a disposable pipette
Times of biological observations	Daily

2.2 Physical Requirements

The following are required for the control sample.

DO	Not less than 4.0 mg/L or 60% saturation
Temperature	25 ± 1ºC
pH	7.8 – 8.2
Salinity	30 ± 2 ppt
Lighting	16 hours light, 8 hours dark (± 15 min.) at 50-100 foot-candles (550-1050 lux)

Table 2. Test Condition Summaries

Species	*Menidia beryllina* (inland silverside)
Life Stage Tested	7-11 days old (24 hour age range)
Feeding	Daily
Temperature (°C)	25±1 ºC
pH	6-9
DO	>4.0 mg/L
Type of physical observations	Temperature and light daily
Types of water quality analyses, and the test concentrations measured	DO, pH, conductivity, and temperature, measured on stock solutions of all concentrations on Day 0 (before distribution to test chambers and introduction of test organisms), and daily thereafter until termination in a surrogate chamber per concentration. Total residual chlorine on control and highest concentration at beginning and end of test (final measurement is not necessary if chlorine undetected in initial).

2.3 Biological Requirements

Feeding	Test organisms will be fed *ad libitum* during the holding period. Feeding rate is 0.10mL of *Artemia* nauplii per chamber (or ~1000 *Artemia* per chamber) on Days 0 – 2, and 0.15mL of *Artemia* nauplii per chamber (or ~1500 *Artemia* per chamber) on Days 3 - 6. Larvae are not fed on Day 7.
Life stage	Juveniles (7 to 11 days post-hatch; 24 hours range in age) will be used
Dilution water	Filtered natural seawater or artificial seawater (Crystal Sea MarineMix™)

2.4 pH Drift

pH drift during the test may contribute to artifactual toxicity when ammonia or other pH-dependent toxicants are present.

As pH increases, the toxicity of ammonia also increases, so upward pH drift may increase sample toxicity. Artifactual toxicity due to pH drift is not likely to occur unless pH is large (more than 1 pH unit) or if concentration of some pH-dependent toxicant in the sample is near the threshold for toxicity. To confirm that toxicity is artifactual and due to pH drift, parallel tests should be conducted, one with controlled pH and one with uncontrolled pH. Total ammonia should also be measured in each treatment at the beginning of parallel testing. During parallel testing, the pH should be measured in each treatment at the beginning and end of each 24 hour exposure period. For each treatment, the mean initial pH and mean final pH should be reported. pH measurements taken during the test should confirm that pH was effectively maintained at the target pH in the controlled pH treatment. For each treatment, the mean initial pH and the mean final pH should be within +/- 0.2 pH units of the target pH.

Results of the parallel tests are compared to demonstrate the presence or absence of artifactual toxicity.

3.0 TEST ORGANISM

The test organism will be *Menidia beryllina*. This organism is used extensively in effluent and product testing.

3.1 Test Organism Specifications

Species:	*Menidia beryllina*
Source:	Aquatic BioSystems, Aquatic Research Organisms, Aquatic Indicators.
Age:	7 to 11-day-old larvae
Identification:	Before exposure to test substances, individuals will be positively identified as *Menidia beryllina*

3.2 Test Organism Care

Records of the stock shipments will be kept, including the original source, feeding regime, and holding water characteristics.

During the test, the organisms in each test chamber will be fed *Artemia nauplii* (less than 24-hour old). Organisms will be fed 0.1 g wet weight (~1000) per replicate on Days 0 to 2; 0.15 g wet weight (~1500) per replicate on Days 3 to 6. For feeding density estimation, two-10uL subsamples of concentrated *Artemia* are pipeted onto a piece of filter paper and counted utilizing a dissecting microscope. When pipeting *Artemia*, the pipet tips need to be trimmed with a blade to enlarge the opening and prevent clogging and damage to the animals. The subsample counts will then be averaged to estimate the number of *Artemia* per 10µL. The following formula will be used to determine the amount of concentrated *Artemia* to deliver the appropriate amount per replicate. This process will be repeated for each batch of *Artemia* collected. Larvae will not be fed on Day 7.

1. Corrected mean count of *Artemia* per µL
   # Mean Count ÷ 10 = corrected mean count
2. Desired Amount (1000 or 1500 *Artemia*) ÷ # corrected mean count

Example
Subsample counts: 38 and 32 = mean count of 35
Corrected mean count: 35 ÷ 10 = 3.5
Desired amount: 1000 ÷ 3.5 = 295.7 µL (amount to deliver per replicate)

4.0 TEST SUBSTANCE

The test substance will be labeled, properly stored, and tracked by internal chain-of-custody procedures throughout its tenure at the laboratory. The test substance will not be heated, filtered, distilled, frozen, or otherwise altered without prior written consent by the Client. The test substance is stored at 0 - 6ºC in a secure and distinct storage area. The test substance will be used within 36 hours of collection. Samples utilized for test solutions renewals shall not exceed 72 hours of sample collection.

5.0 EQUIPMENT

5.1 Instrumentation

Thermometer
Light meter
Electronic meters and probes (DO, Temp, Cond/Sal, pH, Ammonia)
Colorimetric titration for water hardness and alkalinity

Dissecting microscope with substage lighting
Analytical balance
Sedgwick-Rafter counting cell (or equivalent)
30-mL plastic cups
600 - 1000mL beakers
Graduated cylinders

5.2 Apparatus

5.2.1 Test Area

The test area consists of a room with constant temperature of 25 ± 1°C and appropriate illumination of 16-hour/8-hour day/night cycle. The facility will be well ventilated and free of fumes.

5.2.2 Lighting

Overhead lighting will be at 50-100 foot-candles (550-1050 Lux), with a photoperiod of 16 hours light and 8 hours dark (± 15 min.).

5.2.3 Test Chambers

500, 600, or 1000mL chambers

6.0 PROCEDURE

Larvae are exposed in a static-renewal system for seven days to different concentrations of effluent or to receiving water. Test results are based on the survival and growth (increase in weight) of the larvae as compared to the control.

6.1 Preparation

6.1.1 Labware Preparation

Labware is described as any plastic or glass material used in the laboratory that will come into contact with any of the test substances or organisms in this evaluation. Labware must be cleaned prior to use. Labware will first be soaked in deionized water then scrubbed with a brush on all surfaces using non-phosphate detergent in deionized water. Alconox® is a widely used established brand of detergent used in laboratory applications. The clean materials will then be rinsed three times with running deionized water. Labware will then be allowed to soak in a 10% hydrochloric acid bath and afterwards rinsed three times with deionized water. Glass labware with also receive a solvent rinse with reagent grade acetone, and finally rinsed three times with deionized water. Some plastic labware is not

resistant to solvents and may be damaged by acetone. Plastic labware such as Teflon can receive a solvent rinse, but all other plastics should be investigated prior to solvent rinsing.

6.1.2 Dilution Water Preparation

The dilution water will be a saltwater source deemed appropriate by the laboratory and may include: natural seawater (Northern Hood Canal, WA; sand filtered and salinity adjusted as needed) or artificial seawater (prepared from deionized water and Crystal Sea Marinemix™).

6.1.3 Test Organism Acclimation

During the holding period, the organisms are acclimated to the temperature and salinity at which the test will be conducted, unless already at the correct values. The water quality conditions will be changed no more than 3ºC or 3ppt per 24 hours to minimize stress. During the holding period, just enough newly-hatched *Artemia* nauplii will be fed twice daily so that some food is constantly present.

6.2 Primary Task

6.2.1 Test Dilution Preparation

Test substance dilutions will be prepared using labware cleaned according to Section 6.1.1 or using pre-cleaned labware of a disposable nature. Dilutions are initially prepared in vessels large enough to contain sufficient volume for all test replicates. These “stock” containers may be used for preparing the test solutions prior to test initiation and for the test solution renewal (if required).

The testing may be either a “screening test” which includes a laboratory control (dilution water) and the undiluted test substance or a “definitive test” which includes a minimum of five test substance concentrations. The definitive test (also referred to as a “dilution test” or “LC_{50} test”) is conducted when a dose response (i.e. LC_{50}) is desired.

The final test substance dilutions for the definitive test will be expressed as percent and typically run in a geometric series with a 0.5x dilution. Other ratios may be selected depending upon the project requirements. When specified by the regulatory permit, specific test substance concentrations targeting the Acute and Chronic Critical Effluent Concentrations (ACEC/CCEC) should be included in the concentration series.

Dilution water will be the only water used in making up all stock and final dilutions (unless receiving water is specified).

After preparation, the “Stock” test dilutions are allowed to equilibrate to the test temperature. Water quality is measured and recorded in the stock dilutions, and once the

conditions are confirmed to be within the test parameters, the solutions will be distributed to the replicate test chambers. Each test chamber will be labeled with a coded test chamber number, representing the specific test, the concentration, and the replicate number.

6.2.2 Reference Toxicant Test

A reference toxicant test will be conducted on each batch of test organisms either concurrently with project samples or monthly, depending upon QA requirements. The reference toxicant test will consist of a 7-day exposure to at least five concentrations of a reference substance (known toxicant) used to assess the health and sensitivity of the test organisms. Dilutions will be selected to bracket laboratory historical 7-dayLC_{50}. The LC_{50} results will be compared with historical data from definitive bioassays with the reference substance. The results of the 7-day survival and growth test, determined during this study, will be reported and used in combination with control mortality to characterize the health of the test organisms.

6.2.3 Test Organism Addition

Fish larvae will be captured using a large bore, pipette equipped with a suction bulb. The volume in the holding chamber will be reduced and the larval fish will be captured, one at a time, and placed into intermediary holding vessels (1oz plastic food cups). The tip of the pipette will be placed below the surface of the intermediary holding vessel during the transfer. Since the larvae are slow moving and small, ten larvae can be easily counted into each cup; however, if the technician feels his or her accuracy is improved by counting fewer fish, only five larvae should be placed in each cup. After the organisms are dispensed, a light table is used to verify the number and health of organisms in each cup. Larvae will be transferred to the test dilutions from the intermediary holding vessels within 90 minutes of the test dilution makeup. The amount of water added to the chambers when transferring the larvae to the compartments will be kept to a minimum to avoid unnecessary dilution of the test concentrations. Test organisms will be transferred to test chambers in a manner to avoid systematic bias. Any organisms remaining after the transfers will be discarded. Test chambers will be arranged randomly in the test area.

6.2.3 Daily Cleaning of Test Chambers

At the time of daily renewal of test solutions, uneaten and dead *Artemia* and other debris are removed from the bottom of the test chambers with a siphon hose. Siphoned water is collected in a white plastic tray so any larvae caught up in the siphon can be carefully retrieved and gently returned by pipette to the appropriate test chamber. If handling mortality occurs, the number and chamber position of the dead larvae will be recorded.

6.2.4 Test Solution Renewal

The test solutions are renewed daily, immediately after cleaning the test chambers. The water level in each chamber is lowered to a depth of 7-10 mm, leaving 15-20% of the test solution. New test solution is added slowly by refilling each chamber with the appropriate amount of test solution without excessively disturbing the larvae.

6.2.5 Test Measurements

Data are recorded on data sheets.

Water Quality. All probes will be cleaned thoroughly before initial use. The probes will be rinsed with deionized water between each measurement. DO, temperature, salinity, and pH will be measured at the beginning and end of each 24-hour period in one test chamber per concentration and in the control.

Biological. The number of live and dead larvae in each test chamber are recorded daily, and the dead larvae are discarded. At the end of the test, the number of surviving larvae in each test chamber are counted as a group for drying and weighing.

Growth and Biomass. Immediately before drying, the preserved larvae are rinsed in distilled water. The rinsed larvae are transferred by forceps to a tared weighing boat and dried at 60°C for 24 hours or at 100°C for a minimum of 6 hours. Immediately upon removal from the drying oven, the weighing boats are placed in a desiccator to cool and to prevent the adsorption of moisture from the air until weighed. All weighing boats containing the dried larvae are weighed to 0.01 mg; the tare weight is subtracted; and the weight is recorded. The dry weight is divided by the number of original larvae per replicate (Biomass) to determine the average individual dry weight. This value is recorded on the data sheets. The mean weight per surviving fish is also calculated and recorded (Growth). For controls, this value is compared to test acceptability criteria.

6.3 Post-task

6.3.2 Data Analysis

The average reproduction is calculated using the original number of test organisms.

Results Needed:

- Survival and growth in controls
- Survival and growth in test concentrations
- LC_{50} value and 95% confidence limits
- IC_{50} value and 95% confidence limits (effects on reproduction)
- Tables showing biological, chemical, and physical data

Concentration-Response Relationship: The concentration-response relationship must be reviewed to ensure that the calculated test results are interpreted appropriately. See Laboratory Protocol LAB061 for guidance in evaluating the WET test variability and concentration response relationship.

Evaluation of Chronic Test PMSDs: The PMSD limits for both the compliance test and the reference toxicant test must be evaluated to determine whether they fall within the upper and lower bound limits specified in EPA/821/B-00/004. These limits are included in Laboratory Protocol LAB061 which also contains guidelines for determining the proper course of action in the event the PMSD exceeds the upper bounds of the specified limits.

6.3.3 Method

The endpoints of toxicity tests using *Menidia beryllina* (inland silverside) are based on the adverse effects on survival and growth. The LC_{50}, the IC_{25}, and the IC_{50} are calculated using point estimation techniques, LOEC and NOEC values, for survival and growth, are obtained using a hypothesis testing approach such as Dunnett's Procedure or Steel's Many-one Rank Test. Separate analyses are performed for the estimation of the LOEC and NOEC endpoints and for the estimation of the LC_{50}, IC_{25}, and IC_{50}. Concentrations at which there is no survival in any of the test chambers are excluded from the statistical analysis of the NOEC and LOEC for survival and growth but included in the estimation of the LC_{50}, IC_{25}, and IC_{50}.

LC_{50} values and 95% confidence limits will be determined using a computer approach published by Norberg-King (1988) of the U.S. EPA and a commercial statistic software program. The Inhibition Concentration percentage, or ICp, approach to calculating point estimates of toxicity (i.e., LC_{50}) is based upon a monotonic smoothing technique of biological response versus concentration. Bootstrapped estimates of mean response at each concentration allow for distribution-free estimates of standard error and confidence intervals. The result is a non-parametric statistical test that requires no assumptions of normality or homogeneous variance and is robust enough to accommodate a wide variety of biological responses.

6.3.4 Waste Management

Upon completion of analysis, any remaining sample material is stored until the holding time has expired. At that point, samples are either returned to the clients at their request or disposed. Date of disposal is recorded in the sample receipt log. Samples are disposed of by putting them down the drain.

PROPRIETARY INFORMATION FOR REVIEW PURPOSES ONLY, DO NOT DUPLICATE OR DISTRIBUTE

6.3.5 Pollution Prevention

For labware cleaning, acid baths are used to minimize quantities of acid that reach the drain. Known quantities of reference toxicant (aqueous metals) are collected for hazardous waste disposal.

7.0 HEALTH AND SAFETY CONSIDERATIONS

Laboratory personnel will practice good personal sanitation and health practices, consistent with the objectives of this protocol.

Any health-related problem or other condition of laboratory personnel that may be considered to affect the study adversely will be reported to the Client.

Any injury to laboratory personnel obtained during this study, which may be considered related to the test material, will be reported to the Client.

Every reasonable precaution will be taken to minimize exposure of personnel, the laboratory, and the environment to the test substance.

8.0 PERSONNEL

Any technician trained in these procedures may perform them.

9.0 QUALITY ASSURANCE REQUIREMENTS (ACCEPTANCE CRITERIA)

This study will be conducted according to the Standard Operating Procedures in effect during the time the study is being performed. In the case where there is a conflict between the other SOPs and this protocol, the protocol will be the definitive procedure.

9.1 Test Acceptability

Test acceptability criterions are as follows:

- ≥ 80% average survival of control larvae
- Average dry weight is 0.50 mg or greater per surviving control larva (when test starts with 7-day-old larvae)

9.2 Corrective Action / Contingencies for Out-of-Control Data

Equipment malfunctions, failure of internal QA/QC checks, failure of follow-up on audit findings, noncompliance with QA requirements, or other problems may result in an out-of-control event and the need for corrective action. Please refer to the QA Manual (Section 13) for criteria used for determination of an out-of-control event, appropriate corrective action, contingencies for handling out-of-control data, and responsible parties.

10.0 REFERENCE DOCUMENTS

Lewis, P.A., D.J. Klemm, J.M. Lazorchak, T.J. Norberg-King, W.H. Peltier, and M.A. Heber (eds). 1994. Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms. U.S. EPA Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, EPA/600/4-91/002.

Norberg-King, T.J. 1988. An interpolation estimate for chronic toxicity: The ICp approach. Technical Report 05-88, National Effluent Toxicity Assessment Center, Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, Minnesota.

U.S. EPA. 2002. Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine Organisms. Forth Edition. Office of Water, U.S. Environmental Protection Agency, Washington, D.C. 20460. EPA-821-R-02-014.

Washington State Department of Ecology. 2008 Revision. Laboratory Guidance and Whole Effluent Toxicity Test Review Criteria. Water Quality Program. Publication No. WQ-R-95-80.

Weber, C.I., editor. 1993. Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, Fourth Edition. U.S. EPA Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, EPA/600-4-90/027F.

PROPRIETARY INFORMATION FOR REVIEW PURPOSES ONLY, DO NOT DUPLICATE OR DISTRIBUTE

1.0 SCOPE

To determine the chronic toxicity to *Americamysis bahia* (opossum shrimp) when exposed to a test substance for 7 days. Procedures are based on the **Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine Organisms. 3th Ed. (EPA 2002)** (**EPA-821-R-02-014).** The implementation of this method is further defined in the Washington Department of Ecology document **Laboratory Guidance and Whole Effluent Toxicity Test Review Criteria (WQ-R-95-80)** for regulatory use on samples originating in Washington State**.**

2.0 SUMMARY OF TEST

2.1 Approach

Table 1. General Test Conditions for Performing Chronic Toxicity Testing on *A. bahia*

Test type	Static Renewal
Test duration	7 Days
Test temperature	26±1 ºC
Test Salinity	30± 2 ppt (recommended); Range = 20 – 30 ppt
Lighting	Ambient laboratory, 16 hours light, 8 hours dark (± 15 min.) at 50-100 foot-candles (550-1050 lux)
Test chamber size	400 mL (recommended)
Test solution volume	150 mL (recommended)
Renewal of test solution	Daily
No. of organisms per chamber	5
No. of replicates per treatment	8
Feeding	375 *Artemia* nauplii twice daily. Once before and once after renewal. Approx. 8 hours apart
Test solution aeration	None unless DO levels fall below 4.0 mg/L
Type of biological observations	Death, growth (dry weight), fecundity
Definition of death for this test	Lack of movement after a pulse of water has been applied from a disposable pipette
Times of biological observations	Daily

2.2 Physical Requirements

The following are required for the control sample.

DO	Not less than 4.0 mg/L or 60% saturation
Temperature	26 ± 1ºC
pH	7.8 – 8.2
Salinity	30 ± 2 ppt
Lighting	16 hours light, 8 hours dark (± 15 min.) at 50-100 foot-candles (550-1050 lux)

Table 2. Test Condition Summaries

Species	*Americamysis bahia* (opossum shrimp)
Life Stage Tested	7 days old
Feeding	Twice Daily
Temperature (°C)	26±1 ºC
pH	6-9
DO	>4.0 mg/L
Type of physical observations	Temperature and light daily
Types of water quality analyses, and the test concentrations measured	DO, pH, conductivity, and temperature, measured on stock solutions of all concentrations on Day 0 (before distribution to test chambers and introduction of test organisms), and daily thereafter until termination in a surrogate chamber per concentration. Total residual chlorine on control and highest concentration at beginning and end of test (final measurement is not necessary if chlorine undetected in initial).

2.3 Biological Requirements

Feeding	Test organisms will be fed *ad libitum* during the holding period. Feeding rate is 375 *Artemia* nauplii per chamber twice daily.
Life stage	Juveniles (7 days old) will be used
Dilution water	Filtered natural seawater or artificial seawater (Crystal Sea MarineMix™)

2.4 pH Drift

pH drift during the test may contribute to artifactual toxicity when ammonia or other pH-dependent toxicants are present.

As pH increases, the toxicity of ammonia also increases, so upward pH drift may increase sample toxicity. Artifactual toxicity due to pH drift is not likely to occur unless pH is large (more than 1 pH unit) or if concentration of some pH-dependent toxicant in the sample is near the threshold for toxicity. To confirm that toxicity is artifactual and due to pH drift, parallel tests should be conducted, one with controlled pH and one with uncontrolled pH. Total ammonia should also be measured in each treatment at the beginning of parallel testing. During parallel testing, the pH should be measured in each treatment at the beginning and end of each 24 hour exposure period. For each treatment, the mean initial pH and mean final pH should be reported. pH measurements taken during the test should confirm that pH was effectively maintained at the target pH in the controlled pH treatment. For each treatment, the mean initial pH and the mean final pH should be within +/- 0.2 pH units of the target pH.

Results of the parallel tests are compared to demonstrate the presence or absence of artifactual toxicity.

3.0 TEST ORGANISM

The test organism will be *Americamysis bahia*. This organism is used extensively in effluent and product testing.

3.1 Test Organism Specifications

Species:	*Americamysis bahia*
Source:	Aquatic BioSystems, Aquatic Research Organisms, Aquatic Indicators.
Age:	7 day-old mysids
Identification:	Before exposure to test substances, individuals will be positively identified as *Americamysis bahia*

3.2 Test Organism Care

Records of the stock shipments will be kept, including the original source, feeding regime, and holding water characteristics.

During the test, the organisms in each test chamber will be fed *Artemia nauplii* (less than 24-hour old). Organisms will be 375 nauplii per replicate, twice daily. For feeding density estimation, two-10uL subsamples of concentrated *Artemia* are pipeted onto a piece of filter paper and counted utilizing a dissecting microscope. When pipeting *Artemia*, the pipet tips need to be trimmed with a blade to enlarge the opening and prevent clogging and damage to the animals. The subsample counts will then be averaged to estimate the number of *Artemia* per 10µL. The following formula will be used to determine the amount of concentrated *Artemia* to deliver the appropriate amount per replicate. This process will be repeated for each batch of *Artemia* collected.

1. Corrected mean count of *Artemia* per µL
   # Mean Count ÷ 10 = corrected mean count
2. Desired Amount (1000 or 1500 *Artemia*) ÷ # corrected mean count

Example
Subsample counts: 38 and 32 = mean count of 35
Corrected mean count: 35 ÷ 10 = 3.5
Desired amount: 375 ÷ 3.5 = 107.1 µL (amount to deliver per replicate)

4.0 TEST SUBSTANCE

The test substance will be labeled, properly stored, and tracked by internal chain-of-custody procedures throughout its tenure at the laboratory. The test substance will not be heated, filtered, distilled, frozen, or otherwise altered without prior written consent by the Client. The test substance is stored at 0 - 6ºC in a secure and distinct storage area. The test substance will be used within 36 hours of collection. Samples utilized for test solutions renewals shall not exceed 72 hours of sample collection.

PROPRIETARY INFORMATION FOR REVIEW PURPOSES ONLY, DO NOT DUPLICATE OR DISTRIBUTE

5.0 EQUIPMENT

5.1 Instrumentation

Thermometer
Light meter
Electronic meters and probes (DO, Temp, Cond/Sal, pH, Ammonia)
Colorimetric titration for water hardness and alkalinity
Dissecting microscope with substage lighting
Analytical balance
Sedgwick-Rafter counting cell (or equivalent)
30-mL plastic cups
beakers
Graduated cylinders

5.2 Apparatus

5.2.1 Test Area

The test area consists of a room with constant temperature of 26 ± 1°C and appropriate illumination of 16-hour/8-hour day/night cycle. The facility will be well ventilated and free of fumes.

5.2.2 Lighting

Overhead lighting will be at 50-100 foot-candles (550-1050 Lux), with a photoperiod of 16 hours light and 8 hours dark (± 15 min.).

5.2.3 Test Chambers

250, 400, or 600mL chambers

6.0 PROCEDURE

Mysids are exposed in a static-renewal system for seven days to different concentrations of effluent or to receiving water. Test results are based on the survival and growth (increase in weight) of the mysids as compared to the control.

6.1 Preparation

6.1.1 Labware Preparation

Labware is described as any plastic or glass material used in the laboratory that will come into contact with any of the test substances or organisms in this evaluation. Labware must be cleaned prior to use. Labware will first be soaked in deionized water then scrubbed with a brush on all surfaces using non-phosphate detergent in deionized water. Alconox® is a widely used established brand of detergent used in laboratory applications. The clean materials will then be rinsed three times with running deionized water. Labware will then be allowed to soak in a 10% hydrochloric acid bath and afterwards rinsed three times with deionized water. Glass labware with also receive a solvent rinse with reagent grade acetone, and finally rinsed three times with deionized water. Some plastic labware is not resistant to solvents and may be damaged by acetone. Plastic labware such as Teflon can receive a solvent rinse, but all other plastics should be investigated prior to solvent rinsing.

6.1.2 Dilution Water Preparation

The dilution water will be a saltwater source deemed appropriate by the laboratory and may include: natural seawater (Northern Hood Canal, WA; sand filtered and salinity adjusted as needed) or artificial seawater (prepared from deionized water and Crystal Sea Marinemix™).

6.1.3 Test Organism Acclimation

During the holding period, the organisms are acclimated to the temperature and salinity at which the test will be conducted, unless already at the correct values. The water quality conditions will be changed no more than 3ºC or 3ppt per 24 hours to minimize stress. During the holding period, just enough newly-hatched *Artemia* nauplii will be fed twice daily so that some food is constantly present.

6.2 Primary Task

6.2.1 Test Dilution Preparation

Test substance dilutions will be prepared using labware cleaned according to Section 6.1.1 or using pre-cleaned labware of a disposable nature. Dilutions are initially prepared in vessels large enough to contain sufficient volume for all test replicates. These “stock” containers may be used for preparing the test solutions prior to test initiation and for the test solution renewal (if required).

The testing may be either a "screening test" which includes a laboratory control (dilution water) and the undiluted test substance or a "definitive test" which includes a minimum of five test substance concentrations. The definitive test (also referred to as a "dilution test" or "LC_{50} test") is conducted when a dose response (i.e. LC_{50}) is desired.

The final test substance dilutions for the definitive test will be expressed as percent and typically run in a geometric series with a 0.5x dilution. Other ratios may be selected depending upon the project requirements. When specified by the regulatory permit, specific test substance concentrations targeting the Acute and Chronic Critical Effluent Concentrations (ACEC/CCEC) should be included in the concentration series.

Dilution water will be the only water used in making up all stock and final dilutions (unless receiving water is specified).

After preparation, the "Stock" test dilutions are allowed to equilibrate to the test temperature. Water quality is measured and recorded in the stock dilutions, and once the conditions are confirmed to be within the test parameters, the solutions will be distributed to the replicate test chambers. Each test chamber will be labeled with a coded test chamber number, representing the specific test, the concentration, and the replicate number.

6.2.2 Reference Toxicant Test

A reference toxicant test will be conducted on each batch of test organisms either concurrently with project samples or monthly, depending upon QA requirements. The reference toxicant test will consist of a 7-day exposure to at least five concentrations of a reference substance (known toxicant) used to assess the health and sensitivity of the test organisms. Dilutions will be selected to bracket laboratory historical 7-dayLC_{50}. The LC_{50} results will be compared with historical data from definitive bioassays with the reference substance. The results of the 7-day survival and growth test, determined during this study, will be reported and used in combination with control mortality to characterize the health of the test organisms.

6.2.3 Test Organism Addition

Mysids will be captured using a large bore, pipette equipped with a suction bulb. The volume in the holding chamber will be reduced and the mysids will be captured, one at a time, and placed into intermediary holding vessels (1oz plastic food cups). The tip of the pipette will be placed below the surface of the intermediary holding vessel during the transfer. Five mysids should be placed in each cup. After the organisms are dispensed, a light table is used to verify the number and health of organisms in each cup. Mysids will be transferred to the test dilutions from the intermediary holding vessels within 90 minutes of the test dilution makeup. The amount of water added to the chambers when transferring the animals to the compartments will be kept to a minimum to avoid unnecessary dilution of the test concentrations. Test organisms will be transferred to test chambers in a manner to

avoid systematic bias. Any organisms remaining after the transfers will be discarded. Test chambers will be arranged randomly in the test area.

6.2.3 Daily Cleaning of Test Chambers

At the time of daily renewal of test solutions, uneaten and dead *Artemia* and other debris are removed from the bottom of the test chambers with a siphon hose. Siphoned water is collected in a white plastic tray so any animals caught up in the siphon can be carefully retrieved and gently returned by pipette to the appropriate test chamber. If handling mortality occurs, the number and chamber position of the dead mysids will be recorded.

6.2.4 Test Solution Renewal

The test solutions are renewed daily, immediately after cleaning the test chambers. The water level in each chamber is lowered to a depth of 7-10 mm, leaving 15-20% of the test solution. New test solution is added slowly by refilling each chamber with the appropriate amount of test solution without excessively disturbing the mysids.

6.2.5 Test Measurements

Data are recorded on data sheets.

Water Quality. All probes will be cleaned thoroughly before initial use. The probes will be rinsed with deionized water between each measurement. DO, temperature, salinity, and pH will be measured at the beginning and end of each 24-hour period in one test chamber per concentration and in the control.

Biological. The number of live and dead mysids in each test chamber are recorded daily, and the dead mysids are discarded. At the end of the test, the number of surviving mysids in each test chamber are counted as a group for drying and weighing.

Fecundity / Egg Development. Live organisms are examined for eggs, and the sexes are determined within 12 hours of the termination of the test. Each replicate is examined under 240X magnification to determine the number of immature animals, the sex of the mature animals, and the presence or absence of eggs in the oviducts or brood sacs of the females. This is done while organisms are alive because they turn opaque upon dying.

The numbers of immature, males, females with eggs, and females without eggs are recorded on data sheets.

Growth and Biomass. Immediately before drying, the preserved mysids are rinsed in distilled water. The rinsed mysids are transferred by forceps to a tared weighing boat and dried at 60°C for 24 hours or at 100°C for a minimum of 6 hours. Immediately upon removal from the drying oven, the weighing boats are placed in a desiccator to cool and to

prevent the adsorption of moisture from the air until weighed. All weighing boats containing the dried mysids are weighed to 0.01 mg; the tare weight is subtracted; and the weight is recorded. The dry weight is divided by the number of original mysids per replicate (Biomass) to determine the average individual dry weight. This value is recorded on the data sheets. The mean weight per surviving fish is also calculated and recorded (Growth). For controls, this value is compared to test acceptability criteria.

6.3 Post-task

6.3.2 Data Analysis

The average reproduction is calculated using the original number of test organisms.

Results Needed:

- Survival and growth in controls
- Survival and growth in test concentrations
- LC_{50} value and 95% confidence limits
- IC_{50} value and 95% confidence limits (effects on biomass and fecundity)
- Tables showing biological, chemical, and physical data

Concentration-Response Relationship: The concentration-response relationship must be reviewed to ensure that the calculated test results are interpreted appropriately. See Laboratory Protocol LAB061 for guidance in evaluating the WET test variability and concentration response relationship.

Evaluation of Chronic Test PMSDs: The PMSD limits for both the compliance test and the reference toxicant test must be evaluated to determine whether they fall within the upper and lower bound limits specified in EPA/821/B-00/004. These limits are included in Laboratory Protocol LAB061 which also contains guidelines for determining the proper course of action in the event the PMSD exceeds the upper bounds of the specified limits.

6.3.3 Method

The endpoints of toxicity tests using *Americamysis bahia* (opossum shrimp) are based on the adverse effects on survival, growth, and fecundity. The LC_{50}, the IC_{25}, and the IC_{50} are calculated using point estimation techniques, LOEC and NOEC values, for survival and growth, are obtained using a hypothesis testing approach such as Dunnett's Procedure or Steel's Many-one Rank Test. Separate analyses are performed for the estimation of the LOEC and NOEC endpoints and for the estimation of the LC_{50}, IC_{25}, and IC_{50}. Concentrations at which there is no survival in any of the test chambers are excluded from the statistical analysis of the NOEC and LOEC for survival and growth but included in the estimation of the LC_{50}, IC_{25}, and IC_{50}.

LC_{50} values and 95% confidence limits will be determined using a computer approach published by Norberg-King (1988) of the U.S. EPA and a commercial statistic software program. The Inhibition Concentration percentage, or ICp, approach to calculating point

estimates of toxicity (i.e., LC_{50}) is based upon a monotonic smoothing technique of biological response versus concentration. Bootstrapped estimates of mean response at each concentration allow for distribution-free estimates of standard error and confidence intervals. The result is a non-parametric statistical test that requires no assumptions of normality or homogeneous variance and is robust enough to accommodate a wide variety of biological responses.

6.3.4 Waste Management

Upon completion of analysis, any remaining sample material is stored until the holding time has expired. At that point, samples are either returned to the clients at their request or disposed. Date of disposal is recorded in the sample receipt log. Samples are disposed of by putting them down the drain.

6.3.5 Pollution Prevention

For labware cleaning, acid baths are used to minimize quantities of acid that reach the drain. Known quantities of reference toxicant (aqueous metals) are collected for hazardous waste disposal.

7.0 HEALTH AND SAFETY CONSIDERATIONS

Laboratory personnel will practice good personal sanitation and health practices, consistent with the objectives of this protocol.

Any health-related problem or other condition of laboratory personnel that may be considered to affect the study adversely will be reported to the Client.

Any injury to laboratory personnel obtained during this study, which may be considered related to the test material, will be reported to the Client.

Every reasonable precaution will be taken to minimize exposure of personnel, the laboratory, and the environment to the test substance.

8.0 PERSONNEL

Any technician trained in these procedures may perform them.

9.0 QUALITY ASSURANCE REQUIREMENTS (ACCEPTANCE CRITERIA)

This study will be conducted according to the Standard Operating Procedures in effect during the time the study is being performed. In the case where there is a conflict between the other SOPs and this protocol, the protocol will be the definitive procedure.

9.1 Test Acceptability

Test acceptability criterions are as follows:

- ≥ 80% average survival of control mysids
- Average dry weight is 0.20 mg or greater per surviving control mysids
- PMSD for growth ≤ 37%

9.2 Corrective Action / Contingencies for Out-of-Control Data

Equipment malfunctions, failure of internal QA/QC checks, failure of follow-up on audit findings, noncompliance with QA requirements, or other problems may result in an out-of-control event and the need for corrective action. Please refer to the QA Manual (Section 13) for criteria used for determination of an out-of-control event, appropriate corrective action, contingencies for handling out-of-control data, and responsible parties.

10.0 REFERENCE DOCUMENTS

Lewis, P.A., D.J. Klemm, J.M. Lazorchak, T.J. Norberg-King, W.H. Peltier, and M.A. Heber (eds). 1994. Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms. U.S. EPA Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, EPA/600/4-91/002.

Norberg-King, T.J. 1988. An interpolation estimate for chronic toxicity: The ICp approach. Technical Report 05-88, National Effluent Toxicity Assessment Center, Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, Minnesota.

U.S. EPA. 2002. Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine Organisms. Forth Edition. Office of Water, U.S. Environmental Protection Agency, Washington, D.C. 20460. EPA-821-R-02-014.

Washington State Department of Ecology. 2008 Revision. Laboratory Guidance and Whole Effluent Toxicity Test Review Criteria. Water Quality Program. Publication No. WQ-R-95-80.

Weber, C.I., editor. 1993. Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, Fourth Edition. U.S. EPA Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, EPA/600-4-90/027F.

1.0 SCOPE

To estimate the chronic toxicity of effluents by measuring echinoderm larval development in a 72-hour static test. Procedures are based on **EPA/600/R-95/136** and **WDOE WQ-R-95-80.**

2.0 SUMMARY OF TEST

2.1 Approach

Number of samples	1
Number of concentrations per sample	5
Number of replicates per concentration	4 minimum
Number of controls	1
Number of replicates per control	4 minimum
Number of reference toxicant concentrations	5
Number of replicates per reference substance concentration	4
Volume of test samples and controls	10 mL
Number of organisms per chamber	25 eggs per mL
Number of test substance renewals	None
Type of biological observations	Survival and normal development
Times of biological observations	72 ± 2 hours
Type of physical observations	Bath and chamber temperature and light
Times of physical observations	Bath temperature continuous; chamber temperature in each concentration and controls at the beginning and end of the test; light at the start of the test
Types of water quality analyses	DO, salinity, and pH measured at the start and end of test in each concentration and controls

2.2 Physical Requirements

DO	Not less than 4.0 mg/L
Temperature	15 ± 1ºC
Salinity	34 ± 2 ppt
pH	6-9
Lighting	Ambient laboratory light (50-100 foot candles); 16 hours light, 8 hours dark

2.3 Biological Requirements

Feeding	Test organisms will not be fed during test
Life stage	< 1 hour old embryos
Dilution water	Filtered (0.45 µm) natural seawater from a clean source, salinity adjusted to test salinity.

2.4 Interferences

Toxic substances may be introduced by contaminants in dilution water, glassware, sample hardware, and testing equipment.

Improper effluent sampling and handling may adversely affect test results.

3.0 TEST ORGANISM

Echinoderm larvae will be the test organisms. These species are widely used in toxicity testing. Standard protocols exist for this species for both product and effluent testing .

3.1 Test Organism Specifications

Species:	*Strongylocentrotus purpuratus* or *Dendraster excentricus*
Source:	M-REP, Steve LePage, Carlsbad, CA. A. Kimbrough Siewers, 619 Washington St., Santa Cruz, CA 95060,
Age:	< 1 hour old embryos
Identification:	Before exposure to test substances, individuals will be positively identified as *Strongylocentrotus purpuratus* or *Dendraster excentricus*.

3.2 Test Organism Care

Adult echinoderms are held in-house or will be obtained in a “ripe” condition from commercial suppliers.

4.0 TEST SUBSTANCE

The test substance will be labeled, properly stored, and tracked by internal chain-of-custody procedures throughout its tenure at Environ’s Port Gamble Laboratory. The test substance will not be heated, filtered, distilled, frozen, or otherwise altered without prior written consent by the Client. The test substance is stored at 4ºC in a secure and distinct storage area. The test substance will be used within 36 hours of collection.

5.0 EQUIPMENT

5.1 Instrumentation/Equipment

Circulating pump
Pasteur pipets and bulbs
1,000 W heater
Compound microscope
Plastic trays
Sedgwick-Rafter (or equivalent) counting cell (1 mL)
100 mL graduated cylinders
Plunger for stirring eggs in 1 L beaker
1-L beakers
Spawning containers
Mohr pipets (10 mL, 5 mL, 1 mL and 0.1 mL)
Oxford mechanical pipetters (0-5 mL, 5-10 mL)
Controlled-temperature water bath (20 ± 1ºC)
Polarographic oxygen probe
SCT meter
pH probe and calibrated meter with scale divisions of 0.1 pH units
Calibrated mercury thermometer
Culture tubes (16 x 100 mm)
Kimwipes®
Nitex screen (75-250 □m)
Large plastic funnel

5.2 Apparatus

5.2.1 Test Area

The test area consists of an incubator, a water bath, or a room with constant temperature and appropriate illumination. The facility will be well ventilated and free of fumes.

5.2.2 Lighting

Overhead lighting will be at 10-20 foot-candles (ambient), 16 hours light and 8 hours dark.

5.2.3 Test Chambers

New 7 dram (26 ml) shell vials.

6.0 PROCEDURE

Echinoderm larvae (< 1 hour old) are exposed for 72 hours to different concentrations of effluent or reference toxicants (copper sulfate) in a static test. Brine controls are employed during effluent testing. The test chambers used are 7 dram shell vials, each containing 10 mL of test solution. Five replicate test chambers, each containing approximately 25 larvae per mL of test substance are employed for each test concentration. Additional test chambers will also be set up as a water quality series to provide data at termination on the water quality in control and test concentrations. Test endpoints are normal development and survival. The bioassay will be performed in accordance with the standard procedures and guidelines specified in EPA 1995.

6.1 Preparation

6.1.1 Glassware Preparation

Glassware will first be soaked in deionized water then scrubbed with a brush on all surfaces using non-phosphate detergent in deionized water. Glassware will be rinsed three times with running deionized water. Glassware will then be rinsed in 10% hydrochloric acid, rinsed three times with deionized water, rinsed once with reagent grade acetone, and finally rinsed three times with deionized water.

6.1.2 Spawning

Every attempt should be made by the laboratory to ensure the availability of multiple spawnable adults.

Prepare filtered seawater at 34 ± 2 ppt. Be sure the solution is saturated to at least 90% DO prior to use.

To collect gametes required for testing echinoderm species, spawning is induced in the adult organisms by the injection of 0.5 to 1.0 mL of 0.5 M KCl into the coelemic cavity through the perisotomal membrane. The injection is performed while the adult animal is out of water. Females will release orange (*S. purpuratus*) or purple (*D. excentricus*) eggs and males of both species will release cream-colored sperm. Once release has been initiated, each adult is inverted over a 50 to 100 mL beaker with filtered seawater at 15 degrees Celsius and gametes are allowed to accumulate for approximately 15 minutes.

Prior to fertilization, examine eggs by microscope to ensure that they are normally shaped. Echinoderm eggs are typically round or oval in shape, with sand dollar eggs having an extracellular coating. During inspection, also ensure that there are no other unusual features that would preclude the use of the eggs (e.g., large vacuoles within the eggs).

Once sufficient eggs and sperm had been collected, the eggs are transferred to a larger beaker with cold filtered seawater and a homogenized sperm solution (taken from several males) is added to the egg solutions. Egg-sperm solutions are periodically homogenized with a perforated plunger during the fertilization process. Approximately one half-hour after fertilization, embryo solutions are checked for fertilization (presence of fertilization membrane). Only those embryo stocks with >90% fertilization are used to initiate the tests. Density of the embryo stock solution is determined by counting the number of embryos in a subsample of stock solution. Approximately 250 embryos will be added to test chambers within 1 hours of fertilization.

In order to determine the initial embryo stocking concentration, five sacrificial vials should be preserved using l-mL 5% buffered formalin.

6.2 Primary Task

6.2.1 Day 0 - Setting Up and Starting the Test

Once successful spawning has begun, prepare test containers. One method that may be used is as follows: with colored tape, label the 4 replicate test tubes for each treatment (e.g., A=red, B=Blue, and C=green) and write the sample number and the effluent concentration on the tape. Alternatively, a blind labeling scheme may be used.

Prepare test solutions by adding the appropriate volumes of effluent and dilution water (totaling 10 mL) to each test tube. The test involves five effluent concentrations and a dilution water control. In addition, prepare a brine control when using brine to adjust salinity at higher effluent concentrations. Prepare brine controls similar to the effluent control, but use deionized water in place of the effluent, and adjust the water to the same salinity as the test water. In addition, set up 5 separate zero-time vials with dilution water for determining initial embryo density.

Since the volume in each test chamber is only 10 mL, water quality measurements must be made on surrogate test chambers (one for each concentration). The parameters will include dissolved oxygen, temperature, salinity, and pH and will be recorded a data sheet.

Within 1 hours of fertilization, inoculate each container with embryo suspension (approximately 250 fertilized eggs) to reach a final concentration of 25 eggs/mL. Ensure that the embryos remain suspended with frequent plunging during pipetting. The amount of suspension should not exceed 10% of test volume.

Immediately after inoculation of the test vessels with embryos, preserve 5 stocking density vials with 5% buffered formalin.

Cover and incubate the containers by partial immersion of the test tubes in a temperature-controlled water bath or an environmental chamber at 15±1ºC for 72 hours, under a 16-hour light, 8-hour dark photoperiod. Do not aerate the test vessels during the bioassay.

6.2.2 Day 1-2 - Test Monitoring

Check and record the temperature of the water bath or environmental chamber.

6.2.3 Day 3 - Test Termination

Near the end of the 72-hour incubation period, examine the control vials under a microscope to check for complete development of control organisms. If development is complete to the pluteus stage, the test is ended.

Terminate the test and preserve by adding 0.5 mL of 5% buffered formalin.

DO, temperature, salinity, and pH of each test concentration are measured in the surrogate containers and recorded.

The time the test is terminated is recorded.

6.3 Test Termination

6.3.1 Larvae Counting Method

The preserved samples are examined on an inverted microscope under 10X - 40X magnification. The use of the inverted microscope eliminates the need for test solution transfer and potential loss of test organism. The normal and abnormal larvae are enumerated, and percent survival and percent abnormality are determined. The stocking density samples are also enumerated. Counting is performed only by trained personnel.

The test vial is placed on the mechanical stage of an inverted microscope, and the contents are examined under 10X-40X magnification. Using the mechanical stage, all

larvae are carefully counted and scored as either normal or abnormal. Live abnormal larvae are those observed at 72 hours (or time of test termination) in which pluteus development is incomplete. Live normal larvae are those observed at 72 hours (or time of test termination) that have completely reached pluteus stage.

Normal Pluteus development is defined as:

1. The larvae have a pyramid shape with a pair of skeletal rods that extend at least half the length of the long axis of the larvae.
2. The gut should be differentiated into three parts. If the gut If the gut appears lobed and constricts distally in specimens with an obstructed view then normal gut development may be inferred.
3. Development of post-oral arms has begun.

The final count is recorded on the data sheet.

6.3.2 Calculations

The percentage of embryos that survived or developed to live larvae reaching pluteus stage will be calculated for each treatment replicate using the formulas:

$$\text{percentage alive} = \frac{100\ (\text{final count})}{\text{initial count}}$$

$$\text{percentage normal} = \frac{100\ (\text{number normally developed})}{\text{final count}}$$

The means will then be obtained for each treatment level, and the latter will then be corrected for control response using Abbott's formula, as follows:

$$E = \frac{100\ (A - M)}{100 - M}$$

where:

E = the mean percent abnormal/dead, or the mean percent mortality corrected for controls

A = the mean percent abnormal/dead, or the mean percent mortality

M = the value of A for the controls

6.3.3 Waste Management

Upon completion of analysis, any remaining sample material is stored until the holding time has expired. At that point, samples are either returned to the clients at their request or

disposed. Permittee and date of disposal are recorded on the chain-of-custody form. Non-toxic samples are disposed by putting them down the drain. Toxic samples are disposed of following standard hazardous waste procedures.

6.3.4 Pollution Prevention

For glassware cleaning, acid baths are used to minimize quantities of acid that reach the drain. Known quantities of sample material and reference toxicant (copper sulfate) are put down the drain after use, in compliance with City regulations.

6.4 Reference Toxicant Test

Concurrent with this chronic toxicity test with bivalve larvae and a test substance, five concentrations of a reference substance (copper sulfate) are used to assess the health of the test organisms. Four replicates per reference concentration will be used. Five concentrations will be selected to bracket the 48-hour LC_{50}. The suggested reference toxicant concentrations are: 2.5, 5, 10, 20, 40 ppb copper sulfate. (Concentrations may be adjusted in cases of long-term changes in organism sensitivity.) The LC_{50} values will be compared with historical data from definitive bioassays. The results of the 72-hour growth and survival test, conducted during this study, will be reported and used in combination with control growth and survival to characterize the health of the test organisms.

7.0 HEALTH AND SAFETY CONSIDERATIONS

Laboratory personnel will practice good personal sanitation and health practices, consistent with the objectives of this protocol.

Any health-related problem or other condition of laboratory personnel that may be considered to affect the study adversely will be reported to the Client.

Any injury to laboratory personnel obtained during this study, which may be considered related to the test material, will be reported to the Client.

Every reasonable precaution will be taken to minimize exposure of personnel, the laboratory, and the environment to the test substance.

PROPRIETARY INFORMATION FOR REVIEW PURPOSES ONLY, DO NOT DUPLICATE OR DISTRIBUTE

8.0 PERSONNEL

Any laboratory personnel demonstrating competence with this method may perform the procedure.

9.0 QUALITY ASSURANCE REQUIREMENTS

9.1 Test Acceptability

Test acceptability criteria are:

- At least 80% normal development in controls.
- %MSD of < 25 %.

9.2 Count Check Acceptability

To demonstrate consistency among staff members' counting methods, a QA check should be performed on each test by having another staff member perform a second (side-by-side) count on 10 percent of the test samples, randomly chosen. These QA counts must be recorded on the data sheet. To be acceptable, the mean of the QA counts must be within 5 percent of the mean of the original counts. If the mean of the QA counts exceeds the 5 percent acceptability, a second series of QA counts will be performed. In the event the second series of QA counts fails to pass the acceptability criterion, the test report must note this fact and warn to use the test results with caution. Documentation in the form of a Corrective Action Report should be filed by the Laboratory Manager. It shall be the responsibility of the Laboratory Manager or their assignee, to evaluate where the discrepancy is occurring and, with concurrence of the Quality Systems Manager, decide on a course of action, which may include retraining of one or more staff members to improve consistency.

9.3 Corrective Action / Contingencies for Out-of-Control Data

Equipment malfunctions, failure of internal QA/QC checks, failure of follow-up on audit findings, noncompliance with QA requirements, or other problems may result in an out-of-control event and the need for corrective action. Please refer to the Quality Manual (Section 13) for criteria used for determination of an out-of-control event, appropriate corrective action, contingencies for handling out-of-control data, and responsible parties.

10.0 ACRONYMS AND DEFINITIONS

°C	Degrees Celsius
Dilution Water	Acceptable dilution water is one that is appropriate for the objectives of the test. This water type will support adequate performance of the test organisms, meet test acceptability criteria for control responses, be consistent in quality, and will not contain contaminants that could produce toxicity.
EC_{50}	Effective Concentration of a tested material or toxicant needed to impact half the organisms in a tested population
Embryo	Fertilized egg cell, also zygote
ft-c	Foot candles; units of illuminance or light falling on object
IC_{25}	Inhibitory Concentration of a tested material or toxicant needed to impact 25% of the organisms in a tested population
IC_{50}	Inhibitory Concentration of a tested material or toxicant needed to impact half the organisms in a tested population
LC_{50}	Lethal Concentration of a tested material or toxicant needed to kill half the organisms in a tested population
lux	Lux; units of illuminance or light falling on object
mg	Milligrams
mL	Milliliters
MSD	Minimum Significant Difference
%	Percent
Pathogenic	causing or capable of causing disease
ppt	Parts per thousand (salinity)
QA/QC	Quality Assurance / Quality Control
Reagent Grade	meets the limits of purity for inorganic chemicals as established by the American Chemical Society
Taring	Processess of zeroing a mechanical weight measurement either with or without a weight boat or other vessel on top of the balance
WET	Whole Effluent Toxicity

PROPRIETARY INFORMATION FOR REVIEW PURPOSES ONLY, DO NOT DUPLICATE OR DISTRIBUTE

11.0 REFERENCE DOCUMENTS

Anderson, B.S., J.W. Hunt, S.L. Turpen, A.R. Coulon, M. Martin, F.H. Palmer. 1990. Marine Bioassay Project Fifth Report. Protocol Development and Inter-Laboratory Testing with Complex Effluents. State of California Water Resources Control Board 90-13WQ.

Chapman, G.A., et al. 1995. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms, 1st edition. U.S. EPA Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, EPA/600/R-95/136.

Hunt, J.W., B.S. Anderson, S. Tudor, M.D. Stephenson, H.M. Puckett, F.H. Palmer, and M.W. Reeve. 1996. Marine Bioassay Project, Eighth Report. State Water Resources Control Board, California Environmental Protection Agency.

Norberg-King, T.J. 1988. An interpolation estimate for chronic toxicity: The ICp approach. Technical Report 05-88, National Effluent Toxicity Assessment Center, Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, Minnesota.

Washington State Department of Ecology. 2008 Revision. Laboratory Guidance and Whole Effluent Toxicity Test Review Criteria. Water Quality Program. Publication No. WQ-R-95-80.

1.0 SCOPE

To estimate the chronic toxicity of effluents and receiving water using echinoderm sperm during a 40-minute exposure period. Procedures are based on **EPA/600/R-95/136** and **WDOE WQ-R-95-80.**

2.0 SUMMARY OF TEST

2.1 Approach

Table 1. General Test Conditions for Performing Chronic Toxicity Testing on Echinoderm Gametes

Test type	Static
Test duration	40 minutes Sperm is exposed to the test solution for 20 minutes; after 20 minutes, eggs are added and allowed 20 minutes for fertilization.
Test temperature	12 ± 1 ºC
Test Salinity	30 ± 2 ppt
Lighting	Ambient laboratory, 16 hours light, 8 hours dark (± 15 min.) at 50-100 foot-candles (550-1050 lux)
Test chamber size	30 mL
Test solution volume	5 mL
Renewal of test solution	None
No. of organisms per chamber	About 1120 eggs and sperm cells per vial not to exceed 3.36×10^6 (6000 sperm per egg)
No. of replicates per treatment	4
Feeding	None
Test solution aeration	None in the test chambers
Type of biological observations	Fertilization
Definition of fertilization for this test	Expression of cell fertilization membrane
Times of biological observations	Post-exposure

2.2 Physical Requirements

The following are required for the control sample.

DO	Not less than 4.0 mg/L
Temperature	12 ± 1ºC
pH	7.8 – 8.2
Salinity	30 ± 2 ppt
Lighting	16 hours light, 8 hours dark (± 15 min.) at 50-100 foot-candles (550-1050 lux)

Table 2. Test Condition Summaries

Species	*Strongylocentrotus purpuratus* or *Dendraster excentricus*
Life Stage Tested	Gametes used within 1 hour of collection
Feeding	None
Temperature (°C)	12 ± 1 ºC
pH	6 - 9
DO	>4.0 mg/L
Type of physical observations	Temperature and light daily
Types of water quality analyses, and the test concentrations measured	DO, pH, conductivity, and temperature, measured on stock solutions of all concentrations on Day 0 (before distribution to test chambers and introduction of test organisms. Total residual chlorine on control and highest concentration at beginning of test.

2.3 Biological Requirements

Feeding	Adult organisms may be fed macroalgae during the holding period. The organisms will not be fed during the test
Life stage	Gametes (egg and sperm cells)
Dilution water	Filtered natural seawater or artificial seawater (Crystal Sea MarineMix™)
Brine	Hypersaline brine from concentrated seawater (prepared by freezing filtered seawater). The test salinity may be adjusted to protocol criteria by using brine. Calculations will be determined using a salinity adjustment worksheet from Excel programming.

2.4 pH Drift

pH drift during the test may contribute to artifactual toxicity when ammonia or other pH-dependent toxicants are present.

As pH increases, the toxicity of ammonia also increases, so upward pH drift may increase sample toxicity. Artifactual toxicity due to pH drift is not likely to occur unless pH is large (more than 1 pH unit) or if concentration of some pH-dependent toxicant in the sample is near the threshold for toxicity. To confirm that toxicity is artifactual and due to pH drift, parallel tests should be conducted, one with controlled pH and one with uncontrolled pH. Total ammonia should also be measured in each treatment at the beginning of parallel testing. During parallel testing, the pH should be measured in each treatment at the beginning and end of each 24 hour exposure period. For each treatment, the mean initial pH and mean final pH should be reported. pH measurements taken during the test should confirm that pH was effectively maintained at the target pH in the controlled pH treatment. For each treatment, the mean initial pH and the mean final pH should be within +/- 0.2 pH units of the target pH.

Results of the parallel tests are compared to demonstrate the presence or absence of artifactual toxicity.

3.0 TEST ORGANISM

Either *Strongylocentrotus purpuratus* or *Dendraster excentricus* will be the test organism. These organisms are widely used in toxicity testing. Standard protocols exist for these species for both product and effluent testing (Dinnel et al. [1987] and USEPA [1995]).

3.1 Test Organism Specifications

Species:	*Strongylocentrotus purpuratus or Dendraster excentricus*
Source:	Marine Research and Educational Products, Carlsbad, CA, or field collected in various locations
Age:	Gravid adults. Sperm used immediately after SW activation
Identification:	Before exposure to test substances, individuals will be positively identified using Ricketts and Calvin 1966.

3.2 Test Organism Care

Adult echinoderms are held in-house or will be obtained in a "ripe" condition from commercial suppliers.

4.0 TEST SUBSTANCE

The test substance will be labeled, properly stored, and tracked by internal chain-of-custody procedures throughout its tenure at Environ's Port Gamble Laboratory. The test substance will not be heated, filtered, distilled, frozen, or otherwise altered without prior written consent by the Client. The test substance is stored at 0 - 6ºC in a secure and distinct storage area. The test substance will be used within 36 hours of collection.

5.0 EQUIPMENT

5.1 Instrumentation

Syringe (to inject KC1) with 18-22 gauge needle
Pasteur pipets and bulbs
Ice bath or refrigerator
Compound microscope
Neubauer hemocytometer
Sedgwick-Rafter (or equivalent) counting cell (1 mL)
1,000-mL beakers
100-mL beakers
50-mL beakers
20-30-mL scintillation vials
Small siphon hose (2 ft. long, 3/16 - 1/4 in diameter)
Pipet selection (10, 5, 1, and 0.1 mL)
Pipet bulb
Racks for scintillation vials
Oxygen probe
pH probe and calibrated meter
Calibrated mercury thermometer
100-mL graduated cylinder

5.2 Reagents

0.5 M KC1
10% buffered formalin

5.3 Apparatus

5.3.1 Test Area

The test area consists of a room, incubator, or bath with constant temperature of 12 ± 1°C and appropriate illumination of 16-hour/8-hour day/night cycle. The facility will be well ventilated and free of fumes.

5.3.2 Lighting

Overhead lighting will be at 50-100 foot-candles (550-1050 Lux), with a photoperiod of 16 hours light and 8 hours dark (± 15 min.).

5.3.3 Test Chambers

30mL shell or scintillation vials

6.0 PROCEDURE

Echinoderm sperm are exposed for 20 minutes to different concentrations of effluent and reference toxicant in a static, nonrenewal test, and then are tested for the ability to fertilize eggs for 20 minutes. The appropriate sperm-to-egg ratio is determined prior to the definitive test through use of a trial fertilization series. The test chambers are 30-mL glass shell vials (new, unwashed) containing 5 mL of test solution that has been adjusted to 30 ± 2 ppt salinity using seawater, brine, or deionized water. Four to five replicate tubes are used at each concentration.

6.1 Preparation

6.1.1 Labware Preparation

Labware is described as any plastic or glass material used in the laboratory that will come into contact with any of the test substances or organisms in this evaluation. Labware must be cleaned prior to use. Labware will first be soaked in deionized water then scrubbed with a brush on all surfaces using non-phosphate detergent in deionized water. Alconox® is a widely used established brand of detergent used in laboratory applications. The clean materials will then be rinsed three times with running deionized water. Labware will then be allowed to soak in a 10% hydrochloric acid bath and afterwards rinsed three times with deionized water. Glass labware with also receive a solvent rinse with reagent grade acetone, and finally rinsed three times with deionized water. Some plastic labware is not resistant to solvents and may be damaged by acetone. Plastic labware such as Teflon can receive a solvent rinse, but all other plastics should be investigated prior to solvent rinsing.

6.1.2 Dilution Water Preparation

The dilution water will be a saltwater source deemed appropriate by the laboratory and may include: 0.45µm filtered natural seawater (Northern Hood Canal, WA; sand filtered and salinity adjusted as needed) or artificial seawater (prepared from deionized water and Crystal Sea Marinemix™).

6.1.3 Test Organism Acclimation

During the holding period, the organisms are acclimated to the temperature and salinity at which the test will be conducted, unless already at the correct values. The water quality conditions will be changed no more than 3ºC or 3ppt per 24 hours to minimize stress. During the holding period, just enough newly-hatched *Artemia* nauplii will be fed twice daily so that some food is constantly present.

6.2 Primary Task

6.2.1 Test Dilution Preparation

Test substance dilutions will be prepared using labware cleaned according to Section 6.1.1 or using pre-cleaned labware of a disposable nature. Dilutions are initially prepared in vessels large enough to contain sufficient volume for all test replicates. These “stock” containers may be used for preparing the test solutions prior to test initiation and for the test solution renewal (if required).

The testing may be either a “screening test” which includes a laboratory control (dilution water) and the undiluted test substance or a “definitive test” which includes a minimum of five test substance concentrations. The definitive test (also referred to as a “dilution test” or “LC_{50} test”) is conducted when a dose response (i.e. LC_{50}) is desired.

The final test substance dilutions for the definitive test will be expressed as percent and typically run in a geometric series with a 0.5x dilution. Other ratios may be selected depending upon the project requirements. When specified by the regulatory permit, specific test substance concentrations targeting the Acute and Chronic Critical Effluent Concentrations (ACEC/CCEC) should be included in the concentration series.

Dilution water will be the only water used in making up all stock and final dilutions (unless receiving water is specified).

After preparation, the “Stock” test dilutions are allowed to equilibrate to the test temperature. Water quality is measured and recorded in the stock dilutions, and once the conditions are confirmed to be within the test parameters, the solutions will be distributed to the replicate test chambers. Each test chamber will be labeled with a

coded test chamber number, representing the specific test, the concentration, and the replicate number.

6.2.2 Reference Toxicant Test

A reference toxicant test will be conducted on each batch of test organisms either concurrently with project samples or monthly, depending upon QA requirements. The reference toxicant test will consist of a 20-minute exposure to at least five concentrations of a reference substance (known toxicant) used to assess the health and sensitivity of the test organisms. Dilutions will be selected to bracket laboratory historical EC_{50}. The EC_{50} results will be compared with historical data from definitive bioassays with the reference substance. The results of the fertilization test, determined during this study, will be reported and used in combination with control mortality to characterize the health and sensitivity of the test organisms.

6.2.3 Spawning

Adult urchins will be selected from the holding area and rinsed with filtered seawater at target test temperature (12 ± 1°C). Inject 0.5 to 1.0 mL of 0.5 M KCl into the perivisceral cavity through the perisotomal membrane (oral side) or the anal opening (ventral). Females will release reddish to purple eggs. Males will release cream-colored semen.

Allow spawning to proceed for approximately 15 minutes. For females, collect gametes by inverting the spawning female on top of a 50 or 100-mL beaker filled with dilution water. Semen should be collected ‘dry” by collecting with an automatic or pastuer pipet and pooled into a micro-centrifuge tube. The tube of sperm is kept on ice.

6.2.4 Preparation of Sperm

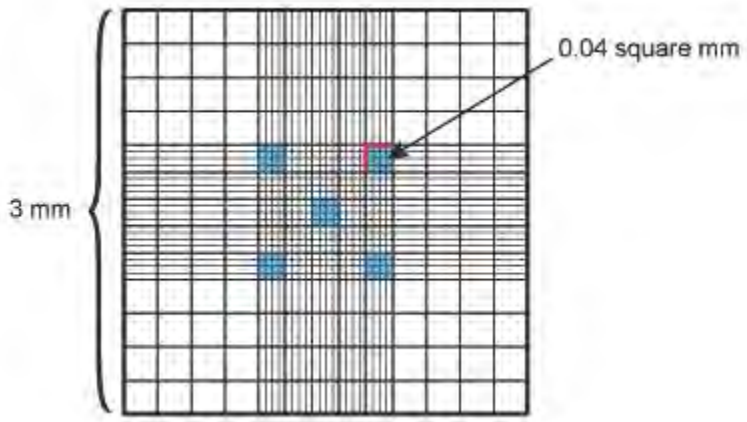
Prepare sperm (diluted with seawater) three times using identical procedures: the first for sperm counting, the second for use in the trial fertilization, and the third for use in the test. The sperm suspensions used for trial fertilization and for the definitive test are made up immediately prior to initiating the trial or test.

A minimum of 100µl of pooled semen should be collected for testing. Subsamples of semen for density calculations and test initiation are withdrawn with an automatic pipet (10-100µl capacity) with a tip cut wide. Prior to extraction, the centrifuge vial containing the semen is mixed with a vortexer.

Place 180 ml of filtered seawater in 250mL beaker. Bring volume up to 200mL with 10% acetic acid. Using a fresh tip with the end cut off; take a 25µl sample of the pooled, vortexed semen. Wipe the outside of the pipet tip with a Kim Wipe ™ and add the 25µl of semen to the beaker. Rinse the tip by repeatedly withdrawing and dispensing with the pitettor. Mix thoroughly with a glass rod. Withdraw a subsample with a Pasteur pitet and load both sides of a hemocytometer with a cover slip.

Count the sperm cells using a microscope at 400X. Count all the sperm in 80 of the small squares (fig 1.), on both sides of the hemocytometer.

Figure 1. Hemocytometer.



If the counts are within 20% of one another, calculate the mean value; if not, refill the hemocytometer and reattempt.

See Section 6.2.7 below for the procedure to determine the appropriate sperm to egg ratio for testing. An alternative method is to target a sperm to egg ratio of 500:1 (560,000 sperm cells per vial) without conducting the trial fertilization described below.

Based upon the sperm density determined from the semen vial, calculate the amount of dilution water to dissolve 25µl of semen to achieve the desired sperm to egg ratio.

Amount of dilution water (mL) = 0.025mL ÷ (5.6×10^6 / Actual Sperm Density)

Deliver 0.100mL of adjusted sperm stock per vial.

6.2.5 Preparation of Eggs

Check quality of eggs released from each female. The eggs should be round, of average size, not clumped, and not fertilized. Eggs from multiple acceptable batched may be pooled into a 600-1000mL beaker with dilutions water. Let the mixture settle and decant or siphon off the supernatant. Repeat twice to completely wash eggs.

Subsamples of the egg stock are then taken for determining egg density. Place 9 mL of dilution water in each of two 30 mL shell vials. Label A and B. Place 1 mL of well-mixed egg stock into vial A. Mix well. (The remaining egg stock is covered with parafilm and stored at 20°C.) Transfer 1 mL of egg suspension from vial A to vial B. Mix

contents of vial B and transfer 1 mL of egg suspension B into a Sedgewick-Rafter counting chamber. Count eggs under a compound microscope. If count is <30, count a 1 mL sample from vial A.

Prepare 100 mL of adjusted egg stock in dilution water at the final target concentration of 2,240 eggs/mL (1,120 eggs in 0.500 mL). If the egg stock is >2,240 eggs/mL (A >224 or B >22 eggs/mL), dilute the egg stock by transferring:

2,240 eggs / __D__ eggs/mL = _____mL

of well-mixed egg stock to a 100 mL graduated cylinder and bring the total volume to 100 mL with dilution water where:

D = (Count A) x 10 or (Count B) x 100.

If the egg stock is <2,240 eggs/mL (A <224 eggs/mL), concentrate the eggs by allowing them to settle and then decant enough water to retain the following percent of the original volume:

(__D__ eggs/mL / 2,240) x 100 = % volume.

Check the adjusted egg stock density. Place 9 mL of dilution water into a 30 mL shell vial; add 1 mL of the final egg stock. Mix well and transfer 1 mL into a Sedgewick-Rafter counting chamber. The egg count should be between 360 and 440. Adjust egg stock volume and recheck counts if necessary to obtain counts within this range. Because some eggs (especially sand dollar eggs) may be sensitive to handling, it is advisable to separately prepare egg stocks for the fertilization trial and the definitive test (but use the same pooled batch of eggs). Calculations may be facilitated using an Excel spread sheet.

Carry out the dilution (or concentration) and keep at 20 ± 1°C in the water bath or environmental chamber.

0.5mL of adjusted egg stock is delivered to each test vial for a final egg concentration of 1,120 eggs/vial.

6.2.7 Trial Fertilization

Following quantitation of sperm and eggs, calculate the volumes of diluted sperm stock necessary to achieve the different sperm-to-egg ratios. Because approximately 1,120 eggs are used in the test, the sperm numbers will be a function of this number. Use between 100 and 2,000 sperm per egg. Never exceed 6,000 sperm per egg.

Sperm to egg ratios of 100, 200, 400, 600, 800, 1200, and 1600 per egg are prepared (see attached Excel spreadsheet. Fig 1.). The 1600:1 dilution is prepared by activating

0.025 mL of dry vortexed semen in the amount of seawater calculated from the initial sperm density counts. The remaining sperm to egg concentrations are prepared by diluting the 1600:1 concentration with the appropriate amount of seawater (total of 10mL).

For each sperm to egg ration to be tested, place 5 mL of dilution water into a single replicate, 20 mL scintillation vial and equilibrate at 12 ± 1°C. Add exactly 0.100 mL of the respective sperm dilution as specified above and incubate for 20 minutes at 12 ± 1°C. After 20 minutes, add exactly 0.5 mL of the adjusted egg stock suspension. Return to the water bath or environmental chamber for an additional 20 minutes.

Terminate the reaction by adding, while swirling, 0.5 mL of 10% formalin. Disperse the preserved eggs with a Pasteur pipet and observe at least 100 eggs using a Sedgwick-Rafter cell and a compound microscope at 10X - 50X magnification. Score the eggs as fertilized (raised fertilization membrane; partial lift-off of the fertilization membrane will be counted as fertilized) or unfertilized (no fertilization membrane). Enter the data on the data sheet, calculating the percent fertilization for each sperm-to-egg ratio. Choose the lowest ratio yielding ~ 90 percent fertilization and conduct the toxicity test using that sperm concentration. The selected sperm concentration will be prepared fresh from the dry semen for conducting the definitive test. The adjusted sperm stock will be prepared by activating 0.025 mL of dry vortexed semen into the appropriate amount of seawater to obtain the desired concentration.

6.2.8 Conducting the Test

Add 0.100mL of adjusted sperm stock to test vials and incubate for 20 minutes at test temperature. After the 20 minute period, 0.500mL of adjusted egg stock is added to each vial and allowed to incubate for 20 minutes.

Three vials containing dilution water should be included in the test that are <u>not</u> stocked with sperm at the beginning of the testing period, but are stocked with eggs only at the 20 minute time point and terminated with the rest of the test. These vials are the “egg blanks” and serve to verify that fertilization did not occur (or become expressed) in the egg stock.

Confirm sperm density in two sacrificial vials. These vials should contain 9 mL of adjusted sperm stock and 1 mL of formalin.

6.2.9 Terminating and Counting the Test

Terminate the reaction by adding, while swirling, 0.5 mL of 10% buffered formalin. Disperse the preserved eggs with a Pasteur pipet and observe at least 100 eggs using a Sedgwick-Rafter cell and a compound microscope at 40X - 100X magnification. Score the eggs as fertilized (raised fertilization membrane; partial lift-off of the

fertilization membrane will be counted as fertilized) or unfertilized (no fertilization membrane).

- - 1120 eggs/mL - For NPDES

ıns value needs to be entered
ıns value is calculated by formula

(Countx8000x4000x1000)/80 — Sperm Density = 47800000000

nts	
1	123
2	116

ɹme counting of 5 little squares of the large square on the hemacytometer
'ferent, the (80) value must be adjusted accordingly
cells are counted then 80 is changed to 400

		Target desity / Actual density	Amount of Seawater to dissolve 0.025mL of dry sperm into to obtain desired ratio (mL)	Ratio	Amount of Seawater	Ar
20/0.1)=	1120000	2.3431E-05	1067.0	100:1	9.5	
20/0.1)=	2240000	4.6862E-05	533.5	200:1	9	
20/0.1)=	4480000	9.3724E-05	266.7	400:1	8	
20/0.1)=	8960000	0.00018745	133.4	800:1	6	
20/0.1)=	13440000	0.00028117	88.9	1200:1	4	
20/0.1)=	17920000	0.0003749	66.7	1600:1	2	
20/0.1)=	22400000	0.00046862	53.3			

target 2240 eggs per mL (Deliver 1120 eggs in 0.5 mL)
If eggs stock is < 2240 eggs mL reconcentrate eggs

sperm to egg ratio
Add 0.025 mL of

A= 1mL of egg stock in 9 mL of seawater — Dilution factor of 10
B= 1mL of A in 9 mL of seawater — Dilution factor of 100

nt whole slide — Count = 262
Enter Dilution Factor (10 or 100) — 100

Amount of eggs stock — 8.5
Dilute in of Seawater — 91.5

Sperm Count Cor
9mL Sperm/1mL
Counts
1
2

Figure 1. Spreadsheet to calculate sperm and egg density for echinoderm fertilization test.

6.2.8 Test Measurements

Data are recorded on data sheets.

Water Quality. All probes will be cleaned thoroughly before initial use. The probes will be rinsed with deionized water between each measurement. DO, temperature, salinity, and pH will be measured in one surrogate test chamber per concentration and in the control.

Biological. At the end of the test, the numbers of fertilized and unfertilized eggs are enumerated for each replicate.

6.3 Post-task

6.3.2 Data Analysis

Results Needed:

- Fertilization in controls
- Fertilization in test concentrations
- IC_{50} value and 95% confidence limits (effects on fertilization)
- Tables showing biological, chemical, and physical data

Concentration-Response Relationship: The concentration-response relationship must be reviewed to ensure that the calculated test results are interpreted appropriately. See Environ's Port Gamble Laboratory Protocol LAB061 for guidance in evaluating the WET test variability and concentration response relationship.

Evaluation of Chronic Test PMSDs: The PMSD limits for both the compliance test and the reference toxicant test must be evaluated to determine whether they fall within the upper and lower bound limits specified in EPA/821/B-00/004. These limits are included in Environ's Port Gamble Laboratory Protocol LAB061 which also contains guidelines for determining the proper course of action in the event the PMSD exceeds the upper bounds of the specified limits.

6.3.3 Method

The endpoint of this toxicity test using echinoderms is based on the adverse effects on fertilization. The LC_{50}, the IC_{25}, and the IC_{50} are calculated using point estimation techniques, LOEC and NOEC values, for survival and growth, are obtained using a hypothesis testing approach such as Dunnett's Procedure or Steel's Many-one Rank Test. Separate analyses are performed for the estimation of the LOEC and NOEC endpoints and for the estimation of the LC_{50}, IC_{25}, and IC_{50}. Concentrations at which there is no fertilization in any of the test chambers are excluded from the statistical analysis of the NOEC and LOEC for survival and growth but included in the estimation of the LC_{50}, IC_{25}, and IC_{50}.

LC_{50} values and 95% confidence limits will be determined using a computer approach published by Norberg-King (1988) of the U.S. EPA and a commercial statistic software program. The Inhibition Concentration percentage, or ICp, approach to calculating point estimates of toxicity (i.e., LC_{50}) is based upon a monotonic smoothing technique of biological response versus concentration. Bootstrapped estimates of mean response at each concentration allow for distribution-free estimates of standard error and confidence intervals. The result is a non-parametric statistical test that requires no assumptions of normality or homogeneous variance and is robust enough to accommodate a wide variety of biological responses.

6.3.4 Waste Management

Upon completion of analysis, any remaining sample material is stored until the holding time has expired. At that point, samples are either returned to the clients at their request or disposed. Date of disposal is recorded in the sample receipt log. Samples are disposed of by putting them down the drain.

6.3.5 Pollution Prevention

For labware cleaning, acid baths are used to minimize quantities of acid that reach the drain. Known quantities of reference toxicant (aqueous metals) are collected for hazardous waste disposal.

7.0 HEALTH AND SAFETY CONSIDERATIONS

Laboratory personnel will practice good personal sanitation and health practices, consistent with the objectives of this protocol.

Any health-related problem or other condition of laboratory personnel that may be considered to affect the study adversely will be reported to the Client.

Any injury to laboratory personnel obtained during this study, which may be considered related to the test material, will be reported to the Client.

Every reasonable precaution will be taken to minimize exposure of personnel, the laboratory, and the environment to the test substance.

8.0 PERSONNEL

Any technician trained in these procedures may perform them.

9.0 QUALITY ASSURANCE REQUIREMENTS (ACCEPTANCE CRITERIA)

This study will be conducted according to the Standard Operating Procedures of Environ's Port Gamble Laboratory which are in effect during the time the study is being performed. In the case where there is a conflict between the other SOPs and this protocol, the protocol will be the definitive procedure.

9.1 Test Acceptability

Test is acceptable only if all these criteria are met:

- At least 70% fertilization in controls
- Fertilization did not occur with the effluent/egg blanks (no sperm) controls.
- Minimum significant difference (MSD) is <25%
- Final sperm stock concentration must be ≤ 33,600,000 sperm/mL AND one of the following conditions:

1) Trial fertilization used
   a. Final sperm stock must not exceed double the target density selected that would provide 80 – 100% fertilization without oversperming
2) Sperm / egg ratio kept at ≤ 500:1 (without trial fertilization) and confirmation of sperm stock ≤ 5,600,000 sperm/mL
3) Use any reasonable sperm stock density and run two extra sets of controls (high and low density). The high density control (0.200 mL of sperm stock) must have at least 5% higher fertilization than the low density control (0.050 mL of sperm stock)

9.2 Count Check Acceptability

To demonstrate consistency among staff members' counting methods, a QA check should be performed on each test by having another staff member perform a second (side-by-side) count on 10 percent of the test samples, randomly chosen. These QA counts must be recorded on the data sheet. To be acceptable, the mean of the QA counts must be within 5 percent of the mean of the original counts. If the mean of the QA counts exceeds the 5 percent acceptability, a second series of QA counts will be performed. In the event the second series of QA counts fails to pass the acceptability criterion, the entire test must be recounted, with the QA procedure again being performed until the QA check is acceptable. In the event recounting of a test becomes necessary, documentation in the form of a Corrective Action Report should be filed by the Laboratory Manager. It shall be the responsibility of the Laboratory Manager or their assignee, to evaluate where the discrepancy is occurring and, with concurrence of the QA Officer, decide on a course of action, which may include retraining of one or more staff members to improve consistency.

9.2 Corrective Action / Contingencies for Out-of-Control Data

Equipment malfunctions, failure of internal QA/QC checks, failure of follow-up on audit findings, noncompliance with QA requirements, or other problems may result in an out-of-control event and the need for corrective action. Please refer to the QA Manual (Section 13) for criteria used for determination of an out-of-control event, appropriate corrective action, contingencies for handling out-of-control data, and responsible parties.

10.0 REFERENCE DOCUMENTS

Anderson, B.S., J.W. Hunt, S.L. Turpen, A.R. Coulon, M. Martin, F.H. Palmer. 1990. Marine Bioassay Project Fifth Report. Protocol Development and Inter-Laboratory Testing with Complex Effluents. State of California Water Resources Control Board 90-13WQ.

Chapman, G.A., et al. 1995. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms, 1st edition. U.S. EPA Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, EPA/600/R-95/136.

Hunt, J.W., B.S. Anderson, S. Tudor, M.D. Stephenson, H.M. Puckett, F.H. Palmer, and M.W. Reeve. 1996. Marine Bioassay Project, Eighth Report. State Water Resources Control Board, California Environmental Protection Agency.

Norberg-King, T.J. 1988. An interpolation estimate for chronic toxicity: The ICp approach. Technical Report 05-88, National Effluent Toxicity Assessment Center, Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, Minnesota.

Washington State Department of Ecology. 2008 Revision. Laboratory Guidance and Whole Effluent Toxicity Test Review Criteria. Water Quality Program. Publication No. WQ-R-95-80.

Appendix B

Field Standard Operating Procedures (EMP)

Field Standard Operating Procedures (EMP)

SOP Number	SOP Title
Field	
FWS SOP-01	Field Documentation
FWS SOP-02	Sample Custody
FWS SOP-03	Sample Packaging and Shipping
FWS SOP-04	Decontamination of Equipment – Sediments
FWS SOP-05	Preparation of Field Quality Control Samples
FWS SOP-06	Surface Sediment Sampling Using a Modified van Veen Grab Sampler
FWS SOP-07	Decontamination of Sampling Equipment
FWS SOP-08	Preparation of Field Quality Control Samples – Tissues
FWS SOP-12	Benthic tissue sampling for chemical analysis using a dredge/rake
FWS SOP-13	Amphipod sampling for chemical analysis using a modified minnow trap
SAM044.01	Sediment Profile Imaging and Plan View Photography Collection
SOP 5-275	At-Sea Collection of Hydrographic Data Using CTD and Rosette System
SOP 5-342	Collecting Sediment Cores with a Piston Push/Hammer Corer
SAM043.01	Benthic Sample Collection and Processing
FIT-0001	Field Collection of Seawater Samples for Dissolved Trace Metals
FIT-6001	Filter Preparation for Suspended Matter Collection and Trace Metal Analysis
FIT-6002	Collection and Digestion of Particulate Samples for Trace Metal Analysis

SOP – 01
Field Documentation

The integrity of each sample collected in the field from the time of collection to the point of data reporting must be maintained throughout the study. Proper record keeping will be implemented in the field to allow samples to be traced from collection to final disposition. All information relevant to field operations must be properly documented to ensure that activities are accounted for and can be reconstructed from written records. Several types of field documents and sample tracking information will be used for this purpose and should be consistently used by field personnel.

FIELD LOGBOOKS

During field sampling events, field logbooks are used to record all daily activities. The purpose of the field logbook is to document events that occur and to record data measured in the field to the extent that someone not present at the site can reconstruct the activity without relying on the memory of the field crew.

A bound, waterproof field logbook with consecutively numbered pages will be completed using indelible ink for each sampling event. All daily field activities will be documented in indelible ink in this logbook and no erasures will be made. All corrections should consist of a single line-out deletion, followed by the sampler's initials and the date. The sampler will initial and date each page of the field logbook. The sampler will sign and date the last page at the end of each day, and a line will be drawn through the remainder of each page. These requirements meet standard Good Laboratory Practices (GLP).

The project name, site name, and location, project contract number, and the dates of sampling activity should be written on the cover of the field logbook. If more than one logbook is used during a single sampling event, then the upper right hand corner of the logbook will be annotated (e.g., 1 of 2, 2 of 2) to indicate the number of logbooks used during the field event.

Field logbooks will be stored in a secure manner when not in use in the field. At a minimum, the sampler will record the following information in the field logbook:

- Project name, location, and number
- Purpose and description of field task
- Project start date and end date
- Date and time of entry (24-hr clock)
- Time and duration of daily sampling activities
- Weather conditions at the beginning of the field work and any changes that occur throughout the day, including the approximate time of the change (e.g., wind speed and direction, wave

action, current, tide, vessel traffic, air and water temperature, ice thickness, any other relevant data)

- Name of field scientist making entries and other field personnel and their duties, including the times that they are present
- Level of personal protection being used
- Onsite visitors, if any, including the times they are present
- The name, agency, and telephone number of any field contacts
- Notation of the system used to determine the station location information
- The sample identifier and analysis code for each sample to be submitted for laboratory analysis
- All field measurements made (or reference to specific field data sheets used for this purpose), including the time that the measurement was collected and the date of calibration, if appropriate
- The sampling location name, date, gear, water depth (if applicable), and sampling location coordinates
- The type of vessel used (e.g., size, power, type of engine) – for aquatic or offshore sampling
- The location and description of the work area, including sketches and map references, if appropriate
- Specific information on each type of sampling activity
- The sample type (e.g., groundwater, soil, benthic sediment (surface or vertical depth)), sample number, and sample tag number
- Preservatives used, if any
- Sample storage methods
- Cross-references of numbers for duplicate samples
- A description of the sample (Source and appearance, such as soil or sediment type, color, texture, consistency, presence of biota or debris, presence of oily sheen, changes in sample characteristics with depth, presence/location/thickness of the redox potential discontinuity (RPD) layer, and odor) and penetration depth
- Estimate of length and appearance of recovered sediment cores (if applicable)
- Photographs (uniquely identified) taken at the sampling location
- Variations, if any, from specified sampling protocols and reasons for deviation
- Details pertaining to unusual events which might have occurred during sample collection (e.g., possible sources of sample contamination, equipment failure, unusual appearance of sample integrity, control of vertical descent of the sampling equipment)
- References to other logbooks used to record information (E.g., field data sheets, health and safety log)
- The signature of the person making the entry.

Upon completion of the field sampling event, the field team leader will be responsible for submitting all field logbooks to be copied and retained for records.

FIELD DATA FORMS

Field data forms, in conjunction with the field lab notes, are an integral component of field work. Examples include station and/or sample logs and sediment core profile forms. Any relevant sample information collected during a sampling event should be recorded on the applicable field data form. Specific instructions relevant to a particular project are included in the project-specific field sampling plan (also sometimes called the Sampling and Analysis Plan (SAP)). Upon completion of the field sampling event, the field team leader will be responsible for submitting all field data forms to be copied and retained for records.

PHOTOGRAPHS

Photographs may often be an integral component of the field documentation process. Photographs allow for documentation of collected samples (visual image for later use) and for documentation of field sampling activities. Photographs should include a measured scale in the picture, when practical. Telephoto or wide-angle shots will not be used because they cannot be used in enforcement proceedings. The following items should be recorded in the field logbook for each photograph taken:

- The photographer's name, the date, the time of the photograph, the general direction faced, and the latitude/longitude (location) relevant to the image in the photo (e.g., sample location for photograph of particular sample collected)
- A brief description of the subject and the field work portrayed in the picture
- The sequential number of the photograph (filename for digital)

Upon completion of the field sampling event, the team leader will be responsible for submitting all photographic materials to be developed (slides, prints) or to be copied (Disks) as appropriate. The appropriate photographic materials will be retained for records, including any photo logs and/or additional supporting documentation from the field logbooks or field forms.

SAMPLE LABELS

Sample labels used in field documentation will provide a unique identification for each sample container that is collected during a sampling event. Field crews will be provided with pre-printed sample labels, which must be placed on each sample container used. The labels should be filled out when the samples are collected and should include the following information:

- Sample number (e.g., indication of sample station, study, year, etc…)
- Site name or project number
- Date and time of sample collection
- Field sampler(s) initials
- Identification of any preservation method used (e.g., acidified, frozen)

- A unique number (i.e., tag number) that is pre-printed on the label consisting of six digits. This is used to identify the individual containers and is included on the chain-of-custody form along with the sample number

SAMPLE TAGS

In some cases, sample tags are required in addition to sample labels. Sample tags are designed to be attached to each container used for a sample. Sample tags are required for environmental samples collected in U.S. Environmental Protection Agency (EPA) Region 5 and Region 10 (EPA 2003). Sample tags must be attached to each individual sample container with a rubber band or wire through a reinforced hole in the tag. All sample tag entries will be made with indelible ink. The tags should be filled out at the time the samples are collected and should consist of the following information:

- Sample number
- Site name or project ID (or project number)
- Date and time sample is collected
- Sampler(s) initials
- Preservation type (e.g., acidification, frozen)
- Type of analysis

There will also be a space for the laboratory sample number, which will be provided by the laboratory at log-in (Contract Laboratory Program, CLP), on the sample tag.

CHAIN-OF-CUSTORY/SAMPLE ANALYSIS REQUEST FORMS

A combined chain-of-custody (COC) and sample analysis request (SAR) form will be used to document the type and number of samples collected, as well as information regarding the particular type of analysis requested for the laboratory. The sample number and the unique number on each sample label will be recorded on the COC/SAR form. The COC/SAR form will also include the sample collection date and time, the type of sample, the project, and the field team leader. In addition, the COC/SAR form provides information on the type of sample preservation (if applicable) and/or other sample pretreatment applied in the field, and the analyses to be conducted on each sample. The SAR references a list of specific analyses (e.g., by method (EPA 8270) or by list) or the statement of work for the laboratory. A COC/SAR form is sent to the laboratory in conjunction with the samples.

Each COC/SAR form is completed in triplicate (either white sheet (remains with the samples), yellow sheet (remains with the samples), and a pink sheet (retained by the field personnel prior to shipping the samples to the laboratory, OR, computer generated forms may be used in triplicate: the original and a copy included with the samples sent to the laboratory and a copy retained by the field personnel). The two copies included with the samples and sent to the laboratory are to be secured in a plastic, sealable bag and taped to the inside top of each sample cooler. The pink (3rd) sheet will be retained by the field personnel for filing after returning from the field.

Upon completion of daily field activities and prior to shipping or storage, COC entries will be completed for all samples. Information on each sample label will be verified against the information logged in the field notebooks and field forms. Upon completion of the field sampling event(s), the field team lead is responsible for submitting at COC/SAR forms for copying and filing after returning from the field.

CUSTODY SEALS

It is imperative (particularly for any projects that may be involved in litigation) that sample integrity be demonstrated and documented from the time of collection to the time of receipt in the laboratory. As security against unauthorized handling of the samples during shipping, two custody seals will be affixed to each sample cooler. The custody seals will be placed across the opening of the cooler (front right and back left) prior to shipping. The seals must be signed and dated and properly attached to the cooler such that they cannot be removed (intentionally or accidentally) during shipping. It is recommended that additional tape be used to ensure the custody seals are attached to the cooler(s).

SHIPPING AIRBILLS

When samples are shipped from the field to the laboratory via a commercial carrier (e.g., FedEx, UPS) and airbill or receipt is provided by the shipper. Upon completion of the field sampling even, the field team lead will be responsible for submitting the sender's copy of all shipping airbills to be copied. The airbill number (i.e., tracking number) should be noted on the applicable COC/SAR forms (if possible) or alternatively the applicable COC/SAR form number should be noted on the airbill to enable the tracking of samples if a cooler is lost.

ACKNOWLEDGEMENT OF SAMPLE RECEIPT FORMS

In most cases, when samples are sent to an analytical laboratory, and an Acknowledgement of Sample Receipt form is faxed to the company and/or the lead scientist on the project. This typically would occur upon receipt of the samples at the laboratory. It is the responsibility of the person receiving the Acknowledgement of Sample Receipt form to review the form and make sure that all the sample that were sent to the laboratory were received by the laboratory and that the correct analyses were requested. If an error is found, the laboratory must be called immediately. Decisions made during the telephone conversation with the laboratory should be documented in writing on the Acknowledgement of Sample Receipt form. In addition, corrections should be made to the COC/SAR form and the corrected version of the COC/SAR form should be faxed to the laboratory and retained for documentation.

FORM COPIES/SCANS FOR DOCUMENT RETENTION

Upon returning from the field, all field notes, field logs, photographs, and COC/SAR forms should be copied and scanned into electronic form. The files should be stored under project folders and backed up on the Fairweather Science server. Once samples have been received at the laboratory, the fully-executed COC/SAR forms should also be scanned and retained on the electronic server. All documents should be retained until otherwise notified by the client and/or the project's principle investigator (PI).

REFERENCES

U.S. EPA. 2003. Quality Management Plan – EPA Region 10. U.S. Environmental Protection Agency, Region 10. Seattle, WA.

Revision No. 0
June 25, 2013

SOP – 02
Sample Custody

A stringent, established program of sample chain-of-custody will be followed during sample storage and shipping activities to account for each sample. The procedure outlined here will be used with SOP – 01, Field Documentation, and SOP-03, Sample Packaging and Shipping. Chain-of-custody record/sample analysis request (COC/SAR) forms ensure that samples are traceable from the time of collection through processing and analysis until final disposition. A sample is considered to be in a person's custody if any of the following criteria are met:

- The sample is in the person's possession
- The samples is in the person's view after being in possession
- The sample is in the person's possession and is being transferred to a designated secure area
- The sample has been locked up to prevent tampering after it was in the person's possession

At no time is it acceptable for samples to be outside of the field leader's custody unless the samples have been transferred to a secure area (e.g., a locked freezer). If the samples cannot be placed in a secure area, then the field team lead (or designate) must physically remain with the samples at all times.

PROCEDURE

The COC portion of the COC/SAR form is the most critical component because it documents sample possession through the life-cycle of the sample. The SAR component of the form provides information to the technical laboratory regarding what analyses are to be performed on the samples that are shipped.

The COC/SAR form will be completed after each field collection activity and before the samples are shipped to the laboratory. Sampling personnel are responsible for the care and custody of the samples until they are shipped. When transferring possession of the samples, the individuals relinquishing and receiving the samples must sign the COC/SAR form(s), indicating the time and date that the transfer occurs. Copies of the forms will be made and kept by the company (e.g., Fairweather Science) or the lead PI, and the originals will be included with the samples in the sample cooler(s). The following guidelines will be followed to ensure consistent shipping procedures and to maintain the integrity of the samples:

- Each COC/SAR form must be appropriately signed by the sampling personnel. The person who relinquishes custody of the samples must also sign this form.
- The COC/SAR form should not be signed until the information has been checked for inaccuracies by the field team leader. All changes should be made by drawing a single line through the incorrect entry and initially and dating it- as per Good Laboratory Practices (GLP). Revised entries should be made in the space below the entries. Any blank lines remaining on the

COC/SAR form after corrections are made should be marked out with single lines. This procedure will preclude any unauthorized additions.

- At the bottom of each COC/SAR form is a space for the signatures of the persons relinquishing and receiving the samples and the time and date that the transfer occurred. The time that the samples were relinquished should match exactly the time they were received by another party. Under no circumstances should there be any time when custody of the samples is undocumented.
- If samples are sent by a commercial carrier not affiliated with the laboratory, such as via FedEx or UPS, the name of the carrier should be entered in the “received by” block. Any tracking numbers supplied by the carrier should also be entered in the “Received by” block. The time of transfer should be as close to the actual drop-off time as possible. After the COC/SAR forms are signed and copied, they should be sealed inside the transfer container.
- If errors are found after the shipment has left the custody of the field personnel, a corrected version of the forms must be made and sent to all relevant parties. Minor errors can be rectified by making a change on a copy of the original with a brief explanation and signature. Errors in the signature block may require a follow-up letter of explanation.

Revision No. 0
June 25, 2013

SOP – 03
Sample Packaging and Shipping

Specific requirements for sample packaging and shipping must be followed to ensure the proper transfer and documentation of environmental samples collected during field operations. Procedures for the careful and consistent transfer of samples from the field to the laboratory are outlined in this Standard Operating Procedure (SOP).

EQUIPMENT REQUIRED

Specific equipment or supplies necessary to properly pack and ship environmental samples include the following:

- Gel packs, frozen Blue Ice, or dry ice (Depending on project and individual sample requirements)
- Sealable airtight bags (Assorted sizes)
- Large, plastic garbage bags
- Paper towels
- Coolers
- Bubble wrap
- Fiber reinforced packing tape
- Duct tape
- Clear plastic packing tape
- Scissors
- Chain-of-custody seals
- Specialized labels (e.g., “Fragile”, “This end up”, or “Handle with care”)
- Mailing/Airbill labels
- Airbills for overnight shipment
- Chain-of-custody record/Sample analysis request (COC/SAR) forms

PROCEDURE

The logistics for sample packaging and shipping should be specifically tailored to each study. In some cases, samples may be transferred from the field to a local storage facility where they can be either frozen or refrigerated. Depending on the logistics of the operation, field personnel may transport samples to the laboratory themselves or utilize an overnight courier service. If a courier service is used, then field personnel need to be aware of any potentially limiting factors to timely shipping (e.g., availability of overnight service and weekend deliveries to specific areas of the country, shipping regulations “restricted articles”, such as dry ice and formalin) prior to shipping the samples.

The following steps should be followed to ensure the proper transfer of samples from the field to the laboratories:

In the Field (Sample Collection Site):

1. Appropriately document all samples using a logbook, the required sample container identification (i.e., sample labels and sample tags) and a COC/SAR form. Fill out the COC/SAR form as per SOP- 02, Sample Custody.
2. Make sure all applicable laboratory quality control sample designations have been made on the COC/SAR form. Samples that will be archived for future possible analysis should be clearly identified on the COC/SAR form by noting the following: "Do Not Analyze: Hold and Archive for Possible Future Analysis", because some laboratories interpret "Archive" to mean continue holding the residual sample (e.g., extract) after analysis.
3. Clean the gross contamination from the outside of all dirty sample containers to remove any residual material that may lead to cross-contamination.
4. Store each sample container in an individual sealable plastic bag that allows the sample label to be read. Volatile organic analyte (VOA) vials for a single sample must be encased in bubble wrap before being sealed in bags.
5. If the samples have a required storage temperature, place a sufficient amount of frozen gel packs (or similar) in the sample cooler to maintain the temperature inside the cooler (e.g., 4° C) throughout the sampling day.

In the Field (Sample Processing):

1. If the samples have a required storage temperature, then the samples should be cooled to and maintained at that temperature prior to shipping. For example, a sufficient amount of frozen gel packs (or similar) must be present in each sample cooler to maintain the temperature inside the cooler at 4° C until processing begins to ship the samples to the testing laboratory.
2. Be aware of any holding time requirements for project-specific analytes and arrange the sample shipping schedule accordingly. For example, some water samples for organics analysis have limited holding time periods of 7-days.
3. Samples will be placed in secure storage or remain in the field personnel's possession until they are shipped to maintain sample integrity and COC requirements.
4. Samples should be stored in the dark (e.g., cooler tops shut and/or inside a dark freezer or refrigerator).

In the Field (Immediately Prior to Shipping):

1. Check sample containers against the COC/SAR form(s) to ensure all samples intended for shipment are accounted for (and that sample label information is correctly entered into COC/SAR form).

2. Choose the appropriate size cooler(s) and make sure that the outside of the cooler is clean of gross contamination. If the cooler has a drain on the outside at the bottom of the cooler, the drain should be capped and thoroughly taped shut with duct tape to prevent leakage.
3. The cooler should be lined with bubble wrap and a large plastic bag should be opened and placed inside the cooler. (Typically commercial carriers will not transport leaking coolers).
4. Individually wrap each glass container (which at the sample collection site had already been placed in an individual sealable plastic bag) in bubble wrap. Place the wrapped samples into the large plastic bag in the cooler; leaving sufficient room for ice to keep the samples cold (e.g., 4°C).
5. If the samples have a required storage temperatures, add enough frozen gel packs (or similar) to keep the samples refrigerated during overnight shipping. Always over-estimate the amount of frozen gel packs that you think will be required. Avoid separating the samples from the gel packs with excess bubble wrap because it will insulate the containers from the ice. After all samples and ice have been added to the cooler, use bubble wrap to fill any empty space to keep the samples from shifting during transport.
6. If possible, consolidate all VOA samples in a single cooler (where applicable) and ship them with a trip blank (or blanks) if the quality assurance project plan (QAPP)_ calls for one.
7. If temperature blanks have been provided by the testing laboratory, include one temperature blank in each sample cooler.
8. Sign, date, and include any tracking numbers provided by the shipper on the COC/SAR form. Remove the back copy of the original COC/SAR form (or the 3rd triplicate copy- if electronically generated) and retain this copy for the project records.
9. Place the rest of the signed COC/SAR form(s) in a sealable bag and tape the bag containing the form to the inside of the cooler lid. Each cooler should contain an individual COC/SAR form(s) for the samples contained in each respective cooler. If time constraints impact sample shipping and it becomes necessary to combine all of the samples into a single set of COC/SAR form(s) and the shipment contains multiple coolers, indicate on the outside of the respective cooler “Chain of Custody Inside”.
10. After the cooler is sufficiently packed to prevent shifting of the containers, close the lid and seal it shut with fiber-reinforced packing tape. The cooler should be taped shut around the opening between the lid and the bottom of the cooler and around the circumference of the cooler at both hinges.
11. As security against unauthorized handling of the samples, apply two chain-of-custody seals across the opening of the cooler lid. Once seal should be placed on the front of the cooler and one seal should be placed on the side of the cooler opposite the first seal. Be sure the seals are properly affixed to the cooler so they are not removed during shipment. Additional tape across the seal may be necessary if the outside of the cooler is wet.
12. Use a mailing label and label the cooler with destination and return address, and add other appropriate stickers, such as “This End Up”, “Fragile”, and “Handle with Care”. If the shipment contains multiple coolers, indicate on the mailing label the number of coolers that the testing laboratory should expect to receive (e.g., 1 of 2, 2 of 2). Place clear tape over the mailing label to

firmly affix it to the outside of the cooler and to protect it from the weather. This is a secondary label in case the airbill is lost during shipment.

13. If an overnight courier is used, fill out the airbill as required and fasten it to either the top of the cooler or to handle tags as provided by the shipper. In addition to the adhesive backing on many airbills, the airbill and/or mailing label should also be taped to the lid, because tracking problems can occur if a sticker is removed during shipment.
14. If samples need to be frozen (e.g., -20°C) during shipping, then dry ice will need to be placed in the sample cooler. Be aware of any additional shipping, handling, and special labeling requirements that may be required by the shipper for these samples.
15. Benthic infauna samples will need to be preserved with formalin in the field prior to shipping. Be aware of any additional shipping, handling, and special labeling requirements that may be required by the shipper for these samples.
16. If samples are shipped that contain “restricted articles” (e.g., dry ice, formalin), a 24-hour emergency contact number must be provided to the shipper by the field personnel.
17. Notify the laboratory contact that the samples will be shipped and the estimated arrival date and time. All environmental samples that are shipped at either 4°C or at -20°C will be shipped overnight for next morning delivery.

FAIRWEATHER SCIENCE

Revision No. 0
June 25, 2013

SOP – 04
Decontamination of Equipment – Sediments

To prevent potential cross contamination of samples, all reusable sediment sampling and processing equipment will be decontaminated prior to the start of sampling each day, and before each use of the sampling equipment. At the sample collection site, a decontamination area will be established in a clean location, upwind of actual sampling locations, if possible. This is where all sediment sampling and processing equipment will be cleaned. Decontaminated equipment will be stored away from areas that may cause recontamination, and rinsate blanks will be collected during field activities. When handling decontamination chemicals, field personnel will follow all relevant procedures and will wear protective clothing as stipulated in the site-specific health and safety plan.

This Standard Operating Procedure (SOP) describes procedures for decontaminating sampling and processing equipment contaminated by either inorganic or organic materials. Sampling equipment (e.g., van Veen grab, Ekman grab, Ponar grab, core tubes) used for both analyte groups follow the decontamination order of a detergent wash, site water rinse, organic solvent rinses, and final site water rinse. Sample processing equipment, such as scoops and spoons, should have a final distilled/deionized water rinse instead of a site water rinse. If the surface of stainless steel equipment appears to be rusting (possibly due to prolonged contact with organic-rich sediment), it should be given an acid and site water rinse at the end of each sampling day to minimize corrosion. If site water contamination is an issue (e.g., visible oil film), the solvent rinse as the final decontamination rinse may be necessary. This decision should be made by the chief field scientist.

REQUIRED EQUIPMENT

Equipment required for decontamination includes the following:

- Polyethylene or polypropylene tub (to collect solvent rinsate)
- Plastic bucket(s), such as 5-gal buckets
- Tap water or site water
- Stainless steel pump (e.g., for on-vessel site water)
- Carboy, distilled/deionized water (Analyte-free; received from testing laboratory of other reliable source)
- Properly labeled squirt bottles
- Funnels
- Alconox®, Liquinox®, or other equivalent industrial detergent
- Pesticide-grade ethanol and heptane (depending on project-specific field sampling plan (FSP) or sampling and analysis plan (SAP), because the solvents may vary by EPA region or state)

- 10 percent (v/v) nitric acid (Reagent grade) for inorganic contaminants
- Baking soda
- Long handled, hard-bristle brushes
- Extension arm for cleaning core liners
- Plastic sheeting, garbage bags, and aluminum foil (except for sampling for trace metals contamination)
- Core liner caps or plastic wrap and rubber bands
- Personal protective equipment as specified in the health and safety plan

DECONTAMINATION PROCEDURES FOR FULL SUITE ANALYSIS (ORGANIC, METAL, AND CONVENTIONAL ANLYTES)

Two organic solvents are used in this procedure. The first is miscible with water (e.g., ethanol) and is intended to scavenge water from the surface of the sampling equipment and allow the equipment to dry quickly. This allows the second solvent to fully contact the surface of the sampler. Make sure that the solvent ordered is anhydrous or has a very low water content (i.e., <%). If ethanol is used, make sure that the denaturing agent in the alcohol is not an analyte of interest in the samples. The second organic solvent is hydrophobic (e.g., heptane) and is intended to dissolve any organic chemicals that are on the surface of the equipment.

The exact solvents used for a given project may vary by EPA region or state (see project- specific Field Sampling Plan (FSP) or Sampling and Analysis Plan (SAP)). Typically ethanol and heptane are preferred solvents for equipment decontamination. If specified in the FSP or SAP, isopropanol and acetone can be substituted for ethanol, and hexane and methanol can be substituted for heptane in the decontamination sequence. The choice of solvents is also dependent on the kind of material from witch the equipment is made (e.g., acetone cannot be used on polycarbonate) and the ambient temperature (e.g., acetone and hexane are quite volatile and may not be appropriate in hot climates). In addition, although methanol and hexane are sometimes slightly more effective than other solvents, their use is discouraged due to toxicity to sampling personnel.

The specific procedures for decontaminating sediment sampling equipment and sediment compositing equipment are as follows:

1. Rinse the equipment thoroughly with tap or site water to remove visible sediment. This step should be performed onsite for all equipment, including sediment core liners that will not be used again until the next day of sampling. After removing visible solids, sampling equipment that does not need to be used again that day may be set aside and thoroughly cleaned in the field laboratory at the end of the day.
2. Pour a small amount of concentrated laboratory detergent into a bucket (i.e., about 1-2 tablespoons per 5-gallon bucket) and fit it halfway with tap or site water. If the detergent is in crystal form, all crystals should be completely dissolved prior to use.

3. Scrub the equipment in the detergent solution using a long-handled brush with rigid bristles. For the polycarbonate core liners, use a round brush attached to an extension arm to reach the entire inside of the liners, scrubbing with a back-and-forth motion. Be sure to clean the outside of core liners, bowls, and other pieces that may be covered with sediment.
4. Double rinse the equipment with tap or site water and set right-side-up (where applicable) on a stable surface to drain. The more completely the equipment drains, the less solvent will be needed in the next step. Do not allow any surface that will come in contact with the sample to touch any contaminated surface.
5. If the surface of stainless steel equipment appears to be rusting (This will occur during prolonged use in anoxic marine sediments), the surface requires passivation. Otherwise, skip to the next step. Using a 10% (v/v) nitric acid solution (ultra-high purity grade), rinse using a squirt bottle, or wipe all surfaces using a saturated paper towel. Areas showing rust may require some rubbing with the paper towel. If using a squirt bottle, let the excess acid drain into the waste container (which may need to be equipped with a funnel). Double-rinse equipment with tap or site water and set it right-side-up (where applicable) on a stable surface to drain thoroughly.
6. Carefully rinse the equipment with ethanol from a squirt bottle and let the excess solvent drain into a waste container (which may need to be equipped with a funnel). These solvents act primarily as a drying agent by scavenging water from the equipment surface and carrying it away, but they also work as a solvent for some organic contamination. Sediment core liners must be held over the waste container and turned slowly so the stream of solvent contacts all of the surface. The sample apparatus (e.g., grab sampler) may be turned on its side (if small enough) and opened to be washed more effectively. In the event that a larger sampling unit (e.g., double van veen grab sampler) is used, it may be necessary to open and close the jaws multiple times and direct site water through a hose from underneath the openings to remove debris entrained in the corners of the unit. The equipment should be allowed to air dry in a clean location (whenever possible). Use only enough solvent to scavenge all of the water and flow off the surface of the equipment (i.e., establish sheet flow) into the waste container. Allow equipment to drain as much as possible. Ideally, the equipment will be dry. The more thoroughly it drains, the less solvent will be required in the following step.
7. Carefully rinse the drained or air-dried equipment with heptane from a squirt bottle, and let the excess solvent drain into the waste container (which may need to be equipped with a funnel). The opening of the squirt bottle may need to be widened to allow enough solvent to run through the sediment core liners without evaporating. Heptane primarily acts to clean the equipment from organic contamination (as opposed to a drying solvent). Ethanol is soluble in heptane, but water is not. If water beading occurs, it means that the equipment was not thoroughly rinsed with ethanol or that the ethanol that was purchased was not free of water. When the equipment has been rinsed with heptane, set it in a clean location and allow the heptane to evaporate before using the equipment for sampling. Use only enough solvent to scavenge all of the ethanol and flow off the surface of the equipment (i.e., establish sheet flow) into the waste container.

8. Under certain sampling conditions (e.g., remote, off-shore field sampling from a vessel), use of large equipment would require excessive use of solvent(s) for the decontamination procedure. In these instances, the solvent rinse process can be replaced by the use of acetone (or similar solvent) wipes. However, in the event that gross contamination (e.g., oiled equipment) is observed, solvent rinsing is imperative.
9. The final rinse is with site water for the sampling equipment (e.g., van veen grab, Ekman grab) and distilled/deionized water for processing equipment (e.g., compositing bowls and spoons). Equipment does not need to be dried before use.
10. If the decontaminated sampling equipment is not to be used immediately, wrap small stainless-steel items in aluminum foil (dull side facing the cleaned area). Seal the polycarbonate core liners at both ends with either core caps or cellophane plastic and rubber bands. Close the jaws of the grab samplers.
11. If the sample collection, processing equipment, or sample jar containers are cleaned/decontaminated prior to the field (or certified by the vendor, e.g., pre-cleaned sample jars), they should be stored covered and protected from field contamination prior to use.
12. Rinse or wipe with a wetted paper towel all stainless-steel equipment at the end of each sampling day with 10% (v/v) nitric acid solution. Follow with a freshwater rinse (site water is fine as long as it is not brackish or salt water).

After decontamination of the sampling equipment, the disposable gloves and used foil will be placed in garbage bags and disposed of in a solid waste landfill. When not in use, keep the waste solvent container closed and store in a secure area. The waste solvent should be transferred to empty solvent bottles and disposed of at a licensed facility per the procedures listed in the FSP or SAP. When not in use, keep the waste acid container closed and store in a secure area. The acid waste should be neutralized with baking soda and disposed of per the procedures listed in the FSP or SAP.

DECONTAMINATION PROCEDURES FOR METAL AND CONVENTIONAL ANALYTES ONLY

The specific procedures for decontaminating sediment sampling equipment and sediment processing equipment are as follows:

1. Rinse the equipment thoroughly with tap or site water to remove the visible sediment. This step should be performed onsite for all equipment including core liners that will not be used again until the next day of sampling. Pieces that do not need to be used again that day may be set aside and thoroughly cleaned in the field laboratory at the end of the day.
2. Pour a small amount of concentrated laboratory detergent into a bucket (i.e., pour about 1-2 tablespoons per 5-gallon bucket) and fill it halfway with tap or site water. If the detergent is in crystal form, all crystals should be completely dissolved prior to use.
3. Scrub the equipment in the detergent solution using a long-handled brush with rigid bristles. For the polycarbonate core liners, use a round brush attached to an extension arm to reach the entire inside of the liners, scrubbing with a back-and-forth motion. Be sure to clean the outside of core liners, bowls, and other pieces that may be covered with sediment.

4. Double rinse the equipment with tap or site water and set right-side-up (where applicable) on a stable surface to drain. The more completely the equipment drains, the less solvent will be needed in the next step. Do not allow any surface that will come in contact with the sample to touch any contaminated surface.
5. If the surface of stainless steel equipment appears to be rusting (This will occur during prolonged use in anoxic marine sediments), the surface requires passivation. Otherwise, skip to the next step. Using a 10% (v/v) nitric acid solution (ultra-high purity grade), rinse using a squirt bottle, or wipe all surfaces using a saturated paper towel. Areas showing rust may require some rubbing with the paper towel. If using a squirt bottle, let the excess acid drain into the waste container (which may need to be equipped with a funnel). Double-rinse equipment with tap or site water and set it right-side-up (where applicable) on a stable surface to drain thoroughly. Double rinse processing equipment with distilled/deionized water and allow to drain.
6. Sample processing equipment used for trace metals analysis should be Teflon or Kynar coated (not metal) and should be stored in plastic bags following decontamination (if not used immediately). Similar to the procedures for organics decontamination, the jaws of the grab(s) should be stored closed prior to decontamination.
7. If the sample collection, processing equipment, or sample jar containers are cleaned/decontaminated prior to the field (or certified by the vendor, e.g., pre-cleaned sample jars), they should be stored covered and protected from field contamination prior to use.

After decontamination of the sampling equipment, the disposable gloves and used foil will be placed in garbage bags and disposed of in a solid waste landfill. When not in use, keep the waste acid container closed and stored in a secure area. The acid waste should be neutralized with baking soda and disposed of per the procedures listed in the project-specific FSP or SAP.

SOP – 05 Preparation of Field Quality Control Samples – Sediment

This SOP describes the purpose, preparation, and collection frequency of field duplicate samples, field replicate samples, matrix spike/matrix spike duplicates, equipment rinsate blanks, bottle blanks, trip blanks, temperature blanks, environmental blanks, and reference materials (i.e., a standard reference material, a certified reference material, or other reference material (SRM acronym applied to all three reference material types) for sediment samples. Not all of the field quality control (QC) samples discussed in this SOP may be required for a given project. The specific field quality control samples will be identified in the project-specific field sampling plan (FSP) or sampling and analysis plan (SAP) and quality assurance project plan (QAPP). For most projects, the recommended field QC samples are: an equipment rinsate blank, a field duplicate, and trip blanks if volatile organic compounds (VOCs) are to be analyzed. Definitions of all potential QC samples are described below.

As part of the quality assurance/quality control (QA/QC) program, all field QC samples will be sent to the laboratories blind. To accomplish this, field QC samples will be prepared and labeled in the same manner as regular samples, with each QC sample being assigned a unique sample number that is consistent with the numbering for regular samples. All of the containers with preservatives that are required to complete the field QC sample for the applicable analyte list shall be labeled with the same sample number. The sample ID for field quality control samples should allow data management and data validation staff to identify them as such and should only be recorded in the field logbook. Under no circumstances should the laboratory be allowed to use FIELD reference materials, rinsate blanks or trip blanks for LABORATORY QC analysis (i.e., lab duplicates, matrix spikes/matrix spike duplicates). To prevent this from happening, regular samples should be selected and marked on the chain-of-custody/sampling analysis request (COC/SAR) form or the laboratory should be instructed to contact the project QA/QC coordinator to select appropriate samples for each sample group.

All field quality control samples will be packaged and shipped with other samples in accordance with the procedures outlined in SOP – 03, Sample Packaging and Shipping. Sample custody will be maintained in accordance with the procedures outlines in SOP – 02 Sample Custody.

Field quality control samples will be prepared at least once per sampling event and certain types will be prepared more often at predetermined frequencies. If the number of samples taken does not equal an integer multiple of the intervals specified in this SOP, the number of field quality control samples is specified by the next higher multiple. For example, if a frequency of 1 quality control sample per 20 is indicated and 28 samples are collected, 2 quality control samples will be prepared. The text below describes the preparation and frequency of field quality control samples required for sediment sampling activities, and shall be followed unless different frequency requirements are listed in the FSP/SAP and QAPP.

The following table (Table 1) lists the quality control sample types and suggested frequencies for sediment sampling programs. Because sediment quality control sampling may require assessment of site cross-contamination, additional blanks may be required. A detailed explanation of each quality control sample type with the required preparation follows this table.

Table 1. Field quality control (QC) sample requirements for sediment sampling.

Quality Control Sample Name	Abbreviation	Preparation		
		Location	Method	Frequency[1]
Duplicate	DUP	Sampling Site	Additional natural sample	One per 20 samples. May not be applicable if REP is being collected.
Replicate	REP	Sampling Site	Additional natural sample	One replicate per 20 samples. May not be applicable if DUP is being collected.
Matrix Spike/Matrix Spike Duplicate	MS/MSD	Sampling Site	Additional sample bottles filled for laboratory quality control requirements	One per 20 samples.
Equipment Rinsate Blank	ER	Sampling Site	Deionized water collected after pouring through and over decontaminated equipment	Minimum of one per sampling equipment used and then 1:20 thereafter.
Bottle Blank	BB	Field	Unopened bottle	One per sample episode or one per bottle type.
Trip Blank	TB	Laboratory	Deionized water with preservative	One pair per each VOC sample cooler shipment.
Temperature Blank	TMB	Laboratory	Deionized water	One per sample cooler.
Environmental Blank	EB	Field	Bottle filled at sample site with DI water	One per 20 samples.
Standard Reference Material	SRM	Field, Laboratory, or Sampling Site	SRM ampules or other container for each analyte group	One set per 50 samples or one per episode.

1. Frequencies provided in this table are general recommendations; project-specific frequencies are provided in the project-specific FSP/SAP and QAPP.

FIELD DUPLICATE SAMPLES

Field duplicate (or split) samples are collected to assess the homogeneity of the samples collected in the field and the precision of the sampling process. Field duplicates will be prepared by collecting two aliquots for the sample and submitting them for analysis as separate samples. Field duplicates will be collected at a minimum frequency of 1 per 20 samples or once per sampling event, whichever is more frequent. The actual number of field duplicate samples collected during a sampling event will be determined on a case-by-case basis by the project QA/QC coordinator and/or Field Team Lead (consult the project-specific FSP/SAP and QAPP). These requirements may vary by EPA region or state.

FIELD REPLICATE SAMPLES

Field replicate samples are co-located samples collected in an identical manner over a minimum period of time to provide a measure of the field and laboratory variance, including variance resulting from sample heterogeneity. Field replicates will be prepared by collecting two completely separate samples from the same station and submitting them for analysis as separate samples. Field replicates will be collected at a minimum frequency of 1 per 20 samples or once per sampling event, whichever is more frequent. If field duplicate samples are collected, then it is unlikely that field replicate samples will also be collected during the field sampling event. The actual number of field replicate samples collected will be determined on a case-by-case basis by the project QA/QC coordinator and/or the Field Team Lead (consult the project-specific FSP/SAP and QAPP). These requirements may vary by EPA region or state.

MATRIX SPIKE/MATRIX SPIKE DUPLICATES

The matrix spike/matrix spike duplicate (MS/MSD) analyses provide information about the effect of the sample matrix on the design and measurement methodology used by the laboratory. To account for the additional volume needed by the laboratory to perform the analyses, extra sample volumes may be required to be collected from designated sediment stations. MS/MSDs may be collected at a minimum frequency of 1 per 20 samples or once per sampling event, whichever is more frequent. The actual number of field replicate samples collected will be determined on a case-by-case basis by the project QA/QC coordinator and/or the Field Team Lead (consult the project-specific FSP/SAP and QAPP). These requirements may vary by analyte group.

EQUIPMENT RINSATE BLANKS

Equipment rinsate blanks will be used to help identify possible contamination from the sampling environment and/or from decontaminated sampling equipment. Equipment rinsate blanks will be prepared by pouring laboratory distilled/deionized water through, over, and into the decontaminated sample collection equipment, then transferring the water to the appropriate sample containers and adding any necessary preservatives. Equipment rinsate blanks will be prepared for all inorganic, organic, and conventional analytes at least once per sampling event per type of sampling equipment used. The actual number of equipment rinsate blanks prepared during an event will be determined on a case-by-

case basis by the project QA/QC coordinator and/or the Field Team Lead (consult the project-specific FSP/SAP and QAPP). These requirements may vary by EPA region or state.

BOTTLE BLANKS

The bottle blank is an unopened sample bottle. Bottle blanks are submitted along with sediment samples to ensure that contaminants are not originating from the bottles themselves because of improper preparation, handling, or cleaning techniques. If required, one bottle blank per lot of prepared bottles will be submitted for analysis. If more than one type of bottle will be used in the sampling (e.g., HDPE and glass), then a bottle blank should be submitted for each type of bottle and preservative. The actual number of bottle blanks analyzed during a project will be determined on a case-by-case basis by the project QA/QC coordinator and/or the Field Team Lead (consult the project-specific FSP/SAP and QAPP). These requirements may vary by EPA region or state.

TRIP BLANKS

Trip blanks will be used to help identify whether contaminants may have been introduced during the shipment of the sediment samples from the field to the laboratory for VOC analyses only. Trip blanks are prepared at the testing laboratory by pouring distilled/deionized water into two 40-mL VOC vials and tightly closing the lids. Each vial will be inverted and tapped lightly to ensure no air bubbles exist.

The trip blanks will be transported unopened to and from the field in the cooler with the VOC samples. A trip blank shall be labeled and placed inside the cooler that contains newly collected VOC samples and it shall remain in the cooler at all times. A trip blank must accompany samples at all times in the field. One trip blank (consisting of a pair of VOC vials) will be sent with each cooler of samples shipped to the testing laboratory for VOC analysis.

TEMPERATURE BLANKS

Temperature blanks will be used by the laboratory to verify the temperature of the samples upon receipt at the testing laboratory. Temperature blanks will be prepared at the testing laboratory by pouring distilled/deionized water into a vial and tightly closing the lid. The blanks will be transported unopened to and from the field in the cooler with the sample containers. A temperature blank shall be included with each sample cooler shipped to the testing laboratory.

FIELD BLANKS

The field blank is prepared in the field to evaluate potential background concentrations present in the air and in the distilled/deionized water used for the final decontamination rinse. If unpreserved bottles are to be used, then the appropriate preservative (i.e., for metals samples use a 10% nitric acid solution to bring sample pH to 2 or less) must be added, as required. Field blanks should be collected at a minimum frequency of 1 in 20 samples. The actual number of field blanks analyzed during a project will be determined on a case-by-case basis by the project QA/QC coordinator and/or the Field Team Lead (consult the project-specific FSP/SAP and QAPP). These requirements may vary by EPA region or state.

To prepare a field blank in the field, open the laboratory-prepared sample bottle while at a sample collection site, fill the sample bottle with distilled/deionized water and then seal. Assign the field blank a unique sample number, label the bottle, and then send the bottle to the laboratory with the field samples according to SOP – 03, Sample Packaging and Shipping.

REFERENCE MATERIALS

Reference materials are samples containing known analytes at known concentrations that have been prepared by and obtained from EPA-approved sources. The SRMs have undergone multi-laboratory analysis using a standard method which provides certified concentrations. When available for a specific analyte, SRM samples provide a measure of analytical performance and/or analytical method bias (i.e., accuracy) of the laboratory. Several SRMs may be required to cover all analytical parameters. For all analytes where available, one SRM will be analyzed at a frequency of 1 per 50 samples. The actual number of SRMs analyzed during a project will be determined on a case-by-case basis by the project QA/QC coordinator and/or the Field Team Lead (consult the project-specific FSP/SAP and QAPP). These requirements may vary by EPA region or state.

SOP – 06 Surface Sediment Sampling Using a Modified van Veen Grab Sampler

This SOP describes the procedures used to collect surface sediment with a modified van Veen grab sampler. For the purposes of this SOP, surface sediment is defined as the upper 10cm of the sediment column, but may vary given the sampling interval specified in the study design (project specific field sampling plan (FSP) or sampling and analysis plan (SAP)). Surface sediment is typically analyzed for various physical and chemical variables so the sampling equipment and sampling procedures must be compatible with all analyses.

A modified stainless-steel van Veen grab sampler is capable of collecting acceptable samples from a variety of substrates such as mud, sand, gravel, and pebbles (APHA 1989, U.S. EPA 2001). The modified van Veen grab sampler incorporates several design improvements over the traditional van Veen grab sampler, which improves the quality of the sediment samples. The modified grab sampler has two doors on top to allow easy access to the sample for visual characterization and subsampling of undisturbed surface sediments. The interiors of the doors are made of screens to minimize the bow wake and the resulting disturbance of the sediment surface when the grab sampler is lowered to the bottom. Rubber flaps cover each screen as the grab sampler is retrieved to prevent disturbing the sediment sample as it is raised through the water column. The arms of the modified grab sampler are lengthened and arced to provide a stronger seal when the grab sampler is closed, thereby minimizing sample leakage when the grab sample is retrieved. Finally, the modified grab sampler has four detachable, epoxy-coated lead weights that allow the weight and penetration of the grab sampler to be optimized with respect to the kind of sediment being sampled. The procedures for collecting surface sediment samples using the modified van Veen grab sampler are described below.

EQUIPMENT AND SUPPLIES REQUIRED

Equipment required for sediment sampling using the van Veen grab sampler includes the following:

- Stainless-steel van Veen grab sampler (typically $0.06m^2$ or $0.1m^2$) and spare parts (also applicable to this SOP would include a double van Veen grab sampler)
- Winch and hydrowire (With load capacities ≥ 3 times the weight of a full sampler)
- Sample collection table
- Teflon® or polyethylene siphon (inner diameter = 1.27cm, length = 60-90cm)
- Stainless-steel ruler
- Stainless-steel spoons/spatulas (or Kynar® coated)
- Stainless-steel mixing bowl or pot (or Teflon® coated)
- Socket and crescent wrenches (for adding or removing the detachable weights of the grab sampler)

- Water pump and hose (for rinsing the grab sampler, sampling utensils, and sample collection table

DECONTAMINATION

To prevent potential cross-contamination of samples, all reusable sediment sampling equipment must be decontaminated. Before each station is sampled, decontaminate the inner surfaces of the grab sampler and all stainless-steel sample compositing equipment. Details on correct decontamination procedures can be found in SOP – 04; Decontamination of Equipment – Sediment. The project-specific FSP or SAP should also be consulted to determine and project-specific decontamination procedures. The personnel performing the decontamination procedures will wear protective clothing as specified in the site-specific health and safety plan (HSP).

All solvent rinsates (if applicable) will be collected into a bucket or tub and allowed to evaporate over the course of the day. Any rinsate that has not been evaporated by the end of the sampling even will be containerized and disposed of in accordance with applicable regulations.

GRAB SAMPLER DEPLOYMENT

[Note: On some vessels, the deployment of the grab sampler will be conducted by marine technicians provided by the vessel operators]

1. Attach the grab sampler to the hydrowire with a swivel. The swivel minimized the twisting forces on the sampler during deployment and ensures that proper contact is made with the bottom. For safety, the hydrowire, swivel, and all shackles should have a load capacity at least 3 times the weight of a full sampler.
2. Place the decontaminated grab sampler on a clean surface (i.e., the sample collection table) and open it.
3. Ensure that the two release chains and the two retrieval chains are hanging free and are not wrapped around the arms of the sampler.
4. Ensure that all doors are firmly latched shut.
5. Attach the ring of the release chains to the release mechanism and insert the safety pin to prevent the mechanism from being activated prematurely.
6. Start the winch, raise the release mechanism and the sampler and swing it outboard.
7. Remove the safety pin from the trigger, and lower the sampler through the water column at a slow and steady speed (e.g., 30cm/second).
8. Allow the grab sampler to contact the bottom gently, with only its weight being used to force it into the sediments. The sampler should never be allowed to “free fall” to the bottom because this may result in premature triggering, and excessive bow wake, or improper orientation upon contact with the bottom.
9. Allow approximately 60 cm of slack in the hydrowire after contact with the bottom to ensure that the release mechanism is activated.

GRAB RETREIVAL

1. After the grab sampler has rested on the bottom for approximately 5 seconds, begin retrieving it at a slow and steady rate (e.g., 30cm/second). Note: the amount of time that the grab sampler rests on the bottom is dependent on the kind of substrate (e.g., sediment with a high moisture content will required less time on the bottom to avoid over-penetration).
2. Ensure that the sampling vessel is not headed into any waves before the sampler breaks the water surface to minimize vessel rolling and potential sample disturbance.
3. Care must be taken to avoid loss of fine-grained surface sediments, mixing or sediment layers upon impact, lack of sediment penetration, and loss of sediment from tilting or washout upon ascent.
4. After the grab sampler breaks the water surface and is raised above the height of the sample collection table, swing the grab sampler inboard, keep the sampler in an upright position and gently lower it onto the table, maintaining the tension of the hydrowire to prevent the grab sampler from rolling when it contacts the table. Avoid quick movements of the sampler, especially rotation, as this could disrupt the interface.
5. When the grab sampler contacts the table, insert wedges under both jaws to that the grab sampler will be help in an upright position when tension on the hydrowire is relaxed.
6. Relax the tension on the hydrowire, and remove the release and retrieval chains from the surface of the grab sampler.
7. As soon as the grab sampler is secured, open the doors on the top of the grab sampler, and inspect the sample for acceptability. The following acceptability criteria should be satisfied:
    a. The sampler is not overfilled with sample to the point that the sediment surface presses against the top of the sampler or is extruded through the top of the sampler
    b. Overlying water is present (indicating minimal leakage)
    c. The overlying water is not excessively turbid (indicating minimal disturbance of the interface or winnowing)
    d. The sediment surface is relatively undisturbed; the sediment-water interface is intact and relatively flat with no sign of channeling or simple washout
    e. The desired penetration depth is achieved
    f. There is no sign of sediment loss (incomplete closure of the sampler, penetration at an angle, or tilting upon retrieval).

    If a sample fails to meet the above criteria, it will be rejected and discarded away from the station. The locations of consecutive attempts and replicate samples (if any) should be as close to the first sample as possible, and if sampling on a river or stream, consecutive attempts should be located upstream of previous samples. Rejected sediment samples should be discarded in a manner that will not affect subsequent samples at that station or other possible sampling stations.

Penetration depth should be determined with a decontaminated stainless-steel ruler by measuring the distance from the top of the sampler to the sediment interface and subtracting this from the inside depth of the sampler. If the sample is fairly level inside the sampler, this measurement can be made at one edge. If the sample is uneven but has an intact interface, then measurements should be made on opposite edges of the sample and the average value is used. This observation (i.e., that the sediment surface is slanted) and subsequent calculation of the average penetration depth should be recorded in the field logbook. If penetration depth is inadequate, add auxiliary weights.

SAMPLE REMOVAL AND PROCESSING

1. For acceptable samples, remove the overlying water by slowly siphoning it off near one or more sides of the grab sampler. Ensure that the siphon does not contact the sediments or that fine-grained suspended sediment is not siphoned off. If sediment is suspended in the overlying water, do not proceed with siphoning until the sediment is allowed sufficient time to settle.
2. After the overlying water is removed, characterize the sample as specified in the study design (FSP or SAP). Characteristics that are often recorded in the field logbook include:
    a. Sediment type (e.g., silt, sand)
    b. Texture (e.g., fine-grain, coarse, poorly sorted sand)
    c. Color
    d. Presence/location/thickness of the redox potential boundaries (a visual indication of black is often adequate for documenting anoxia)
    e. Approximate percentage of water
    f. Presence of biological structures (e.g., amphipods, tubes, macrophytes)
    g. Approximate percentage of biological structures
    h. Presence of debris (e.g., twigs, leaves, drill cuttings)
    i. Approximate percentage of organic debris
    j. Presence of shells
    k. Approximate percentage of shells
    l. Stratification, if applicable
    m. Presence of a sheen
    n. Odor (e.g., hydrogen sulfide, oil, creosote)
3. After the sample is characterized, remove the top 10cm using a stainless-steel spatula or spoon (or a Kynar® coated scoop, or equivalent). Unrepresentative material (e.g., large shells, stones) should be carefully removed without touching the sediment sample, under the supervision of the field team leader. This removal should be noted in the field logbook.
4. Remove subsamples for analysis of unstable constituents (e.g., volatile organic compounds, acid-volatile sulfides), and place them directly into sample containers without homogenization. Sediment must be placed in these containers with no headspace and no entrapped bubbles (i.e., completely fill the sample container).

5. Transfer the remaining surface sediment to a stainless-steel mixing bowl or equivalent (based on FSP or SAP) for homogenization. Additional grab samples may be required to collect the volume of sediment specified in the FAP/SAP. If it is necessary to collect additional grab samples to meet the project-specific volume requirements, the mixing bowl should be covered with aluminum foil (Dull side down), or clean plastic (depending on analytes of interest) to prevent sample contamination (e.g., from precipitation, splashing water) and placed out of the sun and away from heat.
6. After the surface sediment for a sample has been collected from the grab sampler, move the sampling vessel away from the station, open the jaws of the grab sample, attach the ring of the deployment chains to the release mechanism, insert the safety pin, start the winch, raise the grab sampler, and allow the remainder of the sediment sample to fall onto the sample collection table or into waste sediment collection buckets/tubs. Discard this material away from the station, and rinse away any sediment adhering to the inside of the grab sampler. The grab sampler is now ready for additional sampling at the same station or decontamination before sampling at a new station.
7. After a sufficient volume of sediment is transferred to the mixing bowl, homogenize the contents of the bowl using stainless-steel or Kynar® coated spoons until the texture and color of the sediment appears to be uniform.
8. After the sample is homogenized, distribute subsamples to the various containers specified in the FSP/SAP and preserve the samples as also specified in the FSP/SAP. The sediment in the mixing bowl should be briefly stirred in between the transfer of sediment to each sample container.
9. After all sediment for testing has been placed in the sample containers, if it is suspected that there is a clay component to the sediment, a “ribbon test” Should be performed on the sediment to confirm this suspicion. In this “texture-by-feel” test, a small piece of suspected clay is rolled between the fingers while wearing protective gloves. If the piece easily rolls into a ribbon, it is clay; it if breaks apart, it is silt. This information should be noted in the field logbook.

FIELD QUALITY CONTROL SAMPLES

Details on collection of field quality control samples and preparation of the certified reference materials, where relevant, are described in the project-specific FSP/SAP and QAPP documents.

FIELD MEASUREMENTS

A water depth measurement must be collected at every sampling location. For sites where tides affect water depth, the time of collection and depth measurement must be recorded simultaneously. Depending on the specific project objectives, it may be necessary to perform field measurements of the in situ environment. Possible field measurements include temperature and pH of the sediment at the sediment-water interface and concentration of dissolved oxygen, salinity, or conductivity in the

overlying water. Required field measurements are project-specific and will be specified in the relevant FSP/SAP documents.

STATION LOCATION COORDINATES

Station locations will be determined in accordance with the project-specific FSP/SAP. Generally, station locations for all field sampling will be determined using a differential global positioning system (DGPS), which is capable of provided latitude and longitude coordinates with an accuracy of approximately 2m. The DGPS consists of two satellite receivers linked to each other by a VHF telemetry radio system. The GPS receiver will be on the sampling vessel and positioned above where the grab sampler is deployed, or, alternatively an off-set specific to the location of deployment on the vessel will be used.

REFERENCES AND OTHER SOURCES

APHA. 1989. Standard methods for the examination of water and waste water. Seventeenth edition. Prepared and published by American Public Health Association, the American Water Works Association, and the Water Pollutant Control Federation.

U.S. EPA. 2001. Methods for collection, storage, and manipulation of sediments for chemical and toxicological analyses. Technical Manual. EPA-823-B-01-002. U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Washington, D.C.

SOP -07 Decontamination of Tissue Sampling Equipment

Whenever possible, it is best to have the analytical laboratory process the tissue sample under clean laboratory conditions to limit possible contamination from field processing. If, however, the tissue sample must be processed in the field, then the following decontamination procedures should be followed (see Sampling and Analysis Plan (SAP) and/or Field Sampling Plan (FSP) to determine if field processing is requires).

To prevent possible cross contamination of samples, all reusable field filleting and tissue processing equipment (e.g., knives, tweezers, spoons) will be decontaminated before each use (i.e., before processing begins and between each sample). The cutting board will be decontaminated before processing begins and a piece of clean, unused aluminum foil (except in the case of sampling for metals analysis) will be wrapped on top of the cutting board (dull side up) for each sample (i.e., the foil will be replaced after each sample has been processed). At the sample collection site, a decontamination area will be established in a clean location, upwind of the actual sampling processing location, if possible. This is where all field filleting and tissue processing equipment will be cleaned. Decontaminated equipment will be stored away from areas that may cause recontamination. Rinsate blanks will be collected according to SOP – 08 Preparation of Field Quality Control Samples – Tissue. When handling decontamination chemicals, field personnel will follow all relevant procedures and will wear protective clothing as stipulated in the site-specific health and safety plan (HSP).

This SOP describes procedures for decontaminating field filleting and tissue processing equipment contaminated by either inorganic or organic materials. Sampling equipment used for both can combine these procedures, following the order of a detergent wash, site water rinse, organic solvent rinses, and final distilled/deionized water rinse with an acid rinse of all stainless-steel equipment at the end of teach tissue processing field day.

EQUIPMENT REQUIRED

Equipment required for decontamination include the following:

- Plastic tub (to collect solvent rinsate)
- Plastic bucket(s)
- Tap water or site water
- Carboy, distilled/deionized water (Analyte-free; received from testing laboratory or oter reliable source)
- Properly labeled spray bottles
- Funnels
- Alconox®, Liquinox®, or equivalent detergent

- Pesticide-grade ethanol and heptane (consult the project specific SAP/FSP because the solvents may vary by EPA region or State)
- 10% (v/v) normal nitric acid (Trace metal grade) for inorganic contaminants
- Baking soda
- Hard-bristle scrub brush
- Plastic sheeting, garbage bags, and aluminum foil
- Core liner caps or plastic wrap and rubber bands
- Personal protective equipment as specified in the HSP

DECONTAMINATION PROCEDURES FOR FULL SUITE ANALYSIS (ORGANIC AND INORGANIC ANALYTES)

The specific procedures for decontaminating field filleting and tissue processing equipment are as follows:

1. Rinse the field filleting and tissue processing equipment thoroughly with tap or site water to remove most of the remaining gross solids. Pieces that do not need to be used again that day may be set aside and thoroughly cleaned in the field laboratory at the end of the day.
2. Pour a small amount (i.e., 0.5 teaspoons) of concentrated industrial detergent into a bucket and fill it with tap or site water. If the detergent is in crystal form, all crystals should be completely dissolved prior to use.
3. Scrub the equipment in the detergent solution using a brush with rigid bristles. Be sure to scrub with a back-and-forth motion.
4. Double rinse the equipment with tap or site water and set right-side-up on a stable surface to drain. Do not allow any surface that will come in contact with the tissue to touch any contaminated surface.
5. Carefully rinse the field filleting and tissue processing equipment with ethanol from a squirt bottle, and let the excess solvent drain into a waste container (Which may need to be equipped with a funnel). Ethanol acts primarily as a drying agent, but it also works as a solvent for some organic contamination. Set the equipment in a clean location and allow it to air dry. Use the ethanol sparingly and allow the ethanol to cascade down the surface of the equipment (i.e., the ethanol will “Sheet” over the equipment surface).
6. Carefully rinse the air-dried field filleting and tissue processing equipment with heptane from a squirt bottle, and let the excess solvent drain into the waste container (Which may need to be equipped with a funnel). The opening of the squirt bottle may need to be widened to allow enough solvent to run through the core liners without evaporating. Heptane acts as the primary organic solvent, but it is insoluble with water. If water beading occurs, it may mean that the equipment was not thoroughly rinsed with ethanol. When the equipment has been rinsed with heptane, set it in a clean location and allow the heptane to evaporate before using the equipment for tissue processing. Use the heptane sparingly and allow the heptane to cascade down the surface of the equipment (i.e., the heptane will “Sheet” over the equipment surface).

7. Rinse the field filleting and tissue processing sampling collection with a final distilled/deionized water rinse.
8. If the field filleting and tissue processing equipment is not to be used immediately, wrap them in aluminum foil (dull side facing the cleaned area), except in the case of analysis for metals (wrap in clean Ziploc® or equivalent plastic bags.
9. If the field filleting and tissue processing equipment are cleaned at the field laboratory and transported to the site, then the decontaminated equipment will be wrapped in aluminum foil (dull side facing the cleaned area) except in the case of metals (use plastic bags) and stored and transported in clean plastic bags until ready for use, unless alternative procedures are listed in the SAP/FSP.
10. Rinse all stainless-steel equipment at the end of each sampling day with 10% (v/v) normal nitric acid solution.

After decontamination of all of the field filleting and tissue processing equipment, the disposable gloves and used foil will be placed in garbage bags and disposed of in a solid waste landfill. When not in use, keep the waste solvent container closed and store in a secure area. The waste should be transferred to empty solvent bottles and disposed of at a licensed facility per the procedures listed in the project-specific SAP/FSP. When not in use, keep the waste acid container closed and store in a secure area. The acid waste should be neutralized with baking soda and disposed of as per the procedures listed in the project-specific SAP/FSP.

DECONTAMINATION PROCEDURES FOR INORGANIC ANALYTES ONLY

The specific procedures for decontaminating field filleting and tissue processing equipment are as follows:

1. Rinse the field filleting and tissue processing equipment thoroughly with tap or site water to remove most of the remaining (i.e., gross) solids. Pieces that do not need to be used again that day may be set aside and thoroughly cleaned in the field laboratory at the end of the day.
2. Pour a small amount (i.e., 0.5 teaspoons) of concentrated industrial detergent into a bucket and fill it with tap or site water. If the detergent is in crystal form, all crystals should be completely dissolved prior to use.
3. Scrub the equipment in the detergent solution using a brush with rigid bristles. Be sure to scrub with a back-and-forth motion.
4. Double rinse the equipment with tap or site water and set right-side-up on a stable surface to drain. Do not allow any surface that will come in contact with the tissue to touch any contaminated surface.
5. Carefully rinse the field filleting and tissue processing equipment with a 10% (v/v) normal nitric acid solution from a squirt bottle, and let the excess solvent drain into a waste container (Which may need to be equipped with a funnel). Use the acid sparingly and allow

the acid to cascade down the surface of the equipment (i.e., the acid will "Sheet" over the equipment surface).

6. Rinse the field filleting and tissue processing sampling collection with a final distilled/deionized water rinse.
7. If the field filleting and tissue processing equipment is not to be used immediately, wrap them in clean Ziploc® or equivalent plastic bags.
8. If the field filleting and tissue processing equipment are cleaned at the field laboratory and transported to the site, then the decontaminated equipment will be wrapped in plastic bags and stored and transported in additional clean plastic bags until ready for use, unless alternative procedures are listed in the SAP/FSP.

After decontaminating all of the field filleting and tissue processing equipment, the disposable gloves and used foil will be placed in garbage bags and disposed of in a solid waste landfill. When not in use, keep the waste acid container closed and store in a secure area. The acid waste should be neutralized with baking soda and disposed of per the procedures listed in the project-specific SAP/FSP.

SOP – 08 Preparation of Field Quality Control Samples – Tissue

This SOP describes the purpose, preparation, and collection frequency of field replicate samples, matrix spike/matrix spike duplicates, equipment rinsate blanks, trip blanks, temperature blanks, and reference materials (i.e., a standard reference material, a certified reference material, or other reference material; for the purposes of this document the acronym SRM will be used for all types of reference materials) for tissue samples. Not all of the field quality control (QC) samples discussed in this SOP may be required for a given project. The specific field quality control samples will be identified in the project-specific field sampling plan (FSP) or sampling and analysis plan (SAP) and quality assurance project plan (QAPP). For most projects, the recommended field QC samples are: an equipment rinsate blank, a field duplicate, and trip blanks if volatile organic compounds (VOCs) are to be analyzed. Definitions of all potential QC samples are described below.

As part of the quality assurance/quality control (QA/QC) program, all field QC samples will be sent to the laboratories blind. To accomplish this, field QC samples will be prepared and labeled in the same manner as regular samples, with each QC sample being assigned a unique sample number that is consistent with the numbering for regular samples. All of the containers with preservatives that are required to complete the field QC sample for the applicable analyte list shall be labeled with the same sample number. The sample ID for field quality control samples should allow data management and data validation staff to identify them as such and should only be recorded in the field logbook. Under no circumstances should the laboratory be allowed to use FIELD reference materials, rinsate blanks or trip blanks for LABORATORY QC analysis (i.e., lab duplicates, matrix spikes/matrix spike duplicates). To prevent this from happening, regular samples should be selected and marked on the chain-of-custody/sampling analysis request (COC/SAR) form or the laboratory should be instructed to contact the project QA/QC coordinator to select appropriate samples for each sample group.

All field quality control samples will be packaged and shipped with other samples in accordance with the procedures outlined in SOP – 03, Sample Packaging and Shipping. Sample custody will be maintained in accordance with the procedures outlines in SOP – 02 Sample Custody.

Field quality control samples will be prepared at least once per sampling event and certain types will be prepared more often at predetermined frequencies. If the number of samples taken does not equal an integer multiple of the intervals specified in this SOP, the number of field quality control samples is specified by the next higher multiple. For example, if a frequency of 1 quality control sample per 20 is indicated and 28 samples are collected, 2 quality control samples will be prepared. The text below describes the preparation and frequency of field quality control samples required for tissue sampling activities, and shall be followed unless different frequency requirements are listed in the FSP/SAP and QAPP.

The following table (Table 1) lists the quality control sample types and suggested frequencies for tissue sampling programs. Because tissue quality control sampling may require assessment of site cross-contamination, additional blanks may be required. A detailed explanation of each quality control sample type with the required preparation follows this table.

Table 1. Field quality control (QC) sample requirements for tissue sampling.

Quality Control Sample Name	Abbreviation	Preparation		
		Location	Method	Frequency[1]
Duplicate	DUP	Sampling Site	Additional natural sample	One per 20 samples. May not be applicable if REP is being collected.
Replicate	REP	Sampling Site	Additional natural sample	One replicate per 20 samples. May not be applicable if DUP is being collected.
Matrix Spike/Matrix Spike Duplicate	MS/MSD	Sampling Site	Additional sample bottles filled for laboratory quality control requirements	One per 20 samples.
Equipment Rinsate Blank	ER	Sampling Site	Deionized water collected after pouring through and over decontaminated equipment	Minimum of one per sampling equipment used and then 1:20 thereafter.
Bottle Blank	BB	Field	Unopened bottle	One per sample episode or one per bottle type.
Trip Blank	TB	Laboratory	Deionized water with preservative	One pair per each VOC sample cooler shipment.
Temperature Blank	TMB	Laboratory	Deionized water	One per sample cooler.
Environmental Blank	EB	Field	Bottle filled at sample site with DI water	One per 20 samples.
Standard Reference Material	SRM	Field, Laboratory, or Sampling Site	SRM ampules or other container for each analyte group	One set per 50 samples or one per episode.

1. Frequencies provided in this table are general recommendations; project-specific frequencies are provided in the project-specific FSP/SAP and QAPP.

FIELD DUPLICATE SAMPLES

Field duplicate (or split) samples are collected to assess the homogeneity of the samples collected in the field and the precision of the sampling process. Field duplicates will be prepared by collecting two aliquots for the sample and submitting them for analysis as separate samples. Field duplicates will be collected at a minimum frequency of 1 per 20 samples or once per sampling event, whichever is more frequent. The actual number of field duplicate samples collected during a sampling event will be determined on a case-by-case basis by the project QA/QC coordinator and/or Field Team Lead (consult the project-specific FSP/SAP and QAPP). These requirements may vary by EPA region or state.

FIELD REPLICATE SAMPLES

Field replicate samples are co-located samples collected in an identical manner over a minimum period of time to provide a measure of the field and laboratory variance, including variance resulting from sample heterogeneity. Field replicates will be prepared by collecting two completely separate samples from the same station and submitting them for analysis as separate samples. Field replicates will be collected at a minimum frequency of 1 per 20 samples or once per sampling event, whichever is more frequent. If field duplicate samples are collected, then it is unlikely that field replicate samples will also be collected during the field sampling event. The actual number of field replicate samples collected will be determined on a case-by-case basis by the project QA/QC coordinator and/or the Field Team Lead (consult the project-specific FSP/SAP and QAPP). These requirements may vary by EPA region or state.

MATRIX SPIKE/MATRIX SPIKE DUPLICATES

The matrix spike/matrix spike duplicate (MS/MSD) analyses provide information about the effect of the sample matrix on the design and measurement methodology used by the laboratory. To account for the additional volume needed by the laboratory to perform the analyses, extra sample volumes may be required to be collected from designated tissue stations. MS/MSDs may be collected at a minimum frequency of 1 per 20 samples or once per sampling event, whichever is more frequent. The actual number of field replicate samples collected will be determined on a case-by-case basis by the project QA/QC coordinator and/or the Field Team Lead (consult the project-specific FSP/SAP and QAPP). These requirements may vary by analyte group.

EQUIPMENT RINSATE BLANKS

Equipment rinsate blanks will be used to help identify possible contamination from the sampling environment and/or from decontaminated sampling equipment. Equipment rinsate blanks will be prepared by pouring laboratory distilled/deionized water through, over, and into the decontaminated sample collection equipment, then transferring the water to the appropriate sample containers and adding any necessary preservatives. Equipment rinsate blanks will be prepared for all inorganic, organic, and conventional analytes at least once per sampling event per type of sampling equipment used. The actual number of equipment rinsate blanks prepared during an event will be determined on a case-by-

case basis by the project QA/QC coordinator and/or the Field Team Lead (consult the project-specific FSP/SAP and QAPP). These requirements may vary by EPA region or state.

BOTTLE BLANKS

The bottle blank is an unopened sample bottle. Bottle blanks are submitted along with tissue samples to ensure that contaminants are not originating from the bottles themselves because of improper preparation, handling, or cleaning techniques. If required, one bottle blank per lot of prepared bottles will be submitted for analysis. If more than one type of bottle will be used in the sampling (e.g., HDPE and glass), then a bottle blank should be submitted for each type of bottle and preservative. The actual number of bottle blanks analyzed during a project will be determined on a case-by-case basis by the project QA/QC coordinator and/or the Field Team Lead (consult the project-specific FSP/SAP and QAPP). These requirements may vary by EPA region or state.

TRIP BLANKS

Trip blanks will be used to help identify whether contaminants may have been introduced during the shipment of the tissue samples from the field to the laboratory for VOC analyses only. Trip blanks are prepared at the testing laboratory by pouring distilled/deionized water into two 40-mL VOC vials and tightly closing the lids. Each vial will be inverted and tapped lightly to ensure no air bubbles exist.

The trip blanks will be transported unopened to and from the field in the cooler with the VOC samples. A trip blank shall be labeled and placed inside the cooler that contains newly collected VOC samples and it shall remain in the cooler at all times. A trip blank must accompany samples at all times in the field. One trip blank (consisting of a pair of VOC vials) will be sent with each cooler of samples shipped to the testing laboratory for VOC analysis.

TEMPERATURE BLANKS

Temperature blanks will be used by the laboratory to verify the temperature of the samples upon receipt at the testing laboratory. Temperature blanks will be prepared at the testing laboratory by pouring distilled/deionized water into a vial and tightly closing the lid. The blanks will be transported unopened to and from the field in the cooler with the sample containers. A temperature blank shall be included with each sample cooler shipped to the testing laboratory.

FIELD BLANKS

The field blank is prepared in the field to evaluate potential background concentrations present in the air and in the distilled/deionized water used for the final decontamination rinse. If unpreserved bottles are to be used, then the appropriate preservative (i.e., for metals samples use a 10% nitric acid solution to bring sample pH to 2 or less) must be added, as required. Field blanks should be collected at a minimum frequency of 1 in 20 samples. The actual number of field blanks analyzed during a project will be determined on a case-by-case basis by the project QA/QC coordinator and/or the Field Team Lead (consult the project-specific FSP/SAP and QAPP). These requirements may vary by EPA region or state.

To prepare a field blank in the field, open the laboratory-prepared sample bottle while at a sample collection site, fill the sample bottle with distilled/deionized water and then seal. Assign the field blank a unique sample number, label the bottle, and then send the bottle to the laboratory with the field samples according to SOP – 03, Sample Packaging and Shipping.

REFERENCE MATERIALS

Reference materials are samples containing known analytes at known concentrations that have been prepared by and obtained from EPA-approved sources. The SRMs have undergone multi-laboratory analysis using a standard method which provides certified concentrations. When available for a specific analyte, SRM samples provide a measure of analytical performance and/or analytical method bias (i.e., accuracy) of the laboratory. Several SRMs may be required to cover all analytical parameters. For all analytes where available, one SRM will be analyzed at a frequency of 1 per 50 samples. The actual number of SRMs analyzed during a project will be determined on a case-by-case basis by the project QA/QC coordinator and/or the Field Team Lead (consult the project-specific FSP/SAP and QAPP). These requirements may vary by EPA region or state.

Go-Flo Bottle Field Decontamination

Written by Amanda Royal & Michelle Briscoe, Brooks Rand Labs

Revision 3 (3/13/15)

The following procedure is to provide field decontamination steps for 10-L Go-Flo Bottles after use and before re-use for collection of low-level metals seawater samples.

Materials Required

- Liquid detergent low in metals, such as Formula 409
- Ultra-pure reagent water (e.g., MilliQ) pre-tested sufficiently low in analytes of interest
- Cleaning brushes, non-metallic
- Plastic tub or tray (secondary containment for acidic waste)
- 50% (v/v) HNO_3
- 50% (v/v) HCl
- 500-mL pre-cleaned squeeze bottle for preparing solution of 0.5% HNO_3 + 1% HCl
- Bench-liners
- 4-L plastic beaker
- Acid-resistant nitrile gloves
- Clean-room vinyl gloves
- Plastic bags large enough to contain Go-Flo bottles, and associated zip-ties
- Safety glasses and goggles
- Lab coats

Procedure to use if sampling equipment has been used only for clean, low-particulate samples (e.g., outside of a plume)

Clean-room vinyl gloves must be worn at all times when cleaning and handling equipment!

1. Prior to cleaning, inspect each bottle for obvious defects to the bottle or the opening/closing mechanism, and remove any debris.
2. Thoroughly rinse the Go Flo bottles with reagent water.
3. In a large non-metallic sink, spray all exposed surfaces of the bottles with 409 detergent. Using a metal-free brush, scrub all areas of the equipment.
4. Drain some of the soapy water out through the spigot.
5. Rinse off detergent with copious amounts of reagent water and drain one liter of reagent water through spigot.
6. Place bottles on bench liners in a laminar flow HEPA-filter clean hood and allow to dry (24 hours is desired, but a shorter time is acceptable).). [Note: drying step is not necessary if equipment is used immediately following cleaning.]
7. If not using immediately, double-bag for next use, close bag with a zip-tie, and label with date of cleaning.

Procedure to use if sampling equipment has been used inside of a plume or if heavy metals or petroleum contamination is suspected

Clean-room vinyl gloves over acid-resistant nitrile gloves must be worn at all times when cleaning and handling equipment!

1. Prior to cleaning, inspect each bottle for obvious defects to the bottle or the opening/closing mechanism, and remove any debris.
2. Remove the mechanisms of the ball valves and O-rings, and soak in a dilute solution of detergent in a 4-L plastic beaker. Agitate periodically to facilitate cleaning. Wearing clean-room gloves, remove parts from beaker and rinse well with copious amounts of reagent water. Place parts on bench liners in a laminar flow HEPA-filter clean hood and allow to dry (24 hours is desired, but a shorter time is acceptable). [Note: drying step is not necessary if equipment is used immediately following cleaning.]
3. Thoroughly rinse the Go Flo bottles with reagent water.
4. In a large non-metallic sink, spray all exposed surfaces of the bottles with detergent. Using a metal-free brush, scrub all areas of the equipment.
5. Drain some of the soapy water out through the spigot.
6. Rinse off detergent with copious amounts of reagent water and drain one liter of reagent water through spigot.
7. Prepare solution of 0.5% (v/v) HNO_3 + 1% HCl.
8. Reassemble bottles, move to fume hood, and fill each bottle 1/3 full with a solution of 0.5% (v/v) HNO_3 + 1% HCl.
9. Close the ball valves, spigot, and vent. Working over a plastic tub or tray (secondary containment for acidic waste), carefully rotate the bottles for a minute or so to coat all internal surfaces with the dilute acid.
10. Drain one liter of the dilute acid through the spigot into the secondary containment tub or tray. Open the end of the ball valve and drain remaining acid in the secondary containment tub for neutralizing and/or disposal.
11. Rinse each bottle with copious amounts of reagent water, opening and closing the ball valves and drain water through spigot to ensure complete rinsing of all parts.
12. Place bottles on bench liners in a laminar flow HEPA-filter clean hood and allow to dry (24 hours is desired, but a shorter time is acceptable).). [Note: drying step is not necessary if equipment is used immediately following cleaning.]
13. If not using immediately, double-bag for next use, close bag with a zip-tie, and label with date of cleaning.

1.0 SCOPE

To define the processes to be followed in collecting, composting, and processing chemical and biological samples using grab and core samplers. This SOP is intended to be in conformance with the Puget Sound Estuary Program guidelines to ensure data quality that is consistent with other Puget Sound programs and the past programs for the CSESP studies in the Chukchi and Beaufort lease areas.

2.1 BACKGROUND

Sediments are collected for a variety of analyses, which may include chemical analyses, toxicity testing, benthic infaunal analyses, or other purposes as specified by program needs. Sediment cores within a benthic grab sampler must be collected with a sampling device, which minimally disturbs the surface sediments and prevents mixing of the vertical stratification, does not contaminate the sample for chemical parameters of interest (e.g., trace metals and organics), and provides adequate sediment volumes for subsampling for these parameters and grain size from the surface and subsurface layers of the core. A double van Veen grab sampler will be used to collect sediment from each station. This sampler is constructed entirely of stainless steel and is appropriate for collecting sediment samples for both biological and chemical analyses. The top of the sampler is hinged to allow for the removal of the top layer (s) of sediment for chemical and toxicity analyses. This gear is relatively easy to operate and requires little specialized training.

2.2 Equipment Required

- Double van Veen grab sampler
- Winch
- Ball bearing swivel
- Decontaminated stainless steel sampling spoons and mixing bowls
- Core or 2 cm deep sediment collecting tool
- Filtered seawater washing system
- Solvents, distilled water, and Alconox for cleaning sampling equipment and tools
- Whirl-Pak Bags
- Ice chests
- Field notebooks/sampling logs
- Navigation system
- Tubing for siphoning
- Gloves (nitrile)
- Borax buffered formalin solution mixed with filtered seawater

3.1 PROCEDURE

The following instructions separate the procedure into collection and processing functions.

3.2 Sediment Collection

1. Prior to commencing sampling for a project, thoroughly clean the sampler with a non-phosphate laboratory detergent (e.g., Alconox®) to remove any sediment, debris, rust, or grease that might otherwise contaminate the sample. Rinse the inner surfaces first with seawater or tap water to remove sediment from sampler, and then with distilled water. Field equipment used to collect samples for chemical analysis will be cleaned at the start of each sampling shift and prior to use at each station. The decontamination procedure involves removing any visible gross contamination, such as sediment adhered to the double van Veen grab from a prior station, scrubbing the equipment with a hard-bristled brush using a Liquinox-detergent and water mixture, rinsing with clean filtered site water, rinsing with distilled water, wiping with acetone wipes, and rinsing again with distilled water. The specific process is described in the SOP for equipment decontamination and in the project-specific QAPP. Once the survey vessel is on station, prepare to deploy the sampler. Secure all vessel discharges and ensure that all exhaust fumes are directed away from the sample collection area (rear deck) until the sample has been collected.

2. Attach the sampler to the end of the winch cable with a ball bearing swivel and shackles, tighten the pin, and wire the clevis pin to the clevis of the shackle. An auxiliary link may be also installed to provide added assurance against loss of the equipment.

3. If necessary, attach one set of weights to the sampler. These can be removed, or additional weights added depending on the sediment type. The grab is then cocked.

4. Lower the grab sampler through the water column such that travel through the water column is slow enough that the increasing length of cable does not descend faster than the sampling device. During the last 5 meters the lowering rate should be no faster than 1 m/sec. This slower speed minimizes the effects of bow wake disturbance of surface sediments. Record the time and location of sample collection when the core/grab hits bottom.

5. Close the sampling device slowly to allow the sampler to completed close within the sediment. The length of that retrieval is consistent with the distance between the depth of the closed and open arms of the sampler.

6. Retrieve the sampler and lower it into its stand on-board and make certain it is secure. Open the hinged top and determine whether the sample is acceptable or not. An acceptable grab is one having relatively level, intact sediment over the

entire area of the grab, and generally a sediment depth at the center in excess of the depth required to sample >90% of species and individuals that would be captured to 20 cm of sediment depth. This depth of penetration varies by sediment coarseness but is generally at least 7 centimeters. Grabs containing no sediment, partially filled grabs, grabs with grossly slumped surfaces, or which leak are unacceptable. Grabs completely filled to the top, where the sediment is in direct contact with the hinged top, may also be unacceptable. It may take several attempts using different amounts of weight to obtain the first acceptable sample. The more weight that is added, the deeper the bite of the grab will be into the sediment. In very soft mud, pads may be needed to prevent the sampler from sinking in the mud. If pads are used, the rate of descent near the bottom should be slowed even further to reduce the bow wake.

7. Open and tie back the vent flaps of the sampler and carefully siphon off any overlying water into an appropriate sieve.

8. Visually inspect the sample for acceptability (an undisturbed surface layer is evident, the overlying water is not excessively turbid, adequate penetration was achieved, and no external leakage from the grab); if the sample is not acceptable, it should be discarded and another sample should be collected. Record whether the sample was retained or rejected.

9. If the sample is acceptable, note the time of collection, the condition of the surface, penetration depth, and any other notable information in the field log notebook and sample log sheets. The time and location of collection of all grabs/cores, and whether they were acceptable or rejected should be recorded. This gives a general record of the level of difficulty in obtaining a sample at a particular location, should the site be sampled again during another survey.

3.3 Field Processing of Samples for Benthic Community Assessment

Grab samples to be used in the assessment of macrobenthic communities are processed in the following manner:

1. Assign a sample number to the sample, and label the Whirl-Pak bags using indelible ink with the following information: project, date, time of sample collection, station, replicate number, sieve size, preservative, and sample collectors. Whirl-Pak bags are made of polythene and are designed for specimen collection; they form an air tight seal when closed. An internal label containing the same information should be placed inside the sample pak. This internal label should be made of 100 percent waterproof rag paper, and should be filled out using a pencil.

2. Measure the penetration depth of the sediment and record the value in the field or sample log. The depth should be 4-5 cm for medium-coarse sand, 6-7 cm for fine sand, and ≥10 cm for muddy sediment. Record descriptive information about the core/grab, such as the presence or absence of a

surface floc, color and odor of surface sediments, sediment texture, presence of debris (wood chips, wood fibers, human artifacts), presence of oily sheen, vertical changes in sediment characteristics, presence of any redox potential discontinuity layer, and visible fauna or biological structures. The descriptions are recorded on a sample log sheet for each replicate sample at each location (Attachment 2). Photographs of each grab may be collected to retain physical evidence of each grab collected. This information will form a basis for providing a direct comparison to the SPI plan view photographs.

3. Process the grab for benthic community analyses. The whole grab, not an aliquot of the sampler is processed. Sediments to be sieved are placed in increments into a 1.0 mm (0.5mm or stacked 1.0 and 0.5 mm may also be used) mesh sieve at a rate to prevent the sieve from clogging and overflowing. The sieve will also be placed on a table, and a gentle flow of water washed over the sample. Extreme care must be taken to assure that no sample is lost over the side of the sieve while agitating or washing the sample. Water used for sieving is filtered seawater supplied at a rate to process the sediment without damage to the infaunal organisms.

4. Drain the water from the sieve box and gently rinse the contents of the tray to one edge. Using a spoon, GENTLY scoop up the bulk of the sample and place it in the labeled Whirl-Pak (which should be placed in the sieve or a bucket in case some of the sample spills over. Rinse the outside of the pak into the sieve, then rinse the contents into the Whirl-Pak using a squirt bottle or gentle hose (optional: a funnel may be used to facilitate this process). No more than half to two thirds of the Whirl-Pak should be filled with sieved 'grunge' material. If the quantity of sample exceeds this volume, place the remainder of the sample in a second, labeled pak. Note on the sample labels that the sample consists of more than one container. This must also be recorded in the log and on chain-of-custody forms.

5. Carefully inspect the sieve to ensure that all organisms are removed using fine forceps (if necessary) to transfer fauna from the sieve to the container with the proper sample number.

6. A ten percent solution of buffered formalin mixed with seawater is used to fix and preserve samples. A buffered formalin solution is generally prepared prior to field sampling by adding borax to a 35% formalin solution. The borax is added until the formalin is saturated with the buffer (approximately 4 heaping tablespoons of borax). When fixing the sample, seawater collected from the sample station is added to the jar until it is 2/3 to 3/4 full, and the 35% buffered formalin solution is then added to the sample pak to approximately 90% full. This creates a 10-15% buffered formalin and seawater solution. Store the sample in a box or cooler. A Rose Bengal or other vital stain may either be added to the samples at the laboratory performing the taxonomic identifications, or may be added to the formalin prior to field sampling. If added prior to sampling, approximately 1/8 teaspoon should be added to each gallon of 35% formalin. This may be accomplished while buffering the solution. The closure wires for the Whirl-Pak

should be taped to ensure that the sample containers will not be punctured by the closure wires.

7. Prior to sieving the next sample, use copious amounts of forceful water and a stiff brush to clean the sieve, thereby minimizing cross-contamination of samples.

8. Five replicate samples will be collected per sampling station. In addition, if sediment contaminant and conventional chemistry analyses are not to be performed on samples collected at a benthic infaunal station, a separate grab should be collected and subsampled for grain size analysis and total organic carbon (depending on project requirements). Approximately 500 ml should be collected for this analysis.

9. Within ~ 2 weeks of fixing the samples, the samples should be transferred to 70% ethanol for preservation. Each sample and internal label is poured into an appropriately sized sieve (preferably one with a smaller sieve size) place over a bowl or pan to collect the formalin. The formalin is then disposed into a hazardous waste drum. The sample is gently washed with tap or distilled water, as is the sample container. Care should be taken not to splash the sample. Once the rinse water has drained from the sieve, the sample should be gently rinsed with 70% ethanol from a squirt bottle, and returned to the sample pak. The sieve should be checked to ensure that the entire sample has been returned to the jar, including the internal label. The Whirl-Pak should then be filled to ~90% of its volume with 70% ethanol, and the container should be sealed and gently shaken and inverted to ensure proper mixing. For long-term storage of crustaceans (so that the exoskeleton remains supple), it is recommended that glycerine be added to the 70% ethanol solution. The alcohol-glycerine solution would consist of 70% ethanol, 25% distilled water, and 5% glycerine. The glycerine would be added to the solution prior to filling the sample jars. The closure wires for the Whirl-Pak should be re-taped to ensure that the sample containers will not be punctured by the closure wires.

4.0 SAFETY CONSIDERATIONS

Sediment grab samplers are potentially dangerous pieces of equipment. All personnel should wear hard hats and steel-toed boots when working with the samplers. Once the device is cocked, it could accidentally trip at any time. The operators must be careful not to place hands or fingers in a position where they could be injured in the event that the device trips prematurely.

The sampler is a heavy piece of equipment (especially when full). The operators must take care when deploying or retrieving this gear under adverse weather conditions. A grab sampler swinging wildly at the end of a boom can be very dangerous. Safety limes are recommended during adverse weather conditions.

All field personnel must read and comply with the site specific health and safety plan prepared for the sampling program. Appropriate levels of personal protection and decontamination procedures must be followed.

5.1 Sorting and Identification of Benthic Infaunal Samples.

Upon arrival at the laboratory samples are logged into the inventory system and the sample numbers are verified with the Chain of Custody form. Any discrepancies are resolved at this point

Alcohol is rinsed from the samples of benthic 'grunge' and from the retained animals prior to removal and sorting of each individual in the sample. The removal and sorting is performed under a dissecting microscope using ~10-20X amplification and small quantities of 'grunge' material (~5 mL). The organisms removed from the sample are sorted into major taxonomic categories (e.g., molluscs, arthropods, annelids, echinoderms, ophiuroids, and miscellaneous phyla); the sorted 'grunge' is retained in labeled containers. Organisms and residual 'grunge' material are preserved in 70% ethyl alcohol (EtOH) with 5% glycerin added for longer term storage.

The sorting efficiency is documented to be at least 95% efficient by performing a resort of 20% of the sorted 'grunge' material from each sample by a different analyst. Any samples falling below that rate are re-sorted and a second outside QA performed.

The percent sorting efficiency is calculated as:

% Sorting Efficiency = [1 – (# in QA re-sort/(# sorted originally + # in QC re-sort)]*100

With the client's agreement, once the sorted sediment has passed sorting QA, the sediment is disposed.

Organisms will be identified to Lowest Practicable Taxonomic Level (LPTL), generally species level by qualified taxonomists with specialized expertise on each of the major taxonomic categories. Most of these identifications will be made by Columbia Sciences with additional help by taxonomists with key specialties for specific groups of species. Two forms of QA will occur. A reference collection for the project is proposed and would be added to specimens verified by Columbia Sciences and other outside taxonomists from BC, Alaska, Washington, Oregon, and California. Secondly, to maintain internal consistency with historical data sets, the data sets will be updated to provide a consistent name for each species among the various groups of taxonomists used during different sampling efforts.

All of the identified individuals, their abundance and biomass will be provided to the ecological analysts in an excel data base. Prior to analyses and interpretation of the data an addition QA step will be performed to highlight those species and individuals that represent pelagic species that were captured from unscreened water used for sieving during the past surveys.

All identified organisms from a discrete sample are held in labeled glass vials containing 70% EtOH and 5% glycerine for long-term storage. Polyfilm often is used to seal the larger vials in addition to the caps. These are held for 5 years and are not disposed without written permission from the client. They can also be transferred to museums or other collections as desired by the client.

1.0 SCOPE

Sediment Profile Imaging (SPI) provides a cross-section photograph of surface and near-surface sediment. Plan view (PV) imaging provides a snapshot of the seafloor surface. This SOP defines the methods and procedures to be followed to collect SPI/PV images as well as the hazards associated with SPI/PV camera deployment and operation.

2.0 SPI & PLAN VIEW CAMERA OPERATION

2.1 Sediment Profile Camera (SPI)

SPI provides a 20 cm high by 14 cm wide "profile" images of surface and near-surface sediment captured digitally by a Nikon D80 or D7200 SLR camera equipped with a 35mm lens. SPI images can provide information describing sediment grain-size, sedimentary fabric, benthic infauna, and physical and biological processes. SPI technology has been used to map the extent of sediment caps and deposits, conduct sediment quality surveys, sedimentation monitoring, and perform impact assessments due to confined aquatic disposal (CAD) sites, aquaculture, and oil platforms.

The Ocean Imaging Systems model 3731 sediment profile camera, equipped with a digital camera, consists of a wedge shaped prism with a Plexiglass face plate and a back mirror mounted at a 45 degree angle. Light is provided by an internal strobe. The mirror reflects the image of the profile of the sediment-water interface up to a 35 mm camera that is mounted horizontally on top of the prism. The prism is filled with distilled water (or 45% alcohol solution under freezing conditions) which allows clear interpretable images to be captured regardless of turbidity in the water column.

The camera prism is mounted on an assembly that can be moved up and down within a stainless steel frame by allowing tension or slack on the winch wire. As the camera is lowered, tension on the winch wire keeps the prism in the up position. Once the camera frame touches the bottom, slack on the winch wire allows the prism to lower and vertically intersect the sediment. The rate of fall of the prism (6 cm/second) is controlled by an adjustable passive hydraulic piston, which minimizes the disturbance of the sediment-water interface.

A trigger is tripped on impact with the bottom, activating a 13 second time-delay on the shutter release; this allows time for the prism to obtain maximum penetration before an image is collected. After an image is collected, the camera is raised from the bottom, a wiper blade automatically cleans off any sediment adhering to the prism faceplate, and the strobes are recharged. The boat is repositioned slightly then the camera is lowered to collect another replicate image.

NEWFIELDS

2.2 Plan View Camera (PV)

Plan view images are captured using a downward facing underwater 1Cam or Chimaera camera system and external flash manufactured by SubC Control, Newfoundland, Canada. The plan view camera and external flash are mounted on the frame of the SPI camera in a downward-looking orientation. Images are taken just before the SPI camera makes contact with the seafloor, using a lead ball and cable attached to a bounce trigger. When the SPI camera is raised from the bottom, the bounce trigger is reset rendering the plan view camera ready to take another image. The 1Cam is equipped with dual lasers located 64mm apart allowing for accurate scale to be applied to each image. Three replicate plan view images will be taken at each location.

3.0 Equipment Required

- Ocean Imaging Systems Model 3731 Sediment Profile Camera Frame
- Ocean Imaging Systems Camera Head
- Nikon D80 or D7200 Digital SLR Camera
- 1Cam or Chimaera Digital plan view camera
- 1Cam or Chimaera Battery pack w/ stainless housing
- 1Cam or Chimaera external strobe
- 12 v Nicad rechargeable battery packs
- Benthos pinger (for deep water tracking)
- 25 lb lead weights (10 sets)
- “Mud” doors
- Distilled water or 45% alcohol solution (for freezing environments)
- Winch and winch line
- Swivel & shackles
- Navigation system
- A vessel with winch and winch wire having a minimum lifting capacity of 150 kilos

3.1 PROCEDURE

The following procedures will be followed when deploying and recovering the SPI camera and collecting SPI images.

3.1 SPI & Plan View Camera Deployment

1. Prior to survey mobilization, the SPI camera head and plan view systems will be "bench-tested" to ensure that the cameras are focused, firing properly, and the strobes are operational. A spare Nikon D80 or D7200 digital camera, fully-charged battery packs, and SD storage cards will be carried in the field to ensure uninterrupted sample acquisition.

NEWFIELDS

2. A thorough check of all cables connecting the battery pack, external strobe and plan view camera housing will then be conducted. The plan view camera will be fired on deck by pulling and releasing the bounce trigger to confirm that it is fully functional.

2. At the beginning of each survey day, the time on the digital cameras (both the SPI and PV) will be synchronized with the navigation system clock. Each SPI/PV station replicate is identified by the time recorded in the digital image file and the corresponding time and position recorded by the navigation system. Redundant sample logs will be kept by the field crew. Test shots will be fired on deck periodically to verify all internal electronic systems are working according to specifications.

3. The SPI camera system is attached to the winch wire. As the camera is lowered to the seafloor, tension on the wire keeps the prism in the 'up' position. Once the camera frame contacts the bottom, slack on the wire will allow the prism to vertically cut the seafloor. The optical prism descends at approximately 6 cm/second.

4. The prism is driven by the weight of the assembly several centimeters into the bottom sediments. The camera trigger is tripped by the impact with the bottom, activating a 13-second time delay on the shutter release, which gives the prism a chance to obtain maximum penetration before a photo is taken.

5. As the camera is raised off the bottom, a wiper blade automatically cleans any sediment off of the prism faceplate. The strobes are recharged, and the camera can be lowered for another replicate image.

6. When the camera is brought to the surface, the frame count will be verified and the camera prism penetration will be estimated from a penetration indicator that measures the distance the prism fell relative to the camera base. If penetration is inadequate, two weight packs, each capable of holding 125 lbs of lead (in 25 lb increments) will be loaded to increase penetration. If penetration is too great, adjustable stops which control the distance the prism can descend will be lowered. In addition, "mud" doors can be attached to each side of the frame to increase the surface bearing of the entire unit.

6. Three replicate images will be taken at each SPI station. The images are downloaded to a laptop computer via the USB port on the Ocean Imaging Systems' camera head at the end of each survey day or more frequently if required to meet real-time sampling objectives.

4.0 SAFETY CONSIDERATIONS

The SPI camera is a heavy piece of sampling equipment. The operator must use caution when deploying and retrieving this gear, especially under adverse weather conditions. Proper safety equipment (hard hat, safety vest, steel-toed boots/shoes) will be worn by

NEWFIELDS

all personnel operating the camera. Under adverse weather conditions, tag lines will be used to secure the camera during deployment and recovery.

NEWFIELDS

Battelle Duxbury Operations
Standard Operating Procedure
for

COLLECTING SEDIMENT CORES WITH A PISTON PUSH/HAMMER CORER

1.0 OBJECTIVE

The Piston Corer is designed to collect minimally disturbed sediment cores, including the sediment-water interface if deployed with that purpose. The corer is constructed with five primary pieces: 1) Poles of various lengths constructed from materials such as aluminum, stainless steel, composite; 2) Stainless steel pole/core attachment head; 3) Double sealed piston with line attached (the line needs to be good quality, low stretch line (e.g. Vectra™, polyester, Kevlar®), stainless steel cable); 4) Core tubing (typically cellulose acetate butyrate (CAB) or polycarbonate) used most often has an outer diameter (OD) of 2¾", a wall thickness of 1/16" resulting in an inner diameter (ID) of 2⅝"; and 5) slide hammer weight(s). Tubing length is determined by the sample plan, the sediment consistency, and the ability to recover the material. The piston seals prevent air and water from passing by the tube wall. When the tubing is pushed into the sediment, the piston is held in position at the sediment surface by a line fixed to the vessel or land. The immobile piston creates suction during insertion of the core tube minimizing core plugging and the pushing sediment away from the tube. The piston suction also limits the ability of the sediment to fall out of the tube during extraction and recovery. By avoiding a one-way check valve, cutter head, and core catcher hardware, the system is less complicated, less likely to cross contaminate, and has the ability to collect minimally disturbed samples including very short (~6 in) cores. The sampler can recover sediments from very light to harder, stiffer clay consistency.

2.0 PREPARATION

Determine the depth of water and the appropriate sediment core target length (target core length is provided in the project Quality Assurance Project Plan and/or the Sampling and Analysis Plan (QAPP/SAP)). Assemble the amount of push rod needed for the water depth, finishing with the 'T' handle on top. Prepare a tube of the necessary length. Account for the length of the piston and any interference from the core head by adding these lengths to your target core tube length. It is a good practice to add some additional length to the core tube as a buffer. Cut the tube with a clean saw or knife if necessary. Clean the tube, the piston, and the core head as described in the QAPP/SAP. When all the equipment is clean, assemble the core system as follows:

1) Loosen the pressure on the piston seals by partially unscrewing the eye bolt that passes through the piston.
2) Make sure the line attached to the piston is routed through a hole in the inside of the core head.
3) Pass line with carabineer through core tube.
4) Attach carabineer to the loosened eyebolt on the piston. Tighten eyebolt so the piston seals snugly inside the tube yet still allows it to move without creating excessive drag while collecting the core. Friction from the seal will hold the piston in place for deployment.
5) Insert the tightened piston into bottom of core tube and push the piston into the tube until the piston is flush or 1/8 deeper than the bottom of the core tube (to allow for capture of loose fines on

BATTELLE

Battelle Standard Operating Procedures are Business Sensitive, Intellectual Property and MAY NOT be reproduced or distributed in any form without written permission from the Battelle Quality Assurance Office.

sediment surface to be captured) This creates friction in the tube preventing easy travel of the piston within the tube during deployment.

6) Loosen the clamp screws and slide the core tube into the core head, feeding the piston line through at the same time (do not allow the line to bunch up in the core tube).

7) Ensure that the core tube is pushed in as far as possible into the core head.

8) When certain the core tube is completely inserted, secure the core tube by tightening the clamp screws.

9) Attach a measuring tape to the core head if using one. Either measure and record the offset from 0 (e.g., water surface) to the tip of the core head, or, extend the tape to the tip of the core so 0 on the tape measure equals the tip and tie the tape off at the head. Secure any loose tape.

10) Before deployment, check the clamp screws for tightness, preventing the loss of the core barrel. Confirm that the water depth has been measured and the calculated insertion depth is known.

3.0 PROCEDURE

3.1 Pre-Deployment Calculations

Critical to core collection is knowing when the tip of the core tube hits the sediment, or is just above the sediment water interface, and knowing when the target depth has been achieved. Transferring the calculated measurements to the core system can be accomplished by either pre-measuring the core and pole system and then marking the pole (marking options include electrical tape and a Sharpie™ Marker) or attaching a fiberglass measuring tape to the core head (often the best alternative in deep water). Good practice is to make the calculations prior to deployment, and have at least one other staff review the calculation assumptions and the results.

3.2 Deployment of the Piston Corer

Proper deployment can be accomplished several ways. Experience and site specific conditions should be factored in to adjust the methods as necessary to meet the project goals specified in the Quality Assurance Project Plan (QAPP) or Sampling and Analysis Plan (SAP).

The corer has three means of driving the barrel into the sediments: pushing by the operator(s), a slide hammer that fits over the top of the pipe assembly or a donut weight(s) that is lifted and uses gravity to hammer the core in, or. The weight(s), if used, need to be slid onto the first section of the pole prior to deployment with a line attached. Several cores may be rejected while determining the most effective driving technique, depending on the particular bottom sediment condition.

Lower the piston core to the target depth (one method is to lower the core until you can feel the bottom), confirm the water depth, re-affirm or adjust the calculations, then move the core away from the area previously disturbed and continue deployment. Hold the lines attached to the piston and the slide hammer (if used) gently but firm enough to remove any slack. When the core is ready to be collected, tie the line attached to the piston to a secure place on the vessel, or to a secure location in wetlands (e.g. tripod, board, shoulder). In deep water, you may want to deploy the core overboard without all of the sections attached, and as the corer is deployed, attach additional sections as needed. The lines attached to the piston and the slide hammer (if used) need to be maintained with care. Do not allow a large amount of extra line to get in the water, potentially tangling and disturbing operations, and do not hold the lines too taut, which can raise the piston or prematurely lift the slide hammer (if used). The line attached to the

BATTELLE

Battelle Standard Operating Procedures are Business Sensitive, Intellectual Property and MAY NOT be reproduced or distributed in any form without written permission from the Battelle Quality Assurance Office.

slide hammer weight should be in good condition and not so small in diameter that it can cut into and injure the hand of the operator. In soft sediments or for short cores, the sampler is usually driven using the "T" handle.

If pushing is not adequate to reach the target depth, the slide hammer or donut weight can be used to gain additional penetration. Two staff are required to collect a core with the slide hammer or donut weight. One person is responsible for holding the core pole plumb and observing the depth of the corer penetration. With the slide hammer, the second person is responsible for sliding the slide hammer over the top of the pole assembly and striking repetitively the top of the assembly by lifting and hammering down. Alternatively, with the donut weight, the second person is responsible for lifting up with the line the weight and releasing the line freely. This allows the donut weight to drop down striking the core head. This process should continue until the core tube is driven into the sediment to the target depth or refusal.

Smooth corer retrieval is important. The deeper the core penetration the more force will be required to pull the corer from the sediments. The material is retained in the core barrel by means of the vacuum provided by the piston seals. To maintain the vacuum, the line attached to the piston must not be allowed to go slack, especially during extraction. Either secure the piston line to the 'T' handle, or have one staff pull equally hard on the piston line as the other staff is pulling on the pole. Prior to putting the core on the vessel, the bottom of the core barrel must manually be capped BEFORE it breaks the air-water interface. Use polyethylene caps or a core plug to seal the core tip. Failure to do this may result in loss of sample. Some materials are cohesive enough, especially with longer cores into firm fine material, that the cap can be placed on the core after retrieval to the vessel. Once on board, the core tube is removed from the core head and capped. Further processing of the core, if necessary, and core holding and shipping conditions, are described in the QAPP/SAP.

4.0 CALCULATIONS

Determining the core penetration/recovery amount begins with the corer deployed with the tip just touching the bottom. Extra care needs to be taken in soft sediments. Reference the air-water interface by either marking the core pole or recording the depth from the attached measuring tape. After penetration is completed, the final air-water interface position on the core pole is marked or the depth is recorded from the attached measuring tape. Depth of penetration is determined by either measuring the length between the two marks on the pole or subtracting the final depth measurement from the pre-penetration depth. When coring without overlying water, the final penetration depth can be marked on the core tube. After recovery, measure from the core tube end (leading edge) to the mark on the core tube to determine penetration depth. The final core penetration and recovery depths and related calculations must be recorded in the field logs.

5.0 QUALITY CONTROL

Careful attention to the procedures described in this SOP by trained personnel will ensure the quality of the samples collected. The need for field quality control samples, (equipment, blanks or field duplicates), is defined in the project QAPP/SAP.

6.0 TRAINING

A technician training in these methods must first read this SOP in its entirety. The trainee will then practice the procedures in the field under the watch of the instructor until proficiency is demonstrated.

BATTELLE

Battelle Standard Operating Procedures are Business Sensitive, Intellectual Property and MAY NOT be reproduced or distributed in any form without written permission from the Battelle Quality Assurance Office.

A qualified sample processor must train individuals performing core sampling. A qualified sample processor is considered to be an individual who has performed the processing in the past (within 2 years), and for whom a training certificate or equivalent documentation of experience exists. The methods explained in 3.0 are used as training standards. The trainee is considered to be qualified once proficiency is demonstrated and a certificate of training (Attachment 1) is completed and submitted to the quality assurance office.

7.0 SAFETY

During training, the qualified operator should explicitly point out the hazards associated with the handling of the equipment and working on the boat (if used).

ATTACHMENTS

1. Battelle Duxbury Operations Certificate Of Training
2. SOP revision history

APPROVALS

	Name	Date
Author		5 Nov 2008
Technical Reviewer	Robert E Mandeville	6 Nov 2008
Quality Systems Manager		11-6-08
Field Operations Manager		11/6/2008

BATTELLE

Battelle Standard Operating Procedures are Business Sensitive, Intellectual Property and MAY NOT be reproduced or distributed in any form without written permission from the Battelle Quality Assurance Office.

Attachment 1
Battelle Duxbury Operations

CERTIFICATE OF TRAINING

FOR

SOP NO. **5-342-01**

TITLE: **Collecting Sediment Cores With a Piston Push/Hammer Corer**

TRAINEE: _____

Date SOP 5-342-01 read _____

Date demonstration conducted by experienced operator _____

Date operation demonstrated by trainee _____

APPROVED: _____ _____
Name Date

BATTELLE

Battelle Standard Operating Procedures are Business Sensitive, Intellectual Property and MAY NOT be reproduced or distributed in any form without written permission from the Battelle Quality Assurance Office.

ATTACHMENT 2

Revision History

Version	Summary of Changes

BATTELLE

Battelle Standard Operating Procedures are Business Sensitive, Intellectual Property and MAY NOT be reproduced or distributed in any form without written permission from the Battelle Quality Assurance Office.

Battelle
Standard Operating Procedure

for

COLLECTING BENTHIC AND EPIBENTHIC INVERTEBRATES WITH A TOWED CLAM RAKE

1.0 OBJECTIVE

This SOP describes the at-sea collection and processing of benthic and epibenthic invertebrate samples with a towed clam rake.

2.0 PREPARATION

2.1 SUPPLIES AND EQUIPMENT

- Clam Rake: Battelle or similar traditional clam/oyster rake (aka clam or oyster dredge) for collecting bivalves (e.g. clams and oysters)
- Net for collecting organisms the rake dislodges from the sediment
    - Typically from 0.25in to 1in mesh size
- Tubs for biota screening and cleaning
- Weight(s) for winch wire to keep head rope at proper tow angle
- Sieving system such as a box sieve
- Hoses and fittings for the sieving process
- Water pump for wash down process
- Smaller sieves for final cleaning and sorting with mesh sizes from 2mm to 10mm
    - Mesh size depends on target organisms, sieve availability and specifications provided in the project QAPP/SAP
- Sample containers: As specified in the project specific QAPP/SAP. Containers typically consist of glass wide-mouth jars with Teflon® lined lids in various sizes for biota of interest.
- Squirt bottles for rinsing organisms with site water, distilled water, and/or solvent for rinsing and decon, as specified by the project specific QAPP/SAP
- Funnels for transferring organisms from sieve to jars
- Nitrile gloves
- Writing tools e.g. ink pens, permanent markers, and pencils
- Scales or electronic balance for estimating biota mass
- Bristle brushes for cleaning rake, net, screens, and buckets between stations (several sizes are helpful for different sediment consistency and different areas of the gear)
- Non-phosphate detergent for cleaning rake between stations if required (e.g. Alconox® or Liquinox®).
- Common equipment and supplies that are not always required: forceps, disposable spoons

2.2 SOLVENTS (FOR CLEANING EQUIPMENT BETWEEN STATIONS)

DRAFT

Solvents and the decontamination process are specified in the QAPP/SAP. Solvents may consist of one or more of the following

- Acetone
- DCM (Dichloromethane)
- Alcohol (e.g. methanol, ethanol)
- Hexane

3.0 PROCEDURE

3.1 DEPLOYMENT OPERATIONS

The QAPP/SAP will specify the target organisms and required tissue mass.

1. Review operations below with deck crew, vessel captain, and mates prior to performing the sampling operations
    - Go over tow speed (as slow as possible to maintain safe vessel operations), trawl course/heading, and trawl duration
    - Trawl duration varies based on sediment accumulation in the net
        - Use any knowledge you have from the site (e.g. associated grab sampling) for initial trawl duration
        - Easier to increase trawl duration than repair a damaged net
    - Establish the station or order of stations to be sampled
        - Confirm first station and direct captain and mate to proceed to that station
2. Place the sieve table or other sample process systems in a convenient location on deck, influenced as minimally as possible by stack emissions, and secure equipment to the vessel as needed for safe operations (e.g. to cleats, rails, deck).
3. If sample sieving is performed, if possible position the outlet stream from the sieving apparatus through a scupper or over the side of the vessel so most sieved sediment runs overboard and not onto the vessel deck.
4. If filtered water is required in the QAPP/SAP, set up the water filter system by inserting a clean filter, connecting the supply and discharge water hoses, and securing it to the vessel and/or sample processing system.
5. Attach the winch cable termination to a lead rope, strap, or chain with a shackle.
    - Add weight, from 50-200 lbs., where the winch cable meets the lead rope to keep the clam rake towing at the correct angle
    - Length of the lead rope depends on ship's crew judgment, typical range is 5-10m.
6. Attach the rake to the lead rope with a shackle.
7. Seize all shackles to secure shackle pins from unscrewing using cable ties, seizing wire, or other suitable method.
    - Use an appropriate swivel with the shackle(s) at the rake when performing operations in water depths >10m, or in >10m depth if available and workable on the winch system.
8. Communicate with the captain/mate that the gear is ready for deployment

DRAFT

- Confirm with captain/mate station location
- Communicate to captain/mate/crew the expected trawl duration and direction

9. Fill out station log form provided in the QAPP/SAP
    - *See Attachment 2 for an example of a biota field collection log*
10. Set the clam rake up on the deck of the ship under the sheave for the cable (place as directly below the sheave pick-up point as possible to minimize swinging when the rake is lifted)
    - Confirm with captain/mate it is ok to launch equipment
    - Confirm with captain/mate vessel is at trawl speed or ready to proceed to trawl speed
11. Lift the clam rake over the stern/side of vessel and lower to the water surface
    - Communicate to captain/mate the gear is in the water
    - Let the rake and net fill with water and set on the surface with the rake tines pointed down
    - Let winch cable out slowly until tow cable length is 3-5 times the water depth (e.g., if the water depth is 20m, the cable should be out 60-100m
    - Tow for planned duration (start with short duration such as 3-5 minutes, extend if net is not over-filled with mud and more organisms are needed
    - Communicate to captain/mate trawl is over
    - Winch in cable until rake and net are visible on the water surface
    - Allow rake and net to wash mud out at surface if a large volume of mud is present and it easily sieves out of the net
    - Recover net to ship by lifting over rail/stern with winch
        - *See Attachment 1 for a photo of clam rake being retrieved*
    - Notify captain/mate the gear is safely on board the vessel
        - Confirm next station if appropriate
12. Place catch in tub or screened tub to clean and sort for target organism(s)
13. Handle and preserve target organisms as described in the project specific QAPP/SAP
14. Complete recording of station log
15. Decontamination procedures are described in Section 3.2.

3.2 DECONTAMINATION CLEANING PROCEDURES

A new net is best to use prior to each survey, unless repeating short surveys close in time at the same site are being performed. Bivalve and other potential benthic/epibenthic organisms are not highly exposed to the rake and net, thus thoroughly rinsing the gear with site water is the primary decontamination method between stations. Sampling apparatus will be decontaminated with soap and solvents in the field only if there are gross to levels of contamination (e.g. visible oil on the rake and/or net) between sampling stations. If the net is heavily oiled, it is best to replace the net. While performing the decontamination procedure, “phthalate-free gloves,” such as nitrile or butyl rubber, will be used to protect the field staff as well as preventing contamination of the sampling equipment or the samples.

DRAFT

If further decontamination is required

1. Rinse equipment with tap water or site water
2. Scrub equipment with 1% non-phosphate soap (e.g. Alconox®) using a stiff brush
3. Rinse with tap or site water, then Milli-Q water
4. Rinse with appropriate solvent (as described in QAPP/SAP). In general, solvent will not be used unless an oily sheen is noted. Typical solvent rinse procedures are as follows:

    a. Begin with a solvent rinse of acetone and then DCM if oily contamination is apparent and will only be used on metal/stainless steel surfaces
    b. Let air-dry if solvent is used.

Note: All waste solvents must be captured and disposed of in labeled liquid waste containers. All equipment that comes into contact with the sample (i.e. syringe, ruler, collection buckets) must be cleaned using the same general procedures as the grab.

3.3 SAMPLE PROCESSING

Follow project specific QAPP/SAP requirements for sample processing. In general:

1. Empty the catch into a clean tub, preferably one with plastic or stainless steel screen at the bottom.
2. Wash sediment off of all organisms in the trawl using site water.
3. Remove target organism by hands covered with clean nitrile or other gloves as specified in the QAPP/SAP.
4. Place target organisms in a secondary sieve.
5. After collecting all the target organisms from the trawl, release unwanted organisms back into the water.
6. Carefully rinse and clean the target organisms in the secondary sieve.
7. Perform final rinses as required in the QAPP/SAP, such as a final deionized water rinse.
8. Place the jars into the appropriate pre-labeled container, as described in the QAPP/SAP.
9. Store the jars in conditions described in the QAPP/SAP

4.0 CALCULATIONS

There are no calculations necessary for this procedure. It is valuable to count the numbers of bivalves placed in each jar and record the percent of the jar filled for assistance in choosing samples to analyze.

5.0 QUALITY CONTROL

Field replicates and equipment blanks for chemical analyses will be collected according to the QAPP/SAP. Any deviations from this SOP must be documented on the station log in the survey logbook. Careful attention to the procedures described in this SOP by trained, qualified personnel will ensure the quality of the samples collected.

6.0 TRAINING

A technician training in these methods must first read this SOP in its entirety. The trainee will then practice the procedures in the field under the watch of the instructor until proficiency is demonstrated.

DRAFT

A qualified sample processor must train individuals performing clam rake sampling. A qualified sample processor is considered to be an individual who has performed the processing in the past (within 2 years), and for whom documentation of training and/or experience exists. The methods explained in 3.0 are used as training standards. Once the procedures described in this SOP are understood and have been demonstrated by the staff member, training is documented in Battelle University. When registering the training as complete, the comment section should be used to indicate the name of the trainer and the date of training.

7.0 SAFETY

All personnel should wear protective clothing, safety glasses, and gloves when handling sample containers or reagent bottles containing solvents. All collectors should wear life vests, steel toed boots, and hard hats when handling the equipment on the vessel.

During training, the qualified sampler should explicitly point out hazards associated with the reagents and or equipment. The trainee should review the material safety data sheets for Ethyl and Methyl Alcohol.

Gloves, safety glasses (with side shields) and protective clothing such as rain gear that protects from chemical exposure must be worn when handling any of the above chemicals. Open containers must remain in a fume hood or used on deck at sea. If the analyst is exposed to any of the above chemicals the following procedures should be followed:

Skin contact. Remove contaminated clothing immediately, directing a stream of water under clothing while it is being removed, if possible. Wash affected area 15-20 min and ensure no evidence of chemical remains.

Eye contact. Wash eyes immediately with large amounts of water while lifting upper and lower lids for at least 15-20 min. Get medical attention immediately.

Ingestion. If victim is conscious, give large quantities of water immediately. **DO NOT INDUCE VOMITING.** Milk or activated charcoal may also be administered by trained medical personnel. Get medical attention immediately. Contact Poison Control Center and adhere to their advice.

Inhalation. Remove from exposure area to fresh air immediately. If not breathing, give artificial respiration. If breathing is difficult, oxygen is required. If near shore, an ambulance should meet the boat at the nearest dock. Otherwise, the coast guard should be called.

Analysts using this procedure must read the material safety data sheets (MSDS) associated with these materials thoroughly. MSDS are located in the laboratory and on the boat. In the event of an emergency, the MSDS should be submitted to the appropriate medical personnel.

ATTACHMENTS

Attachment 1. Photo of Clam Rake Being Retrieved
Attachment 1. Example of Biota Field Collection Log

DRAFT

APPROVALS

Author	_____	_____
Technical Reviewer	_____	_____
Quality Systems Manager	_____	_____
Resource Manager	_____	_____
	Name	Date

DRAFT

Attachment 1.

<u>Photo of Clam Rake Being Retrieved</u>

Attachment 2.

Example of Biota Field Collection Log

(Includes Clam Rake Trawl and Amphipod Trap Field Collections)

Project Name

Tissue Sample Log Form

Battelle Project No.	**Vessel:**	**Recorder:**
Station ID:	**Battelle Sampling Staff:**	**Sample Analyses:** PAH S/T

Amphipod Collection

Action	**# of Traps**	**Date/Time (local)**	**Water depth** (ft):	**Latitude** (N; WGS84):	**Longitude** (W; WGS84):
Deploy Traps					
Retrieve Traps					
Species (circle one) *Anonyx* Other		**Sample Collection time** (local)		**Sample ID**	
Deploy Traps					
Retrieve Traps					
Species (circle one) *Anonyx* Other		**Sample Collection time** (local)		**Sample ID**	

Clam Collection

Action	**Date/Time (local)**	**Water depth** (ft):	**Latitude** (N; WGS84):	**Longitude** (W; WGS84):
Deploy Dredge				
Retrieve Dredge				
Species (circle one) *Astarte* *Macoma* x Other		**Sample Collection time** (local)		**Sample ID**
Deploy Dredge				
Retrieve Dredge				
Species (circle one) *Astarte* *Macoma* x Other		**Sample Collection time** (local)		**Sample ID**

Field Activities / Comments / Observations:

Field Team Leader Signature and Approval _____ Page ____ of ____

Reviewed/Approved Date _____/_____/_____

DRAFT

Battelle
Applied Coastal and Environmental Services
Standard Operating Procedure

for the

Sea-Bird Electronics SBE 25plus Sealogger and SBE 32 Carousel Water Sampler System

1.0 APPLICATION

The Sea-Bird Electronics (SBE) 25plus Sealogger System and the SBE 32 Carousel Water Sampler System are used to provide real-time acquisition of high-resolution water column profiles and collect discrete samples of water for physical, chemical, and biological analyses.

The SBE 25plus Sealogger System is composed of the SBE 25plus main electronics unit, three primary sensors (a SBE 3F Temperature Sensor, a SBE 4C Conductivity Sensor, and the 25P.122 strain gauge Pressure Sensor) and a Sea-Bird Model 5P pump. The pump is required for the conductivity and temperature sensors, as well as optional sensors requiring water flow e.g. dissolved oxygen sensors. The CTD System described in this SOP is designed for use at up to 600 meters (m), however, the originally installed strain gauge limits the system range to 100m for accurate depth data. *Deploying the system below 100m may physically damage the strain gauge resulting in seawater leaking into the electronics chamber and damaging the system beyond repair at sea.* This SOP is intended to augment the manufacturers' manuals and software programs. The SBE manuals and software are the primary source of information for operations and maintenance of the various facets of the system.

The SBE 25plus can interface with up to ten auxiliary sensors (eight voltage output sensors and two RS-232 serial output sensors). The list of originally installed sensors is shown below. Sensor configurations can change. Therefore, inspect the system prior to use and confirm you have documentation and training on all of the installed sensors.

- Sea-Bird Model 43 Dissolved Oxygen Sensor (SOP No. 3-180)
- Sea-Bird Model 18 pH Sensor
- WET Labs ECO Triplet (Fluorescence, Turbidity, CDOM (Colored Dissolved Organic Matter)
- WET Labs C-Star Transmissometer (SOP No. 3-174)
- Seapoint Turbidity Meter (SOP No. 3-162)
- Valeport VA-500, Altimeter

These instruments require specific cable assemblies to interface to the main electronics unit. Cables are provided by SBE or outside vendors (e.g. Impulse Cables). Battelle may also fabricate specialty cables. For a list of cables and their cross-references, refer to Attachment 1.

The main function of the electronics unit is to provide power to the modular sensors, and to collect and multiplex their data, then send a single coherent data stream to the surface via a waterproof cable system.

The SBE 25plus is typically interfaced to a PC via the Sea-Bird SBE 32 Carousel and the SBE 33 Deck Unit (see diagram in Section 3.1). In certain circumstances, it is possible to gather data directly from the SBE 25plus using only a PC and the appropriate power supply and hookups (see Section 3.2.). The SBE 25plus may also run autonomously, via internal batteries. However, that is beyond the scope of this SOP.

DRAFT

Detailed information on the systems, such as wiring diagrams and specifications are provided in the manufacturer equipment manuals. A list of all equipment and sensor manual files is provided in Attachment 1. These files are necessary to have on the field computer as well as a back-up computer or media drive/device prior to beginning a survey.

Note[1]

This SOP must be used in conjunction with the SBE 25plus, SBE 32, and SBE 33 Instrument Manuals, along with the appropriate modular sensor manuals, and Application Notes as appropriate. Refer to Attachment 1 for a list of files that pertain to the Sea-Bird instrumentation.

2.0 CALIBRATION

The modular sensors interfaced to the SBE 25plus system (i.e., Temperature, Pressure, Conductivity and other auxiliary modular Sensors) are calibrated annually by SBE or by the sensor manufacturer. The calibration coefficients determined during this calibration by SBE or the sensor manufacturer are entered into the SBE software prior to use on a survey.

In certain cases, the coefficients for the Sea-Bird Model 43 Dissolved Oxygen Sensor and the Sea-Bird Model 18 pH Sensor may be determined in the field, but factory calibration is preferred and recommended. The suite of sensors may be calibrated post-survey if the specific project requires that process or the data collected during a survey is not within the expected range of values.

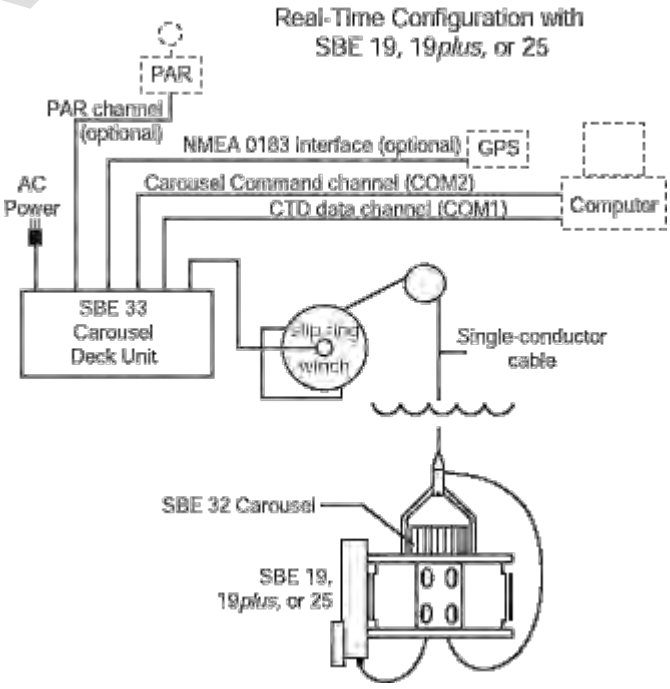
3.0 OPERATION

3.1. TYPICAL SETUP

The most common setup situation for the SBE 25plus CTD System is via a SBE 33 Deck Unit and the SBE 32 Carousel.

The SBE 33 Deck Unit provides 250 VDC power to the SBE 32 Carousel, which in turn provides 15VDC to the SBE 25plus CTD System.

The Deck Unit also controls firing of the sample bottles on the SBE 32 Carousel, and receives and filters the CTD data stream to eliminate external noise, then routes the data to a field computer.



[1] Notes and Cautions are inserted at the end of each section.

DRAFT

The SBE 33 may be pre-programmed to trigger sampling bottles.

3.2. OPTIONAL SETUP

When sampling bottles are not required, such as when trying to operate the SBE 25plus from a small boat where only minimum equipment (and no bottle sampling) is required, an optional setup may be used. The SBE 25plus may be powered directly from the surface via an external power supply providing 14-16VDC at 2A or greater or water column profile data can be stored internally without a power connection using internal batteries ((12) D cell batteries). Power and data hookup would be via a cable assembly such as EBOS613 or equivalent.

When operating at less than 14VDC, the SBE 25plus will default to, and consume, its own internal alkaline battery pack. See Caution 1 below.

3.3. OPERATIONAL PARAMETERS

The Shell SBE 25plus CTD system, as a whole, is limited to 100M deployment depth. This is to avoid damage to the mechanical strain-gage pressure transducer for this system (e.g., 0-100M range). Lowering the system to >100m depth can cause damage to the strain gauge such that water can penetrate the sealed system and damage the electronics. See Caution 2 and 3 below.

The system is also limited by the crush depth of the various instrument housings. As supplied, the limiting factor for the SBE 25plus CTD system is 600M. This can be extended by purchasing a stronger-rated housing from Sea-Bird for the SBE 25plus main unit, and alternative sensors.

The SBE25plus pumps water past several sensors. If this water freezes, the sensors can be damaged. Maintain the system >2deg C if at all possible. If this is not possible, blow the water out of the pump and tube system with dry air.

Depth ratings for various units of the SBE 25plus system are given below. Consult sensor specific operating manuals for their operating limitations.

3.4. INITIALIZING ACTIVITIES

The SBE 33 requires 120 or 240VAC at 50/60 Hz (selectable) for operation.

3.4.1 Zeroing the Depth

Allow the SBE 25plus to equilibrate (with power on) in a reasonably constant temperature environment for at least 5 hours before starting. Pressure sensors exhibit a transient change in their output in response to changes in their environmental temperature. Sea-Bird instruments are constructed to minimize this by thermally decoupling the sensor from the body of the instrument. However, there is still some residual effect; allowing the SBE 25plus to equilibrate before starting will provide the most accurate calibration correction.

1. Place the 25plus in the orientation it will have when deployed.
2. In Seasave, in the .xml con file, set the pressure offset to 0.0.

DRAFT

3. Acquire data, and display the 25plus pressure sensor output in decibars.
4. Compare the 25plus output to the reading from a barometer at the same elevation as the 25plus' pressure sensor. Calculate offset = barometer reading – 25plus reading
5. Enter calculated offset (positive or negative) in the .xml con file.

Due to the sensitivity of these instruments, the readings will vary by some small amount inherent in the signal. For depth, an on-deck reading of ±0.2m is acceptable. If values begin falling outside that range, re-zeroing is recommended.

3.5. POWER

The electrical power for the system can electrocute a person. Use extreme caution when handling the electric conductor winch cable and the CTD/Carousel system, especially when the power is energized (see Caution 4 below).

3.5.1 Switch

The SBE 25plus main unit has an external magnetic slide switch controlling an internal switch. This external switch must be in the 'ON' position to enable the SBE 25plus main unit to power the modular sensors and to transmit data to the surface.

3.5.2 Power Sources

When the SBE 33 deck box is energized, the SBE 33 Deck Unit provides the required power and the alkaline batteries in the SBE 25plus are bypassed. If the SBE 33 Deck Unit is switched off but the SBE 25plus switch is allowed to remain in the 'ON' position, the batteries will continue to energize the SBE 25plus and will become depleted over time.

When the SBE 25plus is powered directly from the internal batteries, when the switch is in the 'ON' position, the batteries will be depleted if left on. Ensure that the SBE 25plus switch is in the 'OFF' position whenever using internal power but not collecting data.

3.5.3 Memory Backup batteries

The SBE 25plus also has two internal lithium batteries for memory backup (6VDC nominal). If the alkaline battery pack is allowed to deplete below the voltage level of the lithium batteries, the lithium memory batteries will take over function of the CTD and will be depleted rapidly. Memory settings will be lost and the CTD will have to be reinitialized. See Caution 7 below.

Note

CAUTION!

1. *If the internal battery pack becomes depleted, fresh batteries should be installed immediately. Depletion of the internal battery pack could cause the batteries to leak after a period of time and corrode the internal circuitry of the SBE 25plus.*

2. *The SBE 25plus system should not be used in depths greater than 100M, in accordance with the rating on the strain-gage (pressure sensor) system. Use of the system below these depths will*

DRAFT

result in serious damage to the SBE 29 Pressure Sensor.

3. *If the CTD system is to be used at depths greater than 100M, the existing depth sensor must be replaced to withstand the new depth, with a current, or a new depth sensor purchased.*

4. *Do not mate or un-mate any connectors while the SBE 25plus system is powered on.*

5. *Do not expose the SBE 25plus modular sensors to air temperatures below -2° C when the instrument and sensors are wet. The freezing of water in the SBE 4 Conductivity Sensor, SBE 43 Dissolved Oxygen Sensor, or WETLabs WETStar flow-through fluorometer probe will damage the cell.*

6. *If temperatures below -2° C are to be encountered, remove any water from the conductivity cell and other plumbed sensors with dry air. Protect all sensors from temperature extremes whenever possible.*

7. *If the slide switch is left on with the SBE 33 Deck Unit off, the SBE 25plus main unit will continue to remain powered, and provide power to the modular sensors as well. This will deplete the internal batteries and could cause damage to the unit. It is imperative to turn off the SBE 25plus slide switch (or the externa1 4-16VDC power supply) when the SBE 33 is off.*

3.6. Deployment and Retrieval

1. Confirm ship as at the correct sampling location
    a. Confirm station code is correctly entered on project specific log form
2. Check all sample bottles for correct triggering position
3. Remove protective sensor covers
4. Turn AC system on
5. Turn battery power on
6. Gently lift system over the ship rail or stern and gently lower into the water
7. Lower system to a depth of ~3 meters
    a. Allow bubbles to escape the system tubing and sensors to equilibrate (~1-2 minutes)
    b. Check data on all sensor channels on field laptop
8. Raise system so top of system is just under water (sensors should be at ~1m water depth)
9. Lower system to target depth of ~2 meters above the seafloor at a winch speed of ~30 m min^{-1}
    a. Use Valeport altimeter unless data are questionable
    b. If altimeter is not appearing accurate, use winch wire counter or marked cable
    c. Review downcast data and determine five target depths for discrete water sample collection based on turbidity and transmissometer data
    d. Either
        i. a) Program system to trigger bottles to collect water at the designated depths

DRAFT

or

ii. b) Prepare to manually fire the bottles for water sample collection

e. Communicate plan to winch operator and deck hands

10. Raise system to lowest of five depths
    a. Stop system
    b. Either
        i. a) winch up slow to allow automatic triggering of bottle
            1. or
        ii. b) manually trigger collection of sample
11. Raise system to second depth up from the seafloor
12. Repeat steps 10a and 10b and 11 until all five depths are sampled
13. Communicate to winch operator and deck hands that the cast is complete
14. Turn the AC system power off
15. Lift the system over the ship rail/stern and set on the deck gently
16. Secure system to deck
17. Turn battery power off
18. Collect water samples into appropriately pre-labeled containers
19. Review electronic cast data for acceptability
    a. Record cast number and electronic file information on project specific log form
20. Communicate to back deck ship crew or bridge the next sampling station
21. Cover any sensors as needed
22. Set water bottle triggering systems for next deployment

4.0 MAINTENANCE

4.1. ROUTINE MAINTENANCE

When mating connectors to the SBE 25plus CTD, the mating surfaces of the connectors should be cleaned and lubricated using a silicone based lubricant (such as DOW-Corning #4). The use of Barium-soap based lubricants is not recommended. Lubricant should be used sparingly. Care should be taken when handling any instrument sensors after using the silicone since transferring silicone to a sensor probe could contaminate the probe, causing it to provide erroneous measurements.

When the instrument is not to be used for extended periods of time (as in, long transits between stations) the system may be powered down if desired. Additionally, rinsing the carousel and instruments with freshwater is recommended.

DRAFT

4.2. FIELD INSPECTION, DISASSEMBLY AND REPLACEMENT

O-rings should be inspected any time that the SBE 25plus is disassembled. Check thoroughly for cracks, splits, nicks, geometry (i.e., loss of its circular cross section due to compression) or any other defect. When in doubt, always replace an O-ring as they are critical to preventing catastrophic damage to the electronics.

Make note of any issues with the system and relay the issues to the field leader so corrective and/or preventative actions can be taken after the survey.

5.0 TRAINING

A qualified technician must train individuals to perform the procedures described in this SOP. A qualified technician is considered to be an individual who has been trained in this process and has performed it in the past (within two years) and for whom a training certificate or equivalent document of experience exists.

The trainee should begin by reading this SOP in its entirety; all questions should be directed to a qualified technician. A qualified technician must then perform the procedures in Section 3.0 in their entirety with the trainee. The trainee must then perform the procedures in their entirety, including completion of documentation, while the qualified technician observes.

Once the procedures described in this SOP are understood and have been demonstrated by the staff member, training is documented in Battelle University. When registering the training as complete, the comment section should be used to indicate the name of the trainer and the date of training.

Users of this instrument are required to read this SOP, as well as be familiar with the SBE 25plus Sealogger CTD User Manual, the SBE 32 Carousel Water Sampler User Manual, and the SBE 33 Carousel Deck Unit User Manual, and be familiar with the individual sensors calibration documentation sheets.

6.0 SAFETY

The operation of the Sea-Bird SBE 25plus SBE 32 Carousel system requires working on the water and with electricity, causing routine field operations risks. All personnel should be aware of the hazards listed below and take necessary precautions to minimize risk. When working with electrofishing equipment, personnel must wear rubber boots and gloves.

• Drowning - When working on or near water, there is always a risk of drowning. Life jackets must be worn during the system deployment and retrieval operations, as well as specific vessel and project safety requirements.

• Fire – It is highly unlikely, but a power shortage could cause a fire. As always working on a vessel, make sure you know where the fire extinguishers are located and what the emergency notification procedures are for the specific vessel.

• Tripping and falling - Cables and ropes must be kept clear of machinery and should be routed so as to avoid tripping deck hands, scientific support staff, and any other people on the vessel.

• Injuring others - Operators working where space is restricted should take care not to injure others when deploying and retrieving equipment.

DRAFT

• Electrical hazards – When working with electrically charged equipment, electric shocks may cause serious injury or death, or may cause indirect injuries by making a worker recoil so that he endangers himself and others by sudden movement. Direct effects include electrical burns, heart failure, or interference with breathing. The main sources of potential risk of electric shock during the SBE 25plus/SBE 32 Carousel/SBE 33 Deck Unit operations are:

• Bodily contact with energized wires.
• Bodily contact with isolated water being energized by an electrical short.
• Shocks from damaged, inadequately constructed, or poorly insulated equipment.

Warning!

- *In the event of actual or suspected instrument flooding, disassembly of the instrument should only be performed by qualified personnel. Pressure buildup inside any flooded instrument housings could result in parts becoming lethal projectiles as internal pressure is released.*

- *The internal circuitry of the SBE 32 CTD Deck Unit contains high AC and DC voltage sources. This voltage could be harmful or possibly fatal if the box is open while power is applied. Ensure that the power to the unit has been turned off and disconnected before opening the box. In addition, 250VDC will be present at the 'wet' end of the sea cable when the box is energized.*

- *Capacitors in the power supply circuitry may still be holding a severe or lethal charge for an unspecified time even with the power cord disconnected. Inspection and repairs should only be undertaken by a qualified technician.*

APPROVALS

Author	_____	_____
Technical Reviewer	_____	_____
Quality Systems Manager	_____	_____
Resource Manager	_____	_____
	Name	Date

DRAFT

Attachment 1

User Manuals

Equipment	User Manual File Name
SBE 25plus Sealogger CTD	25plus_004.pdf
SBE 32 Carousel	32_022.pdf
SBE 33 Deck Unit	33_014.pdf
SBE Model 43 Dissolved Oxygen Sensor (SOP No. 3-180)	Appnote64-2Jun12.pdf 67326Q.pdf
SBE Model 18 pH Sensor	appnote18-2Sep14.pdf
WET Labs ECO Triplet (Fluorescence, Turbidity, CDOM (Colored Dissolved Organic Matter)	WETLabs-ECOMaster=3en.pdf
WET Labs C-Star Transmissometer (SOP No. 3-174)	C-Star-Rev-V-Manual.pdf
Seapoint Turbidity Meter (SOP No. 3-162)	Seapoint Turbidity Meter stm_um.pdf
Valeport VA-500, Altimeter	Valeport 0430831e_VA500_Altimeter_Manual.pdf

DRAFT

Battelle
Standard Operating Procedure

for

COLLECTING AMPHIPODS FOR CHEMICAL ANALYSIS USING BAITED TRAPS

1.0 OBJECTIVE

This SOP describes the at-sea collection and processing of amphipods collected with baited traps.

2.0 PREPARATION

2.1 SUPPLIES AND EQUIPMENT

- One anchor per set of traps
  - Size weight dependent on sea conditions and vessel
  - Typically a 15-20 lb Danforth type anchor is effective
- Chain for connecting to anchor and float line
  - ~3/8" chain, 5-10ft long
- Line from anchor to surface floats
  - Typically 3/8-5/8" Poly/Dacron line or similar is preferred
  - Allow adequate length so the floats will not submerge during high tide and the floats will not put undo lifting force on the anchors
- Two bullet floats (the type routinely used for crab and lobster pots)
- Short lines for attaching traps, smaller diameter e.g. ¼" is acceptable.
- Plastic minnow traps
  - Traps get lined with nylon or similar mesh, mesh size ~1mm
- Sardines for bait
  - Sardines packed in oil are preferred
  - Ancient Arctic myth says mustard soaked sardines are most successful
  - Bait needs to be placed into nylon (e.g. Nytex®) or similar plastic bags made from mesh
  - Bait bag mesh should be ~0.5mm mesh size
- Weight (e.g. rocks) for keeping traps on the seafloor
  - ~1-2lbs is fine, does not need to be very much weight (~1-3 rocks, each ~½ of a fist size)
- Cable ties (assume ≥10 per deployment)
- Plastic sieves for collecting and rinsing amphipods
  - Sieves are typically ~30cm diameter with 0.5-1.0mm mesh
- Funnels screened and unscreened for transferring amphipods to sample jars
- Hoses and fittings for the rinsing process
- Water pump for rinsing process
- Sample containers: As specified in the project specific QAPP/SAP. Containers typically consist of glass wide-mouth jars with Teflon® lined lids; typically 125ml, 250ml, and 500ml sizes
- Squirt bottles for rinsing organisms with site water, distilled water, and/or solvent for rinsing and decon, as specified by the project specific QAPP/SAP
- Nitrile gloves
- Writing tools e.g. ink pens, permanent markers, and pencils

DRAFT

- Bristle brushes for cleaning traps and mesh liner
- Non-phosphate detergent for cleaning traps between stations if required (e.g. Alconox® or Liquinox®).
    - Detergent is also useful for oil contamination (e.g. Joy® dish detergent)
- Common equipment and supplies that are not always required: forceps, disposable spoons

2.2 SOLVENTS (FOR CLEANING EQUIPMENT BETWEEN STATIONS)

Solvents and the decontamination process are specified in the QAPP/SAP. Solvents may consist of one or more of the following

- Alcohol (e.g. methanol, ethanol)
- Hexane

3.0 PROCEDURE

3.1 DEPLOYMENT OPERATIONS

The QAPP/SAP will specify the target organisms and required tissue mass.

1. Review operations below with deck crew, vessel captain, and mates prior to performing the sampling operations
    - Go over deployment needs such as the vessel needs to stay on station without dragging float line and floats into the propellers or side thrusters during deployment
    - Establish target deployment duration
        - Duration varies based on several factors, including but not limited to:
            - Project logistics
            - Success at collecting organisms
            - Local vessel traffic (can run over and cut floats)
            - Ice (can pass over trap lines and move/destroy traps
            - Typically a 12-24 hour set is adequate, but often less time is sufficient if cruise logistics dictate moving away from the area
    - Establish the station or order of stations to be sampled
        - Confirm first station and direct captain and mate to proceed to that station
2. Organize location to wash and process samples at a convenient location on deck, influenced as minimally as possible by stack emissions, and secure equipment to the vessel as needed for safe operations
3. If filtered water is required in the QAPP/SAP, set up the water filter system by inserting a clean filter, connecting the supply and discharge water hoses, and securing it to the vessel and/or sample processing system.
4. Assemble the anchor-trap-float system
    - *See Attachment 1 for a schematic of trap system*

DRAFT

- Attach chain to the anchor with a shackle
- Attach chain to the float line with a shackle
- Seize all shackles to secure shackle pins from unscrewing using cable ties, seizing wire, or other suitable method.
- Attach two floats to float line, leaving 3-5m of line between floats
  - The two floats allows a floating section of line for the deck crew to hook onto with a grapnel hook for retrieval
- Place bait in two bait bags (one for each of two traps) and seal ends of bags with cable ties or other low contamination mechanism
  - ~1 typical can of sardines per bag per trap
- Place bait bags and rock(s) into each of the two traps
- Connect two sides of the minnow traps together with cable ties
  - Do <u>not</u> use clips supplied with some minnow traps to connect the two sides
- Attach two minnow traps to anchor chain or float line
  - Use 2-3m lengths of float line, or smaller line (~1/4" diameter)
  - Secure knots with cable ties or electrical tape

5. Deploy traps one of several ways:
   - By hand
   - Using a fisherman 'pot puller' style winch
   - Using ships' normal winch with a pelican hook or other release system
6. Communicate with the captain/mate that the gear is ready for deployment
   - Confirm with captain/mate station location
7. Fill out station log form provided in the QAPP/SAP as much as possible
   - *See Attachment 3 for an example of a field log form*
8. Set the anchor and chain on the deck of the ship where it needs to be for deployment
   - Confirm with captain/mate it is ok to launch equipment (e.g. vessel is at location and in position to hold steady during deployment)
9. Deployment:
   - Lift the amphipod trap system over the stern/side of vessel and lower to the water surface
   - Communicate to captain/mate the gear is in the water
   - Let the anchor and traps descend under a controlled rate of speed (not a free fall)
   - Communicate to captain/mate when anchor and traps are on the bottom and the floats are clear of the vessel
   - Recover net to ship by lifting over rail/stern with winch
   - Notify captain/mate the gear is safely on board the vessel
   - Confirm next station if appropriate

DRAFT

10. Recovery:
    - *See Attachment 2 for a photo of trap recovery*
    - Prepare grapnel hook and line system
    - Confirm with captain/mate what station you need to recover
    - Have captain/mate navigate to location
        - Keep watch for floats on surface
        - Communicate to captain/mate when visual siting is made (or conversely, the captain/mate will communicate to deck crew they have the floats in visual range)
    - When approaching floats, confirm with captain/mate it is ok to throw grapnel hook
    - When in range, throw the grapnel hook
        - Repeat as many times as it takes to capture line between the floats
        - This may require the vessel to move away and return
    - When the grapnel hook was captured the float line, pull the float line to the vessel
    - Once upper part of float line is on vessel, use the pot puller, other winch system, or manual labor to retrieve the traps, chain, and anchor
    - Notify captain/mate when gear is safely onboard
    - Confirm next station or alternative operation with captain/mate
11. Untie traps from lines attaching to float line
12. While wearing clean nitrile or similar gloves:
    - Place traps in mesh sieve
    - Cut cable ties
    - Separate two halves of minnow trap
    - Remove bait bag and rocks
        - Rinse amphipods off of rocks into sieve
    - Pour/rinse amphipods into sieve
    - Rinse amphipods with site water
    - Remove any non-target species animals (e.g. shrimp, crabs)
    - Transfer amphipods to funnel screen
    - Rinse amphipods with de-ionized water
    - Transfer amphipods to pre-labeled sample jars
    - Repeat steps in #12 for second trap
13. Handle and preserve target organisms as described in the project specific QAPP/SAP
14. Complete recording of station log
15. Decontamination procedures are described in Section 3.2.

DRAFT

3.2 DECONTAMINATION CLEANING PROCEDURES

All minnow traps, mesh liners, and bait bags should be cleaned with a non-phosphate detergent such as Alconox® or Liquinox® prior to the survey, and as necessary between stations. Traps and mesh can be reused if carefully decontaminated prior to each survey. Amphiods do not highly interact (e.g. feed) on the traps, thus thoroughly rinsing the gear with site water is the primary decontamination method between stations. Sampling apparatus will be decontaminated with soap and solvents in the field only if there are gross to levels of contamination (e.g. visible oil on the traps or line) between sampling stations. If the float line is heavily contaminated, it is best to replace the line. While performing the decontamination procedure, "phthalate-free gloves," such as nitrile or butyl rubber, are used to protect the field staff as well as preventing contamination of the sampling equipment or the samples.

If further decontamination is required

1. Rinse equipment with tap water or site water
2. Scrub equipment with 1% non-phosphate soap (e.g. Alconox®) using a stiff brush
3. Rinse with tap or site water, then Milli-Q water
4. Rinse with appropriate solvent (as described in QAPP/SAP). In general, solvent will not be used unless an oily sheen is noted. Typical solvent rinse procedures are as follows:

    a. Begin with a solvent rinse of acetone and then DCM if oily contamination is apparent and will only be used on metal/stainless steel surfaces
    b. Let air-dry if solvent is used.

Note: All waste solvents must be captured and disposed of in labeled liquid waste containers. All equipment that comes into contact with the sample (i.e. syringe, ruler, collection buckets) must be cleaned using the same general procedures as the grab.

3.3 SAMPLE PROCESSING

Follow project specific QAPP/SAP requirements for sample processing. In general:

1. Empty the catch into a clean plastic or other non-metallic material sieve
2. Wash any sediment or other material off of all organisms using site water.
3. Remove non-target organism by hands covered with clean nitrile or other gloves as specified in the QAPP/SAP.
    a. Release unwanted organisms back into the water
4. Rinse organisms with de-ionized water
5. Transfer organisms to pre-labeled sample jars either by:
    a. Within the larger sieve
        i. Perform final rinses as required in the QAPP/SAP, such as a final deionized water rinse
    b. Transfer the organisms to a funnel sieve
        i. Perform final rinses as required in the QAPP/SAP, such as a final deionized water rinse
6. Store the jars in conditions described in the QAPP/SAP.

DRAFT

4.0 CALCULATIONS

There are no calculations necessary for this procedure. However, it is useful to estimate volume of tissue sample by using the percentage filled of the known volume jar.

5.0 QUALITY CONTROL

Field replicates and equipment blanks for chemical analyses will be collected according to the QAPP/SAP. Any deviations from this SOP must be documented on the station log in the survey logbook. Careful attention to the procedures described in this SOP by trained, qualified personnel will ensure the quality of the samples collected.

6.0 TRAINING

A technician training in these methods must first read this SOP in its entirety. The trainee will then practice the procedures in the field under the watch of the instructor until proficiency is demonstrated.

A qualified sample processor must train individuals performing clam rake sampling. A qualified sample processor is considered to be an individual who has performed the processing in the past (within 2 years), and for whom documentation of training and/or experience exists. The methods explained in 3.0 are used as training standards. Once the procedures described in this SOP are understood and have been demonstrated by the staff member, training is documented in Battelle University. When registering the training as complete, the comment section should be used to indicate the name of the trainer and the date of training.

7.0 SAFETY

All personnel should wear protective clothing, safety glasses, and gloves when handling sample containers or reagent bottles containing solvents. All collectors should wear life vests, steel toed boots, and hard hats when handling the equipment on the vessel.

During training, the qualified sampler should explicitly point out hazards associated with the reagents and or equipment. The trainee should review the material safety data sheets for Ethyl and Methyl Alcohol.

Gloves, safety glasses (with side shields) and protective clothing such as rain gear that protects from chemical exposure must be worn when handling any of the above chemicals. Open containers must remain in a fume hood or used on deck at sea. If the analyst is exposed to any of the above chemicals the following procedures should be followed:

Skin contact. Remove contaminated clothing immediately, directing a stream of water under clothing while it is being removed, if possible. Wash affected area 15-20 min and ensure no evidence of chemical remains.

Eye contact. Wash eyes immediately with large amounts of water while lifting upper and lower lids for at least 15-20 min. Get medical attention immediately.

Ingestion. If victim is conscious, give large quantities of water immediately. **DO NOT INDUCE VOMITING.** Milk or activated charcoal may also be administered by trained medical personnel. Get medical attention immediately. Contact Poison Control Center and adhere to their advice.

DRAFT

Inhalation. Remove from exposure area to fresh air immediately. If not breathing, give artificial respiration. If breathing is difficult, oxygen is required. If near shore, an ambulance should meet the boat at the nearest dock. Otherwise, the coast guard should be called.

Analysts using this procedure must read the material safety data sheets (MSDS) associated with these materials thoroughly. MSDS are located in the laboratory and on the boat. In the event of an emergency, the MSDS should be submitted to the appropriate medical personnel.

ATTACHMENTS

Attachment 1. Schematic of Amphipod Traps
Attachment 2. Photo of Amphipod Traps Being Recovered
Attachment 3. Example of Biota Field Collection Log Form

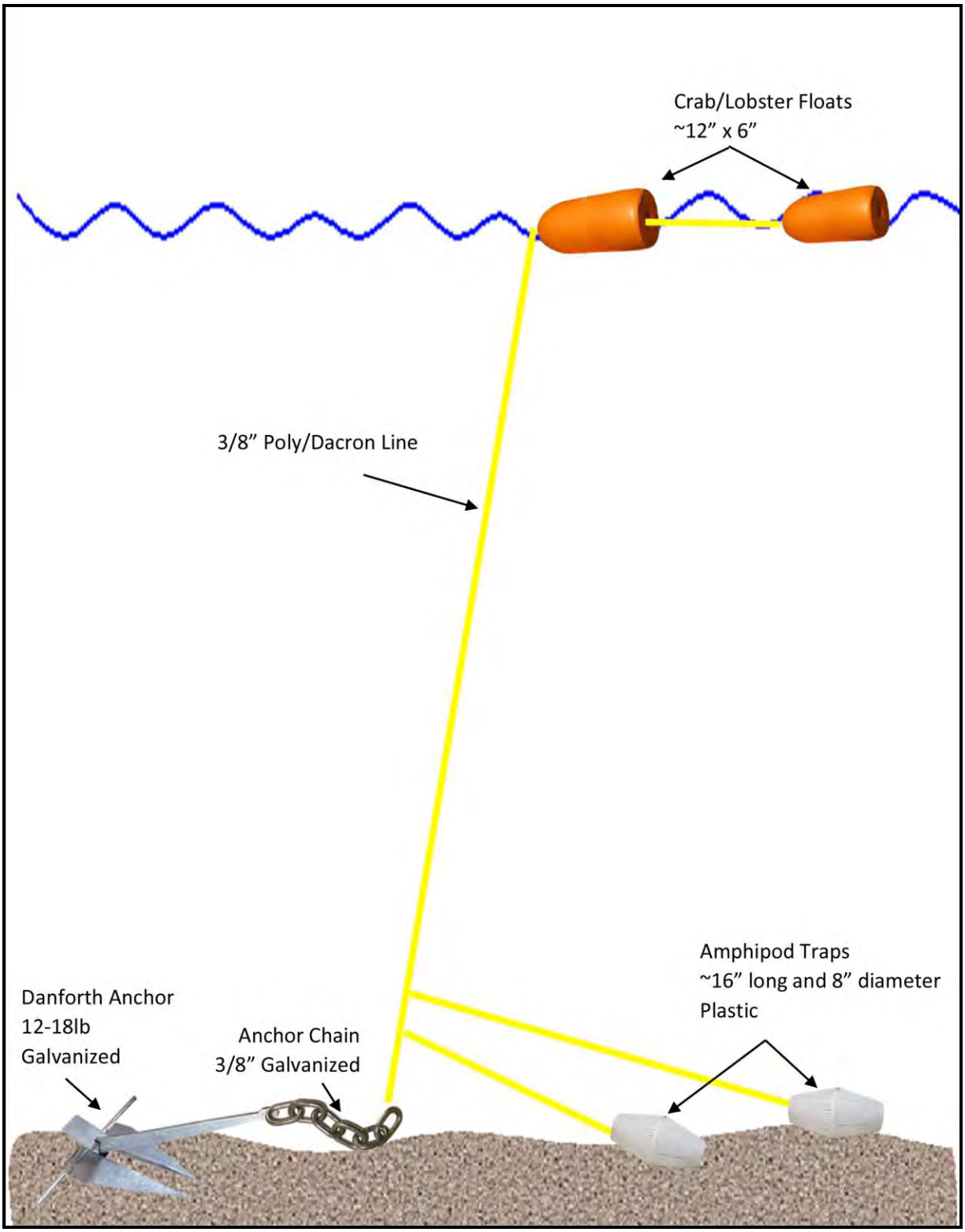
APPROVALS

Author	_____	_____
Technical Reviewer	_____	_____
Quality Systems Manager	_____	_____
Resource Manager	_____	_____
	Name	Date

DRAFT

Attachment 1.

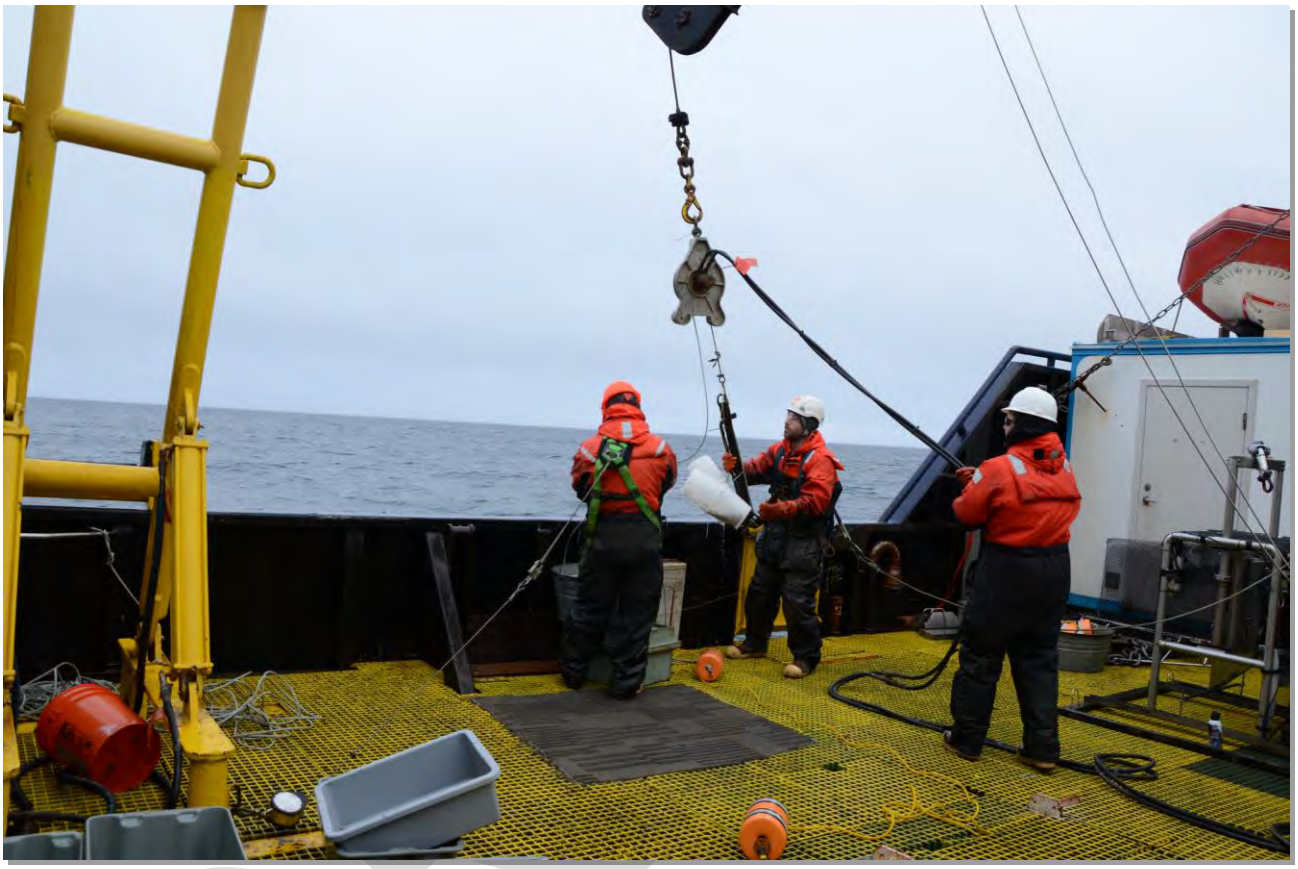
Schematic of Amphipod Traps



Attachment 2.

<u>Photo of Amphipod Traps Being Recovered</u>

(note amphipods in bottom of trap)



DRAFT

Attachment 2.

Example of Biota Field Collection Log Form

(Includes Amphipod Trap and Clam Rake Trawl Field Collections)

Project Name

Tissue Sample Log Form

Battelle Project No.	**Vessel:**	**Recorder:**
Station ID:	**Battelle Sampling Staff:**	**Sample Analyses:** PAH S/T

Amphipod Collection

Action	**# of Traps**	**Date/Time (local)**	**Water depth** (ft):	**Latitude** (N; WGS84):	**Longitude** (W; WGS84):
Deploy Traps					
Retrieve Traps					
Species (circle one) *Anonyx* Other		**Sample Collection time** (local)		**Sample ID**	
Deploy Traps					
Retrieve Traps					
Species (circle one) *Anonyx* Other		**Sample Collection time** (local)		**Sample ID**	

Clam Collection

Action	**Date/Time (local)**	**Water depth** (ft):	**Latitude** (N; WGS84):	**Longitude** (W; WGS84):
Deploy Dredge				
Retrieve Dredge				
Species (circle one) *Astarte* *Macoma* Other		**Sample Collection time** (local)		**Sample ID**
Deploy Dredge				
Retrieve Dredge				
Species (circle one) *Astarte* *Macoma* Other		**Sample Collection time** (local)		**Sample ID**

Field Activities / Comments / Observations:

Field Team Leader Signature and Approval _____ Page ____ of ____

Reviewed/Approved Date _____/_____/_____

DRAFT

FIELD COLLECTION OF SEAWATER SAMPLES FOR DISSOLVED TRACE METALS

1.0 Purpose

This standard operating procedure (SOP) presents the techniques used to collect seawater samples for dissolved trace metal analysis if not received from a collection agency. Several options are described to fit a variety of sampling requirements and conditions.

2.0 Application

This SOP applies to the collection of seawater samples containing dissolved trace metals in the ng/L (part per trillion) to mg/L (par per million) range. In summary, seawater is collected and filtered to remove particulate matter. It is then acidified to preserve the metals in solution.

3.0 References

Patterson, C.C. and Settle, D.M. 1976. The reduction of orders of magnitude errors in lead analyses of bio Special Publication 422, Accuracy in Trace Analysis: Sampling, Sample Handling, Analysis. Vol. 1., P.D. LaFleur (Ed.), pages 321-351.

4.0 Associated SOPs

None

5.0 Preparation

5.1 Supplies and Equipment

The following labware and equipment may be needed to perform the sample collection:

» Class 100 laminar-flow hood

» Powder-free polyvinyl gloves

» Tevek protective clothing

» 30 mL, 500 mL and/or 1 L low density polyethylene and Teflon bottles

» 1 mL Eppendorf pipet and tips (or equivalent)

» Polycarbonate filters, 47 mm diameter, 0.4 µm pore size (Poretics or Nuclepore)

» Solid Teflon filter forceps (Bel-Art)

» All-glass filtration glassware (Millipore XX15-047-00 or equivalent)

» Vacuum tubing (_" inner diameter)

» Oil-free vacuum pump (Gast 1HAB25BM100X or equivalent)

» Teflon wash bottle

» GO-FLO Niskin water samplers (General Oceanics)

» In-line filter holders, 47 mm diameter (Millipore XX43-047-00 or equivalent).

» High flow-rate peristaltic pump and tubing (Cole-Parmer)

» Polypropylene tubing (_" inner diameter)

» Kevlar hydrowire (¼" to _" diameter)

» Teflon messengers (General Oceanics)

» pH meter (Orion Ionalyzer Model 501 or equivalent) and pH buffers

» Non-contaminating acid resistant gloves

» Safety glasses or goggles

5.2 Acids, Gases and Reagents

» Reagent water: Distilled/deionized water with an electrical resistance of 18 megohm/cm or greater.

» Nitric acid: Ultrex II ultrapure reagent grade (J.T. Baker)

» Nitric acid: Trace metal grade (J.T. Baker)

» Hydrochloric acid: Trace metal grade (J.T. Baker)

» Pressure filtration gas: High purity nitrogen

6.0 Cleaning and Safety

6.1 Cleaning

All low-density polyethylene and Teflon bottles are cleaned by filling with hot (~70°C), concentrated nitric acid for 24 hours. Three successive rinses, of at least 6 hour duration, with reagent water then follow to remove residual acid and recondition the bottles (Patterson and Settle, 1976). The bottles are air-dried in a cleanroom facility and then sealed in plastic bags until use. Filtration glassware is washed in ~70°C 8 N nitric acid and rinsed with reagent water. Filters are washed in freshly prepared 5 N nitric acid for 24 hours and rinsed with reagent water as with the bottles. Niskin samplers are rinsed with 2 N hydrochloric acid followed by rinses with reagent water and ambient seawater.

6.2 Safety

When handling acids, reagents or samples, wear protective clothing, gloves and eye protection.

7.0 Procedure

7.1 Sample Collection

7.1.1 Surface Waters. (1) Collect surface seawater samples directly in acid-washed low density polyethylene or Teflon bottles from the bow of a small boat while wearing plastic gloves and moving slowly against the current. The bottles should not be opened until at least 10 cm below the sea surface and they should be rinsed with the ambient water on site immediately before collecting the final sample. (2) Use an acid-washed GO-FLO Niskin sampler lowered on a Kevlar hydrowire and tripped with a Teflon messenger. If possible, mount the bottle horizontally on the line and lower from a boom extended as far from the ship as practical. (3) Use a peristaltic pump with polypropylene tubing and a weight that is sealed in plastic and mounted on a boom. The pump should be located in a clean area and the polypropylene line flushed for several minutes with ambient seawater before collecting the sample.

7.1.2 Subsurface Waters. (1) Use an acid-washed GO-FLO Niskin sampler lowered on a Kevlar hydrowire and tripped with a Teflon messenger. If possible, mount the bottle horizontally
on the line and lower from a boom extended as far from the ship as practical. (2) Use a peristaltic pump with polypropylene tubing and a weight sealed in plastic and mounted on a boom. The pump should be located in a clean area and the polypropylene line flushed for several minutes with ambient water before collecting the sample. (3) A SCUBA diver may collect the samples at depths of less than 33 m using 1 L low density polyethylene bottles or a small hand-held Niskin water sampler.

7.2 Sample Filtration.

7.2.1 Vacuum Filtration. Transfer the collection bottles to a clean area, preferably a laminar-flow hood isolated from ship operations, exhaust gases and general traffic. All subsequent handling of the samples should be with plastic gloves and Tevek protective clothing. Filter the samples through acid-washed 47 mm diameter, 0.4 µm pore size, polycarbonate filters mounted on acid-washed glassware in a laminar-flow hood. Use an oil-free vacuum pump. Transfer the filtrate to acid-washed low density polyethylene or Teflon bottles (rinse the bottle with a small aliquot of filtrate first).

7.2.2 Pressure Filtration. If large volume Niskin sample bottles are used, pressure filtration in a clean and isolated environment with filtered N_2 gas is acceptable. Use 47 mm, acid-washed, in-line polypropylene or Teflon filter holders containing acid-washed, 0.4 µm pore size filters to remove particulates. The first few hundred mL of filtrate should be used as a collection bottle rinse and discarded.

7.3 Sample Preservation

Acidify the seawater filtrate to ~pH 2 with 1 mL of Ultrex II nitric acid/L if the samples are to be stored and not concentrated or analyzed immediately. The pH of the sample should be checked by transferring a few mL of sample to a small container to prevent contamination from the pH probe. If the pH is >2, add an additional 0.5 mL of nitric acid to the sample and re-measure the pH. Continue the 0.5 mL additions of nitric acid until a pH <2 is achieved.

7.4 Sample Storage

Acidified samples for dissolved trace metals are to be stored in sealed plastic bags and protected from high temperatures.

8.0 Calculations

There are no calculations involved with this SOP.

9.0 Quality Assurance/Quality Control

9.1 Quality Control Samples

Process quality control samples in the same manner as actual samples.

9.1.1 Equipment Blank. A minimum of one equipment blank should be prepared with each set of seawater samples. This blank consists of reagent water run through the same sample collection and filtration equipment used with the experimental samples. Separate blanks of sample collection and filtration apparatus are preferred. If the equipment blank is not less than 5 times the Method Detection Limit (MDL) for the required analyses, the source of contamination must be determined, corrected and documented before proceeding.

9.1.2 Travel Blank. A minimum of one travel blank should be prepared with each group of seawater samples. This blank consists of reagent water placed in a sample container under field conditions, acidified, and shipped with the experimental samples. If the travel blank is not less than 5 times the MDL for the required analyses, the source of contamination must be determined, corrected and documented before proceeding.

9.1.3 Reagent Water Blank. If reagent water is produced in the field, a minimum of three reagent water blanks should be placed in sample containers and acidified during the field collection process for analysis along with the experimental samples. If the reagent water blank is not less than 5 times the MDL for the required analyses, the source of reagent water should not be used until purity is restored and documented.

9.1.4 Duplicate Samples. Duplicate samples will be collected at a frequency of 5% or 1 per set of samples to establish collection reproducibility. If the relative percent difference is not within 20%, the sampling strategy should be reevaluated in terms of the project goals and (if necessary) corrective action taken and documented.

9.2 Interferences

Interferences which may result in sample contamination are a function of sampling location, field equipment/work area, and trace elements of interest. In general, the more isolated the sample collection and filtration process is from other activities, the easier the prevention or correction of contamination will be.

9.3 Documentation

The field identification will be maintained in all sample labeling, chain-of-custody and shipping documentation. Signed copies of all chain-of-custody forms will be retained by the collection and recipient agencies.

FILTER PREPARATION FOR SUSPENDED MATTER COLLECTION AND TRACE METAL ANALYSIS

1.0 Purpose

This standard operating procedure (SOP) presents the technique used to prepare filters for the collection of particulate matter from water samples for subsequent trace metal analysis, if not received from another agency.

2.0 Application

This SOP applies to the preparation of polycarbonate filters from 10 to 90 mm in diameter for the collection of suspended matter samples which will be digested and analyzed for trace metals analysis. In summary, filters are acid-washed, dried and weighed under cleanroom conditions.

3.0 References

Trefry, J.H. and Trocine, R.P. 1991. Collection and analysis of marine particles for trace elements. In Marine Particles: Analysis and Characterization, Chapter 5, Geophysical Monograph 63, D.C. Hurd and D.W. Spencer (Eds.) American Geophysical Union, Washington, DC., pages 311-316.

4.0 Associated SOPs

FIT-0001 FIELD COLLECTION OF SEAWATER SAMPLES FOR DISSOLVED TRACE METALS

FIT-5001 FIELD COLLECTION OF FRESHWATER SAMPLES FOR DISSOLVED TRACE METALS

5.0 Preparation

5.1 Supplies and Equipment

The following labware and equipment may be needed to perform the sample collection:

» Class 100 laminar-flow hood

» Powder-free polyvinyl gloves

» Tevek protective clothing

» 20-dram plastic vials with caps (or equivalent)

» Plastic drying basket (located in cleanroom or equivalent)

» Digital temperature and relative humidity monitor

» Polonium antistatic ionizing units (StaticMaster)

» Solid glass rod (≥4 inches long)

» Polycarbonate filters, 47 mm diameter, 0.4 µm pore size (Poretics or Nuclepore)

» Solid Teflon filter forceps (Bel-Art)

» Plastic petri dishes (Gelman)

» Teflon wash bottle

» Plastic bags (Ziplock, quart size)

» Non-contaminating acid resistant gloves

» Safety glasses or goggles

» Lint-free laboratory towels

» Electronic balance (6-place minimum) and calibration weights

» Marking pens, felt-tip, fine-point, black

5.2 Acids and Reagents

» Reagent water: Distilled/deionized water with an electrical resistance of 18 megohm/cm or greater.

» Nitric acid: Trace metal grade (J.T. Baker)

6.0 Cleaning and Safety

6.1 Cleaning

Plastic petri dishes and vials are washed by immersion in, hot (~70°C), 4 N nitric acid for 24 hours. Three successive rinses, of at least 6 hour duration, with reagent water then follow to remove residual acid and recondition the dishes. All Teflon materials are cleaned by filling with, or immersion in, hot (~70°C), concentrated nitric acid for 24 hours, followed by three reagent waters rinses as above. The plastic and Teflon materials are air-dried in a cleanroom facility and then sealed in plastic bags until use.

6.2 Safety

When handling acids wear protective clothing, gloves and eye protection.

7.0 Procedure

7.1 Filter Washing

1. Fill acid-washed 20-dram vials _ full (~20 ml) with concentrated trace metal grade nitric acid. With a Teflon wash bottle, add reagent water to the vials until almost full. Use a glass rod to immerse ten filters in each vial (discard the blue filter separators), then fill the remainder of the vial with reagent water and seal. Swirl vials gently to mix the acid-wash. Seal the vials in plastic bag and let sit for 24 hours at room temperature.

2. After the acid-washing is complete, pour off the acid and begin three successive, 12 hour, reagent water rinses. Completely fill the plastic vial with water, cap, swirl and store in a plastic bag each time.

3. At the end of the final reagent water rinse, use Teflon forceps to transfer the filters to acid-washed plastic petri dishes (in the laminar-flow hood). Place the filters, with the dishes cracked open, in a plastic drying basket, cover the basket with a plastic sheet and place the basket on the cleanroom drying rack.

4. After 24 hours of drying time at 21-23°C and 50% relative humidity, flip the filters in their petri dishes and return them to the drying rack for another 24 hours. At this point either seal the petri dishes and store the filters in plastic bags, or begin weighing the filters (**Section 7.2**). If the filters have been store for some time, crack open the petri dishes and let the filters equilibrate to cleanroom conditions on the drying rack for at least

12 hours before weighing.

7.2 Filter Weighing Before Sampling

1. Turn on the 6-place balance 12 hours prior to weighing the filters (go to Standby Mode) so it will be at thermal equilibrium and put two polonium antistatic units in the weighing chamber of the 6-place balance.

2. Just prior to weighing the filters, calibrate the scale using its internal electronic calibration and then follow up with external calibration weights. Record the calibration results and the temperature and relative humidity of the cleanroom.

3. Mark the lid of each petri dish with a unique, sequential number using a black marking pen. Weigh each filter (in random order) three times and record the weights. Calculate and record each filter's mean weight and standard deviation.

4. Reseal the petri dishes, group in lots of 20-24 filters, and store double-bagged in plastic.

7.3 Filter Weighing After Sampling

1. Return the filters to the cleanroom, crack open the petri dishes and let the filters dry to cleanroom conditions for 24 hours on the drying rack.

2. After 24 hours, use Teflon forceps to break loose the filters from the bottom of the petri dishes (but do not flip them in the dishes) and let dry for another 24 hours before weighing the filters as describes in **Section 7.2** (numbers 1 to 3).

3. Reseal the petri dishes and store bagged in plastic, in the cleanroom, for trace metal analysis.

8.0 Calculations

Mean filter weights (MFW) are determined using the equation:

$$MFW = (filter_{weight\ \#1} + filter_{weight\ \#2} + filter_{weight\ \#3}) / 3$$

The standard deviation (SD) of the mean filter weight is calculated using the equation:

COLLECTION AND DIGESTION OF PARTICULATE SAMPLES FOR TRACE METAL ANALYSIS

1.0 Purpose

This standard operating procedure (SOP) presents the techniques used to collect and digest particulate samples for trace metal analysis if not received from a collection agency. Several options are described to fit a variety of sampling requirements and conditions.

2.0 Application

This SOP applies to the collection and digestion of particulates for trace metal analysis from saline and freshwater samples containing suspended solids in the µg/L (part per billion) to mg/L (par per million) range. In summary, particulate matter is deposited on acid-washed filters, rinsed of residual salts and digested by refluxing in concentrated nitric, hydrofluoric and hydrochloric acids.

3.0 References

Patterson, C.C. and Settle, D.M. 1976. The reduction of orders of magnitude errors in lead analyses of biological materials and natural waters by evaluating and controlling the extent and sources of industrial lead contamination introduced during sample collection, handling, and analysis. In National Bureau of Standards Special Publication 422, Accuracy in Trace Analysis: Sampling, Sample Handling, Analysis. Vol. 1., P.D. LaFleur (Ed.), pages 321-351.

4.0 Associated SOPs

FIT-0001 FIELD COLLECTION OF SEAWATER SAMPLES FOR DISSOLVED TRACE METALS

FIT-5001 FIELD COLLECTION OF FRESHWATER SAMPLES FOR DISSOLVED TRACE METALS

FIT-6001 FILTER PREPARATION FOR SUSPENDED MATTER COLLECTION AND TRACE METAL ANALYSIS

5.0 Preparation

5.1 Supplies and Equipment

The following labware and equipment may be needed to perform the sample collection:

» Class 100 laminar-flow hood

» Powder-free polyvinyl gloves

» Tevek protective clothing

» 15-mL, 500-mL and/or 1-L low density polyethylene and Teflon bottles

» Assorted Eppendorf pipets and tips (or equivalent)

» Polycarbonate filters, 47 mm diameter, 0.4 µm pore size (Poretics or Nuclepore)

» Solid Teflon filter forceps (Bel-Art)

» Stoppered Teflon test tubes, round and conical bottomed (Berghof/America)

» Plastic test tube racks

» All-glass filtration glassware (Millipore XX15-047-00 or equivalent)

» Plastic petri dishes (Gelman)

» Vacuum tubing (_" inner diameter)

» Oil-free vacuum pump (Gast 1HAB25BM100X or equivalent)

» Teflon wash bottle

» Hotplate or heated water bath

» GO-FLO Niskin water samplers (General Oceanics)

» In-line filter holders, 47 mm diameter (Millipore XX43-047-00 or equivalent).

» High flow-rate peristaltic pump and tubing (Cole-Parmer)
» Polypropylene tubing (_" inner diameter)

SOP No.: FIT-6002
Date Initiated: April 16, 1997

» Kevlar hydrowire (¼" to _" diameter)

» Teflon messengers (General Oceanics)

» pH meter (Orion Ionalyzer Model 501 or equivalent) and pH buffers

» Non-contaminating acid resistant gloves

» Safety glasses or goggles

» Rubber wading apparel

» Plastic coated weight

» Lint-free laboratory towels

» Electronic balance (4-place minimum) and calibration weights

» Thermometer (0 to 110°C)

5.2 Acids, Gases and Reagents

» Reagent water: Distilled/deionized water with an electrical resistance of 18 megohm/cm or greater.

» Nitric acid: Ultrex II ultrapure reagent grade (J.T. Baker)

» Nitric acid: Trace metal grade (J.T. Baker)

» Hydrochloric acid: Ultrex II ultrapure reagent grade (J.T. Baker)

» Hydrochloric acid: Trace metal grade (J.T. Baker)

» Hydrofluoric acid: Ultrex II ultrapure reagent grade (J.T. Baker)

» Ammonium hydroxide: Ultrex ultrapure reagent grade (J.T. Baker)

» Pressure filtration gas: High purity nitrogen

6.0 Cleaning and Safety

6.1 Cleaning

All low-density polyethylene and Teflon materials are cleaned by filling with, or immersion in, hot (~70°C), concentrated nitric acid for 24 hours. Three successive rinses, of at least 6 hour duration, with reagent water then follow to remove residual acid and recondition the bottles (Patterson and Settle, 1976). The bottles are air-dried in a cleanroom facility and then sealed in plastic bags until use. Filtration glassware is washed in ~70°C 8 N nitric acid and rinsed with reagent water. Filters are washed in freshly prepared 5 N nitric acid for 24 hours and rinsed with reagent water as with the bottles. Niskin samplers are rinsed with 2 N hydrochloric acid followed by rinses with reagent water and ambient freshwater.

6.2 Safety

When handling acids, reagents or samples, wear protective clothing, gloves and eye protection.

7.0 Procedure

7.1 Sample Collection

7.1.1 Surface Waters. (1) Collect surface freshwater samples directly in acid-washed low density polyethylene or Teflon bottles from the bow of a small boat while wearing plastic gloves and moving slowly against the current. The sample bottles should not be opened until at least 10 cm below the water's surface and they should be rinsed with the ambient water on site immediately before collecting the final sample. (2) Wear wading apparel to move into the water body, allow several minutes for resuspended material to dissipate before collecting the sample. (3) Use an acid-washed GO-FLO Niskin sampler lowered on a Kevlar hydrowire and tripped with a Teflon messenger. If possible, mount the bottle horizontally on the line. (4) Use a peristaltic pump with polypropylene tubing. If a weight is used, it should be plastic coated. The pump should be located in a clean area and the polypropylene line flushed for several minutes with ambient freshwater before collecting the sample.

7.1.2 Subsurface Waters. (1) Use an acid-washed GO-FLO Niskin sampler lowered on a Kevlar hydrowire and tripped with a Teflon messenger. If possible, mount the bottle horizontally on the line. (2) Use a peristaltic pump with polypropylene tubing and a weight sealed in plastic. The pump should be located in a clean area and the polypropylene line flushed for several minutes with ambient water before collecting the sample. (3) A SCUBA diver May collect the samples at depths of less than 33 m using 1 L low density polyethylene bottles or a small hand-held Niskin SOP No.: FIT-6002
Date Initiated: April 16, 1997
Revision No.: 2
Revision Date: December 16, 2013

water sampler.

7.2 Sample Filtration.

7.2.1 Vacuum Filtration. Transfer the collection bottles to a clean area, preferably a laminar-flow hood isolated from other operations, exhaust gases and general traffic. All subsequent handling of the samples should be with plastic gloves and Tevek protective clothing. Filter the samples through acid-washed 47 mm diameter, 0.4 µm pore size, polycarbonate filters mounted using Teflon forceps on acid-washed glassware in a laminar-flow hood. Record the volume filtered and use an oil-free pump as the vacuum source. If the samples are saline, residual salts are removed by repeated rinsing with pH 8 reagent water. The filters are then transferred to acid-washed petri dishes and sealed for return to the laboratory.

7.2.2 Pressure Filtration. If large volume Niskin sample bottles are used, pressure filtration in a clean and isolated environment with filtered N_2 gas is acceptable. In a laminar-flow hood, acid-washed, 47 mm diameter 0.4 µm pore size, polycarbonate filters are loaded with Teflon forceps into acid-washed, in-line polypropylene or Teflon filter holders which are attached to the lower port of the Niskin sample bottles. Once the filtration is complete, record the volume filtered and return the filter holders to the laminar-flow. Carefully open the filter holders, apply a vacuum and rinse the filters of residual salts with pH 8 reagent water (if saline). Transfer the filters to acid-washed petri dishes and seal for return to the laboratory.

7.3 Sample Storage

Filters bearing suspended matter and digested suspended samples are to be stored in sealed plastic bags at a temperature above freezing but <25°C.

7.4 Sample Digestion

1. Dry and re-weigh the filters (FIT-6001) in the cleanroom to determine the amount of suspended matter to be digested. Calculate the total suspended solid (TSS) concentrations of the water samples.

2. Weigh milligram quantities of selected standard reference materials (SRMs) into round-bottomed Teflon test tubes. Use Teflon forceps to placed the suspended matter samples and filter blanks into conical Teflon test tubes. Reagent blanks are not tube specific.

3. Add 1 ml of Ultrex II nitric acid and 0.1 ml of Ultrex II hydrofluoric acid to each of the tubes in such a way that the filters are wetted with the acids. Use the Teflon stoppers to

seal the digestion tubes and then place them in a 1-liter beaker and fill it with reagent water up to the top of their conical section.

4. Seal the top of the beaker with a plastic bag. Poke a hole in the bag for a thermometer. Place the beaker on a hotplate and heat slowly to a temperature of 70-75°C. Remove the beaker from the hotplate and let the tubes cool slowly.

5. In the laminar-flow hood, use a lint-free laboratory towel to wipe reagent water condensation of the cooled tubes, tap the tubes in the hood to bring all the acid to the bottom and them swirl the tubes gently to help wash the suspended matter off the filters. Put the tubes back in the 1-liter beaker, add more reagent water if necessary, seal the beaker, reheat slowly to 70-75°C and then let the tubes slowly cool again.

6. Repeat Step 5, but stop after swirling the tubes. Tap the tubes in the laminar-flow hood again and place them in a plastic test tube rack. Gently remove the Teflon stoppers and add 0.2 ml of Ultrex II hydrochloric acid. Reseal the tubes, swirl gently and place them back in the rack (no heating). Pressure will build slowly in the tubes, forcing the stoppers to the top. At this point carefully remove the stopper to release the pressure and decant the digestion into a tarred 15 ml low-density polyethylene bottle. Add several small reagent water rinses of the digestion tube to the digestion (discard the filter), record the final weight of the solution, label the bottle and store for trace metal analysis.

8.0 Calculations

Total suspended solids (TSS) for the water samples are determined using the equation:

$$TSS_{mg/L} = (\text{particulate weight}_{mg} / \text{volume filtered}_{liters})$$

The Digestion Dilution Factors (DDF) for the suspended matter samples are determined using the equation:

$$DDF_{sample} = (\text{digest solution}_{grams} / \text{particulate weight digested}_{mg} \text{ X } 1000)$$

9.0 Quality Assurance/Quality Control

9.1 Quality Control Samples

Process quality control samples in the same manner as actual samples.

9.1.1 Filter Blanks. A minimum of two filter blanks should be prepared with each set of SOP

particulate samples. These blanks consist of acid-washed filters from the lot used with the experimental samples and are digested with each group of samples. If the filter blanks are not less than 5 times the Method Detection Limit (MDL) for the required analyses, the source of contamination must be determined, corrected and documented before proceeding.

9.1.2 Travel Blank. A minimum of one travel blank should be prepared with each group of particulate samples. This blank consists of an acid-washed filter placed in a sealed petri dish which accompanies the experimental filters to the field and back and is then digested. If the travel blank is not less than 5 times the MDL for the required analyses, the source of contamination must be determined, corrected and documented before proceeding.

9.1.3 Reagent Blanks. A minimum of two reagent blanks should be prepared with each set of particulate samples. These blanks consist of the digestion acids used to dissolve the particulates and are carried through the digestion process in the same manner as the experimental samples. If the reagent blanks are not less than 5 times the Method Detection Limit (MDL) for the required analyses, the source of contamination must be determined, corrected and documented before proceeding.

9.1.4 Duplicate Samples. Duplicate samples will be collected at a frequency of 5% or 1 per set of samples to establish collection reproducibility. If the relative percent difference is not within 20%, the sampling strategy should be reevaluated in terms of the project goals and (if necessary) corrective action taken and documented.

9.1.5 Method Accuracy Check. Milligram quantities of a sediment SRM provided by the National Institute of Standards and Technology or National Research Council of Canada are digested and analyzed at a frequency of 5% or 2 per batch of samples to verify method accuracy. If the experimental value of the SRM is not within the certified confidence interval, the source of error must be determined, corrected and documented.

9.2 Interferences

Interferences which may result in sample contamination are a function of sampling location, field equipment/work area, and trace elements of interest. In general, the more isolated the sample collection and filtration process is from other activities, the easier the prevention or correction of contamination will be.

9.3 Documentation

The field identification will be maintained in all sample labeling, chain-of-custody and shipping

documentation. Signed copies of all chain-of-custody forms will be retained by the collection

and recipient agencies.