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September 23, 2021

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SUBJECT: Final Report on the Joint Industry Project Study of Well Treatment, Completion, and Workover Effluents

Ms. Zavala and Ms. Staples,

The participants in the Joint Industry Project Study of Well Treatment, Completion, and Workover Effluents ("the JIP") are pleased to submit the attached final report in fulfillment of their requirement to conduct Characteristic Assessments of treatment, completion and workover (TCW) discharges under the industry-wide study alternative as required by NPDES Permits GMG290000 and GEG460000. The study participants are listed in Attachment 1 of this letter.

The JIP was organized and managed by the Offshore Operators Committee and was carried out in accordance with a study plan approved by the U.S. Environmental Protection Agency (EPA) Regions 4 and 6. The JIP involved collection of discharge information from participants, sampling of TCW discharges from a subset of participant discharges during 2019-2021, and laboratory analysis of sampled discharges for acute whole effluent toxicity and chemical composition.

Highlights from the results of this study are as follows:

- TCW discharges were brief in duration and small in volume. The median sampled discharge duration was 1 hour (h) and the median sampled discharge volume was 473 barrels (bbls). Based on an order-of-magnitude estimate of the total industry TCW discharges, the total volume of TCW discharges during 2019-2020 amounted to 0.01% of the volume of produced water discharges during the same period.
- Acute aquatic toxicities of TCW fluids were highly variable, with median lethal concentration (LC50) values ranging from 0.05% to > 50% effluent. No observed effect concentration (NOEC) values for a majority of samples were greater than the applicable NPDES permit critical dilutions.
- Reducing toxicity test exposure times from 48 h to 2 h tended to reduce toxicity. Considering the brief duration of TCW discharges, this result suggests that a 48-h acute exposure test provides a conservative metric for the risk of aquatic toxicity from TCW discharges.

- Acute aquatic toxicities of TCW fluids measured in this study were not significantly different than the acute toxicity of Gulf of Mexico produced water reported in the literature. Considering the brief duration and small volume of TCW discharges, this suggests that TCW discharges are not likely to pose a greater environmental risk than produced water discharges.
- Chemical analysis showed that calcium concentrations were associated with the toxicity of clear brine completion fluids. Concentrations of total organic carbon, dissolved organic carbon, and total suspended solids were correlated with the toxicities of workover and treatment fluids. The upper confidence limits of concentrations of metals and bromide ion at the critical dilution did not exceed available marine criteria for protection of aquatic life indicating that these substances did not have a potential to cause acute toxicity at the edge of the mixing zone.

Due to the large file size of the collected redacted toxicity test and lab reports (noted as Appendices D, F, and I of the attached report), we will arrange to transmit this information to EPA in electronic form.

After you have reviewed this report, the JIP participants would be happy to schedule a teleconference between EPA staff and the project team to discuss any questions regarding the results of this study. Please contact me if EPA would like to have such a meeting so that we can schedule it at a convenient time.

Sincerely,

Greg Southworth
Associate Director
Offshore Operators Committee

cc: EPA Region 6:
Ms. Nichole Young
Ms. Mitty Mohon

EPA Region 4:
Ms. Karrie-Jo Shell

Attachment 1

Participants in the Joint Industry Project Study of Well Treatment, Completion, and Workover Effluents

The following companies are participants in the Joint Industry Project Study of Well Treatment, Completion, and Workover Effluents and are jointly submitting this report in fulfillment of their requirement to conduct Characteristic Assessments of discharged treatment, completion and workover fluids under the industry wide study alternative as required by NPDES Permits GMG290000 and GEG460000.

- Anadarko Petroleum Corporation
- ANKOR Energy to ANKOR Energy, LLC , and including ANKOR E&P Holdings
- Arena Offshore
- bp
- BHP Billiton
- Beacon Offshore
- Byron Energy
- CETCO Energy Services
- Chevron USA, Inc. including Union Oil Company of California
- Contango
- Deepwater Abandonment Alternatives (DAA)
- ENI US Operating
- EnVen Energy Ventures, LLC
- Equinor
- ExxonMobil
- Fieldwood Energy, including QuarterNorth Energy and GOM Shelf LLC
- Halliburton
- Helis Oil & Gas Company, L.L.C.
- Hess
- LLOG
- Marubeni
- Medco Energi
- Murphy E&P
- Newpark
- Sanare Energy Partners, LLC
- Petrobras America
- Shell Offshore Inc., including Shell Gulf of Mexico Inc.
- Talos Energy including Talos Energy Offshore LLC, Talos ERT LLC, Talos Petroleum LLC, Talos Oil & Gas LLC, Talos Third Coast LLC
- TETRA
- TotalEnergies E&P USA, Inc.
- W&T Offshore, including W&T Energy VI, LLC
- Walter Oil & Gas

Final Report: Joint Industry Project Study of Well Treatment, Completion, and Workover Effluents

USEPA Region 4 Gulf of Mexico NPDES General Permit No. GEG460000
USEPA Region 6 Gulf of Mexico NPDES General Permit No. GMG290000

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Date: September 23, 2021

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Acronyms and Abbreviations List

Acronym	Explanation
%	Percent
API	American Petroleum Institute
bbl	Barrel
bbl/day	Barrel per Day
BOEM	Bureau of Ocean Energy Management
CAS	Chemical Abstracts Service
CD	Critical Effluent Dilution
cm	Centimeter
CMC	Criterion Maximum Concentration
COD	Chemical Oxygen Demand
CORMIX	Cornell Mixing Zone Expert System
CV	Coefficient of Variation
DDAC	Didecyldimethylammonium Chloride
DOC	Dissolved Organic Carbon
DQO	Data Quality Objective
EEUSA	Environmental Enterprises USA, Inc.
EPC	Exposure Point Concentration
ESV	Ecological Screening Value
GAC	Granular Activated Carbon
GHS	Globally Harmonized System
GOM	Gulf of Mexico
ICp	Inhibition Concentration
JIP	Joint Industry Project
LC25	25 Percent Lethal Concentration
LC50	50 Percent Median Lethal Concentration
LCSW	Laboratory Control Seawater
LDEQ	Louisiana Department of Environmental Quality
L(E)C50	Median Lethal (or Effects) Concentration
LHS	Latin Hypercube Sampling
LOEC	Lowest Observed Effect Concentration
m	Meter
Mbbl	Millions of Barrels
meq/L	Milliequivalents per Liter
mg/L	Milligrams per Liter
MVI	Marine Ventures International
NOEC	No Observed Effect Concentration
NPDES	National Pollutant Discharge Elimination System
OOC	Offshore Operators Committee
PAH	Polycyclic Aromatic Hydrocarbon
PP	Priority Pollutant
ppt	Parts per Thousand
PW	Produced Water
QAC	Quaternary Ammonium Compound
R_s	Spearman's Rank Correlation Coefficient
RL	Reporting Limit
RPM	Revolutions per Minute
SD	Standard Deviation
SDS	Safety Data Sheet
TAC	Test Acceptability Criteria
TBP	Tributyl Phosphate
TCW	Treatment, Completion, and Workover
TDS	Total Dissolved Solids

Acronym	Explanation
THPS	Tetrakis (Hydroxymethyl) Phosphonium Sulphate
TOC	Total Organic Carbon
TQ	Toxicity Quotient
TSS	Total Suspended Solids
TTPC	Tributyl Tetradecyl Phosphonium Chloride
TUa	Acute Toxic Unit
UCL	Upper Confidence Limit
USEPA	U.S. Environmental Protection Agency
VOC	Volatile Organic Compound
WAF	Water Accommodated Fraction
WET	Whole Effluent Toxicity
WRS	Wilcoxon Rank-Sum
w/w	Weight by Weight

Executive Summary

This report presents the results of a two-year joint industry project (JIP) study of well treatment, completion, and workover (TCW) effluents discharged directly to Gulf of Mexico (GOM) surface waters. This study was organized by the Offshore Operators Committee (OOC) to enable study participants to meet their National Pollutant Discharge Elimination System (NPDES) general permit requirements for characteristic assessments of TCW fluids under the Industry-Wide Study Alternative in permits GMG290000 and GEG460000. The study characterized TCW discharges and assessed the potential for TCW effluents to contribute to acute whole effluent toxicity. The study provides a better understanding of TCW effluent characteristics, their aquatic toxicity, and substances that potentially contribute to this toxicity. A summary of the study scope and key findings, organized by the study questions posed in the Introduction, is provided below:

- **What was the scope of the JIP study?** Twenty-eight samples were evaluated from November 2019 to May 2021. Samples were collected from the GOM western and central planning areas and represent a typical range of well operation and TCW effluent types. No samples were collected from the GOM eastern planning area because TCW effluents were not discharged in the eastern planning area during the study. Facility operators provided data on the discharge scenario, the type of fluid used, and the substances added to the fluids. The toxicity and chemical composition of sampled effluents were evaluated in laboratory tests.
- **How are TCW discharges typically handled and their discharge to GOM surface waters managed?** TCW effluents at sampled structures were discharged through a single port outfall or in a few cases, a diffuser. Most outfalls were situated just above or just below the ocean surface. One discharge occurred near the seafloor. Some effluents were subjected to end-of-pipe treatments such as granular activated carbon (GAC) or filtration. The median discharge duration and volume were 1 hour and 473 barrels (bbl), respectively. TCW discharges represent a small input to the GOM. An order-of-magnitude estimate of the volume of all TCW discharges in 2019-2021 was 0.01 percent (%) of the volume of produced water (PW) discharges during the same period.
- **What is the typical chemical composition of discharged TCW effluents? How variable is the chemical composition of a discharge?** Of the four categories of fluids identified during planning for this study, only TCW Category I (brine-based completion fluids) and Category III (workover and treatment fluids) were sampled during the study period. TCW Category I and Category III fluids are composed of chloride and bromide brines and may contain chemical products comprised of organic substances. TCW Category III fluids contained more added chemical products than did TCW Category I fluids. Pronounced variability in salinity, bromide, and calcium concentrations in effluents was observed among samples collected at different times during the same discharge.
- **How toxic are TCW discharges towards marine biota?** Acute 48-hour (48-h) whole effluent toxicity (WET) testing was conducted with *Menidia beryllina* (Inland silverside minnow) and *Americamysis bahia* (Mysid). The toxicity of TCW effluents to these organisms was highly variable, with acute 50% median lethal concentrations (LC50s) ranging from 0.2 to >50% effluent for the Inland silverside minnow and from 0.05 to 35% effluent for the Mysid. This variability appears to be influenced by end-of-pipe treatment, well operation type, stage of the

discharge, brine type, and the chemical additives used for each well operation. The Mysid was generally more sensitive to TCW effluents than the Inland silverside minnow. NOEC values of a majority (16 of 28) of samples were greater than the applicable NPDES permit critical dilutions.

Recognizing that the median duration of the sampled TCW discharges was 1-h, a series of toxicity tests using a 2-h exposure was performed. These tests showed that toxicity for 2-h exposures was generally less than toxicity in 48-h exposure tests. This suggests that, since TCW discharges are of short duration, a comparison of a 48-h NOEC with a critical effluent dilution (CD) as an indicator of potential acute toxicity has a high degree of conservatism.

Based on a comparison of JIP study and literature data, there are no significant differences in the acute toxicity of TCW and PW effluents to the Mysid. Thus, as TCW effluents are similar in potency and variability but have demonstrably smaller and shorter duration discharges, TCW effluents are unlikely to present a greater risk to the receiving environment than PW effluents.

- **What can be said about the cause of toxicity? Can general toxicity-composition connections be made?** Multiple lines of evidence were used to identify individual substances and classes of substances potentially contributing to toxicity, and potential sources of these substances. Ionic composition, specifically Ca^{2+} concentration, appeared to be associated with the toxicity of TCW Category 1 effluents to Mysids, whereas organics (based on the dissolved organic carbon (DOC) and total organic carbon (TOC) concentrations used as surrogate for organic chemical products or organics picked up downhole) were associated with Inland silverside minnow toxicity. DOC, TOC, and total suspended solids (TSS) appeared to contribute to toxicity to Mysid and Inland silverside minnow in most TCW Category III effluents. Chemical products present in TCW effluents contain primarily organic substances that, based on hazard classification and not considering actual environmental concentrations, could potentially contribute to aquatic toxicity of the TCW effluent samples.
- **What are the estimated concentrations of substances in GOM surface waters at the critical effluent dilution (CD), i.e., the concentration predicted to exist in the effluent plume at the edge of the 100-meter (m) mixing zone?** The composition of effluents diluted to the critical dilution applicable to discharges sampled for this study (0.1 to 1.25% effluent) mainly reflected the composition of the laboratory control seawater (LCSW) used as a diluent. Components displaying highly variable concentrations likely reflected contributions from the effluent, including substances used in formulating the fluids and substances picked up downhole. For TCW Category I effluents, these components included bromide, DOC, TOC, zinc, thallium, and barium. For TCW Category III effluents, these components included bromide, DOC, TOC, thallium, arsenic, and cadmium. Safety data sheet information provided by operators did not indicate that any priority pollutant metals were used in formulating fluids. No priority pollutant organics were detected in any effluent diluted to the Critical Dilution.
- **What substances are currently used in TCW fluids? What are their general aquatic hazard characteristics?** Substances used in TCW fluids include $CaCl_2$ and $CaBr_2$ brines and chemical products. Brine components can contribute to aquatic hazard by causing ionic imbalances.

Participants reported seventy-five (75) chemical products that were used in formulating TCW fluids discharged to GOM surface water and sampled during this study. Substances and their aquatic hazard characteristics can be summarized as follows:

- Safety Data Sheets (SDSs) for a minority of chemical products used in TCW fluids provided aquatic hazard information. For these products, an aquatic hazard assessment was conducted using the United Nations (2019) guidance *A Guide to The Globally Harmonized System of Classification and Labeling of Chemicals (GHS) 8th Edition*. Among the chemical products whose SDSs presented GHS classifications, there were products in each of the three GHS acute aquatic toxicity categories: GHS Category 1 – Very toxic; GHS Category 2 – Toxic; and GHS Category 3 – Harmful.
- Of the 75 chemical products reported, most (81%) were identified as "Not Assessed." For chemical products where GHS classification information was not provided in SDS Section 2, no aquatic hazard assessment could be made, and no conclusion about potential for aquatic toxicity is implied.
- The most frequently used chemical products in TCW Category I effluents were defoamers, oxygen scavengers, and corrosion inhibitors. The most frequently used products in TCW Category III effluents were fluid additives, defoamers, pH control, clay stabilizers, and viscosifiers. TCW Category III effluents contained more added chemical products than did TCW Category I effluents, including those with a GHS acute aquatic toxicity category of 1-3.

- **What substances could potentially be associated with acute aquatic toxicity at the CD?** A screening of measured concentrations of substances against acute ecological screening values (ESVs) was conducted. The screening was based on comparison of measured concentrations and estimates of the upper confidence limit (UCL) of concentrations for substances in TCW fluids as a group, with ESVs reported in the literature. For substances with measured concentrations, the screening evaluation did not identify any with the potential to cause acute toxicity at the edge of the mixing zone.

1.0 Introduction

This report presents the results of a two-year joint industry project (JIP) study of well treatment, completion, and workover (TCW) effluents discharged directly to Gulf of Mexico (GOM) surface waters. The JIP study was commissioned by Offshore Operators Committee (OOC) to enable JIP study participants to meet their National Pollutant Discharge Elimination System (NPDES) general permit requirements for characteristic assessments of TCW fluids under the Industry-Wide Study Alternative described in *Section B.6.c* of the general permit. The objectives of the JIP study are to characterize the chemical composition and acute aquatic toxicity of TCW effluents, and their potential to be a source of acute aquatic toxicity to GOM aquatic biota.

1.1 Study Questions

To achieve JIP study objectives, this report addressed the following study questions:

- What substances are currently used in TCW fluids? What are their general aquatic hazard characteristics?
- How are TCW effluents typically handled and their discharge to GOM surface waters managed? What is the duration and volume of a typical discharge?
- What is the typical chemical composition of discharged TCW effluents? How variable is the chemical composition of a discharge?
- What are the estimated concentrations of substances in GOM surface waters at the critical effluent dilution (CD), i.e., the concentration predicted to exist in the effluent plume at the edge of the 100-meter (m) mixing zone?
- How toxic are TCW effluents to exposed marine biota? Is exposure duration important?
- What can be said about the cause(s) of toxicity? Can general toxicity-composition connections be made?
- What substances could potentially be associated with acute aquatic toxicity at the CD?

1.2 Report Approach

This report presents an aquatic hazard identification with multiple lines of evidence, a risk assessment, and conclusions regarding sources of aquatic hazard in TCW discharges (**Figure 1**). Hazard is defined as a source of adverse effects to the aquatic environment, whereas risk is the probability that hazard will result in an observed adverse effect (Chapman, 2000). The aquatic hazard identification evaluations were conducted consistent with the U.S. Environmental Protection Agency (USEPA) Region 4 and Region 6-approved August 2019 study plan (AECOM and Marine Ventures International [MVI], 2019) and built upon evaluations presented in the February 2021 *Year 1 Interim Report*. Deviations from the study plan and the rationale for the deviation are noted in the text, where applicable.

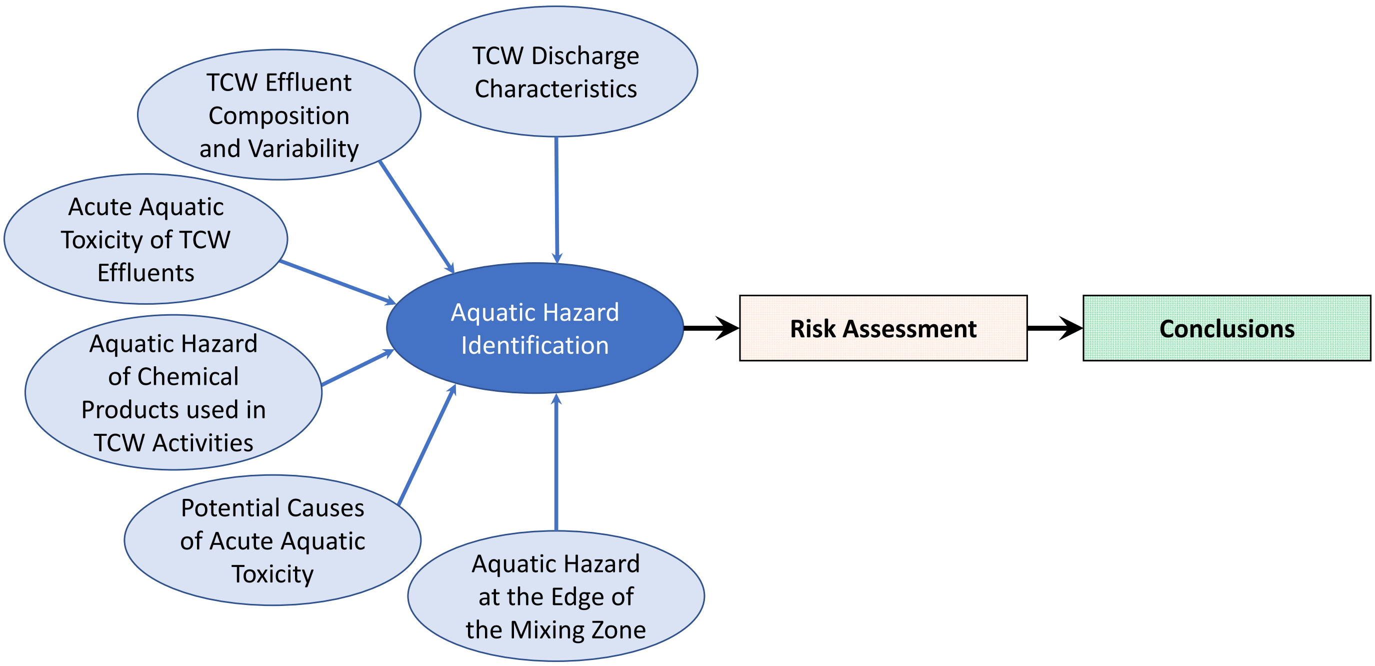


Figure 1. Conceptual framework of the JIP study.

2.0 Selection of Structures for Sampling

This section describes the approach used to select offshore platforms and vessels ("structures") for sampling in Year 1 (2019 to 2020) and Year 2 (2021). The general permit requirements for TCW fluid characteristic assessments (USEPA, 2017 a, b) under the Industry-Wide Study Alternative specify examination of a "*statistical[ly] valid number of samples of wells in the Western and Central [for USEPA Region 6] and Eastern [*for USEPA Region 4] *areas of the GOM.*" Structure selection was objective and intended to yield representative data that characterize the likely range of discharged TCW effluents.

2.1 Approach for Year 1

Nineteen structures were sampled within the GOM central planning area in Year 1. The structures were selected from a database of 95 planned discharges generated by JIP study participants using a survey questionnaire (**Appendix A**). Samples were collected between November 2019 and May 2020. In 2019, three structures were identified by JIP study participants and were sampled. In 2020, a larger number of structures were available and statistical sub-sampling consistent with the USEPA-approved study plan was warranted. The statistical approach was *n*-dimensional Latin hypercube sampling (LHS) (McKay et al., 1979). LHS is a stratified random procedure that provides an efficient way of sampling multiple input variables (Minasny and McBratney, 2006). Raw LHS output for the selected variables is provided in **Appendix B**.

2.1.1 Data Screening

Each of the 95 planned TCW effluent discharges were screened for consistency with JIP study data quality objectives (DQOs). Discharges were eliminated from consideration for sampling if the TCW effluents were comingled with PW or if the available information had insufficient detail to conduct the LHS analysis. The screened discharges were carried forward for LHS evaluation.

2.1.2 Input Variables for Sample Selection

Sixteen input variables (**Table 1**) deemed important for generating representative data were selected from the JIP study participant survey responses. The input variables fell into the following categories: geographical, TCW fluid category, presence/absence of chemical products, and presence/absence of TCW effluent treatment.

Table 1. LHS Input Variables Used to Select Structures for Sampling.

Input Variable Category	Input Variable	Data Type	Rationale for Selection
Geographical	Block No.	Discrete	Spatial aspect; position within the study area.
	Water Column Depth	Continuous	
TCW Fluid Category	Category I	Discrete: "Absent" = 0; "Present" = 1	May influence chemical makeup of discharge toxicity.
	Category II		
	Category III		
	Category IV		
Chemical Products	Corrosion Inhibitors		
	Non-emulsifiers		
	Surfactants		
	Defoamers		
	Biocides		
TCW Effluent Treatment	No Treatment or Tank Storage		
	Tank Storage		
	Filtration		
	Other Treatment, e.g. polishing step		

2.2 Approach for Year 2

Sampling was conducted from late February through early May 2021. Five structures were available for sampling in Year 2; samples were collected as they became available. LHS analysis was not performed in Year 2 due to the smaller number of discharges planned in the available study period. All available TCW discharges were tested.

2.3 Samples Evaluated

In total, 28 samples were evaluated across 23 structures during the 2-year study; each sample was assigned a sample code (**Table 2**). It was found that an additional sample that was collected had not been discharged. Samples were collected from the GOM western and central planning areas and represent a typical range of well operation and TCW effluent types in the GOM. The lease area, block, and American Petroleum Institute (API) well number for each sample are provided in **Table A1**; individual sample locations are shown in **Figure A1.**

Table 2. Sample Collection Year and Sample Code.

Year Collected	Sample Code
2019	HV63
	JK70
	RD67
2020	RU61
	XP62
	NY50
	LC54
	YO64[1] AU71
	FP89
	ZG57
	GQ67
	YU91
	LX98[1] IS88
	RU72
	IH80[2]
	BT52
	SH87
	EP57 (Begin)[3] TR84 (End) CM89 (Code for mean results for samples EP57 and TR84).
	RC74 (Begin)[3] OD76 (Middle) TF74 (End) NZ96 (Code for mean results from samples RC74, OD76, and TF74)
2021	QK91
	DO57
	PO80
	JH68
	UP92

Notes: [1] Samples of different types of TCW effluents were collected from separate discharges. [2] After collecting sample IH80, the Operator determined that the sample was not discharged to GOM surface water. This sample was therefore not representative of TCW effluents. Results from this sample are presented in Appendix E but were not included in the overall analysis. [3] Effluent samples EP57 and TR84 were collected from the beginning and end of a discharge from a single structure. Samples RC74, OD76, and TF74 were collected at the beginning, middle, and end of a discharge from a single structure. Multiple samples were collected to characterize variability in effluent composition and aquatic toxicity during a single discharge

3.0 TCW Discharge Characteristics

This section addresses the following JIP study questions:

- *What substances are currently used in TCW fluids?* This question is addressed by identifying the categories of TCW fluids discharged to GOM surface waters and describing the type and general composition of TCW brines and chemical products that make up the fluids.
- *How are TCW effluents typically handled and their discharge to GOM surface waters managed? What is the duration and volume of a typical discharge?* These questions are addressed by describing the effluent discharge configuration; effluent discharge duration, volume, and rate; and treatment of effluents before discharge to surface water, where applicable. An informal estimate of the total volume of TCW discharges was compared with the total volume of PW discharges to provide perspective on the magnitude of TCW discharges.

3.1 Well Operation Type

Well operation types represented by the sampled structures were well treatment, completion, and workover. Detailed information associated with each well operation e.g., TCW fluid category and discharge characteristics is provided in **Table A2**.

3.1.1 Well Treatment

Of the 28 TCW effluent samples collected, 9 were associated with treatment well operations such as hydraulic fracturing, chemical treatment, wellbore cleanout, and acidizing.

3.1.2 Well Completion

Thirteen TCW effluent samples were associated with completion well operations. Completion well operations involve using solids-free brines to complete a well and facilitate final operations before production. The brine’s density is selected to provide sufficient hydrostatic pressure to control the well. Completion fluids may also contain polymers and other additives.

3.1.3 Well Workover

Five TCW effluent samples were identified by JIP study participants as being from workover well operations. Workover refers to the process of performing major maintenance or remedial treatments on a well or to set packers. Workover fluids are typically brines that are free of solids and that will not adversely affect either the reservoir fluids or the formation.

3.2 TCW Fluid Composition

There are four categories of TCW fluids (TCW Categories I-IV). The choice of fluid category depends on the type of well operation. A description of each TCW fluid category is provided in **Table 3**. Individual anions and cations, and other substances potentially present in chemical products used in sampled fluids are presented by TCW effluent sample in **Table A3**.

Table 3. Categories of TCW Fluids and Fluids Sampled.

TCW Category	Description	No. of Sampled Discharges
I	Typically clear, brine-based fluids use to treat, complete, or workover a well. May be comprised of fresh water or saltwater brines of appropriate density for well control. May contain some chemical products.	13
II	Organic (acetic and formic acids) and inorganic acids (hydrochloric and hydrofluoric) and/or blends of each.	0 (No TCW Category II fluid discharges were planned by project participants during the study period.)
III	TCW Category III fluids typically use a TCW Category I fluid as the base component. One or more additional chemical products are added to achieve desired properties: • Small amounts of polymers, e.g., guar, are used to give the fluid viscosity. • Cross-linkers, e.g., boron, are used to create a gel-like fluid consistency. Supporting additives used to improve the cross-link function or improve the performance of the fluid include buffers to maintain favorable fluid pH to stabilize the cross-link; surfactants to improve reservoir wettability and fluid recovery; and breakers that ensure that the cross-link breaks as designed.	15[1]
IV	Can be classified as a treatment, completion or workover fluid depending on how it is used. • The use of hydrocarbon-based fluids in TCW fluids is infrequent and normally limited to the removal of waxes and asphaltenes from the wellbore and/or sand face. • Some hydrocarbons can be gelled to act as fracturing fluids, but that is only when water-based fluids are damaging to the reservoir. This is not common in the offshore environment. • Gelled hydrocarbons may also be used as packer fluids to control convective heat transfer in wells that have high bottom hole temperatures or high flow rates that create a high-temperature environment that could damage ancillary equipment. • Base oils can be used to perform negative pressure testing for regulatory compliance.	0 (No TCW Category IV fluid discharges were planned by project participants during the study period.)

Notes: [1] After collecting sample IH80, the Operator determined that the sample was not discharged to GOM surface water. This sample was therefore not representative of TCW effluents and is not included in the total for Category III effluents. Results from this sample are presented in Appendix E but were not included in the overall analysis.

3.2.1 Brines

Brines form the base for TCW fluids:

- **TCW Category I**: TCW Category I fluids are used in completion well operations. The two classes of brines observed during the study are chloride brines: calcium chloride ($CaCl_2$), sodium chloride (NaCl), and potassium chloride (KCl); and bromide brines: calcium bromide ($CaBr_2$) and sodium bromide (NaBr).

- **TCW Category III**: TCW Category III fluids are used in workover, treatment, and fracturing well operations. In addition to a chloride or bromide brine base, TCW Category III fluids contain additional components that provide needed functional properties.

3.2.2 Chemical Products

In addition to chloride and bromide inorganic salts, chemical products are added to TCW fluids to support well operations and protect piping and associated infrastructure from fouling and corrosion. Seventy-five distinct chemical products with 31 product functionalities were used during the study (**Table 4**). The types of chemical products used varied with the type of well operation.

Table 4. Functionality and Number of Chemical Products used during the Study.

Functionality	Number of Chemical Products
Biocide	7
Defoamer	6
Viscosifier	6
Acid	5
Solvent	4
Breaker	3
Clay stabilizer	3
Corrosion inhibitor	3
Fluid additive	3
Non-emulsifier	3
Oxygen Scavenger	3
pH Control	3
Surfactant	3
Iron control	2
Linear gel	2
Proppant	2
Scale Inhibitor	2
Well cleaner	2
Activator	1
Base fluid	1
Completion Fluid Additive	1
Crosslinker	1
Diagnostic additive	1
Fluid stabilizer	1
Gellant	1
Hydrogen sulfide scavenger	1
Initiator	1
Intensifier	1
Oil Tracer	1
Stabilizer	1
Synthetic Mud Casing Scrubber	1
Total	**75**

Product Safety Data Sheets (SDSs) were consulted for information on chemical composition of the chemical products used. A summary of the dominant functionalities provided by chemical products is provided below by TCW category. Trade names of chemical products are not provided to ensure that proprietary information and/or trade secrets are not inadvertently revealed. Instead, chemical additive codes based on chemical functionality are used to identify chemical additives used in the study. SDSs sometimes only list chemicals by functionality, e.g., “surfactant” rather than by chemical name; this limitation is reflected in the following discussion:

- **TCW Category I**: Completion chemical products are used to clean wells after drilling, to control them while they are being perforated, and to make them operational when essential equipment such as packers and tubing are added (Boehm, et al., 2001). In some instances, no chemical products other than inorganic salts were present in TCW Category I fluids. When present, chemical products included biocides, acid treatments, scale inhibitors, non-emulsifiers, de-foamers, viscosifiers, pH control agents and well cleaners as described below:
    - Biocides are used to control microbiological growth in piping and other infrastructure to prevent fouling. The chemical product “Biocide 1” was an example of a biocide present in TCW Category I effluents and contains the aldehyde glutaraldehyde.
    - Acidification: In one instance, a treatment with acetic and hydrochloric acids was observed for a completion well operation with a TCW Category I brine. Acetic acid is used in high-temperature wells, typically in conjunction with hydrochloric acid. The acids are often pumped ahead of a frac or as a stand-alone treatment. Frac acids are not reversed out of the well; however, they and stand-alone treatments may be present in well flowbacks.
    - Scale inhibitors: Seawater often reacts with formation water to produce inorganic scales or deposits of barium or calcium salts that must be controlled with scale inhibitors. One anti-scaling product that was present in TCW Category I effluents is “Scale inhibitor 2”, which is composed of the inorganic salt sodium molybdate and the organic solvent ethylene glycol.
    - Non-emulsifiers: Non-emulsifiers are surfactants that are sometimes added to TCW Category I fluids to prevent the formation of emulsions between completion brines containing calcium, e.g., $CaBr_2$, $CaCl_2$, and crude oil. For example, the product “Non-emulsifier 1” contains proprietary quaternary ammonium compounds (QACs) that are cationic surfactants.
    - De-foamers: De-foamers are used to prevent unwanted foaming when using surfactants. The chemical product “Defoamer 1” was one product used in TCW Category I fluids. The phosphate ester tributyl phosphate (TBP) (30 to 60 percent [%] weight by weight [w/w]) is a key component of this product.
    - Viscosifiers: The product “Viscosifier 1” was used in a TCW Category I fluid in support of a workover well operation to increase the viscosity of low weight brines.
    - pH Control: pH control agents can be used to control bacterial growth or to raise the pH of acidic fluids. Addition of sodium hydroxide is used to control pH. A commercial pH control product used in TCW Category I samples for this study was “pH Control 3.”
    - Fluid stabilizer: A fluid stabilizer was used to control alkalinity of the brine and extend temperature stability of drilling fluid systems containing polymers. A commercial fluid stabilizer product used in TCW Category I samples for this study was “Fluid stabilizer 1.”

  - Hydrogen sulfide scavenger: These products are used to remove H_2S from brine-based fluid systems. A commercial fluid stabilizer product used in TCW Category I samples for this study was “Hydrogen sulfide scavenger 1.”
  - Non-aqueous base fluids: A non-aqueous base fluid (“Base fluid 1”) was used in a single workover well operation. The base fluid consists of synthetic fluids, e.g., olefins.
  - Oxygen scavengers: Oxygen scavengers remove soluble oxygen from water-based drilling and completion fluids. “Oxygen Scavenger 2” is a product used for corrosion control; this product contains a proprietary substituted alkylamine, ethylene glycol, and 2-butoxyethanol.
  - Well casing cleaner: One TCW effluent sample containing well casing cleaner was observed. The product used was “Well Cleaner 1,” which is comprised of surfactants and solvents used in fluid displacement and cleanup operations.
  - Breakers: Drilling fluids are commonly emulsified such that cuttings are carried back to the surface. A breaker was used to reduce the viscosity of a fluid. One product was observed in TCW Category I fluids (“Breaker 3”).
  - Corrosion inhibitors: Corrosion protection is necessary to ensure safe drilling operations. “Corrosion Inhibitor 1” is one product that was used as a corrosion inhibitor in TCW Category I fluids and consists of reducing agents, alcohols, and acids.
  - Surfactant: Surfactants are used to lower the surface tension between a fluid and a solid, and encompass emulsifiers, dispersants, oil-wetters, water-wetters, foamers, and defoamers. One surfactant product was observed in TCW Category I fluids (“Surfactant 3”).

- **TCW Category III**: TCW Category III fluids used in well treatment operations contain chemical products added to a brine base to achieve specific functional properties. Chemical products are present in all TCW Category III effluents. Synthetic mud casing scrubbers, clay control chemicals, polymers, cross-linkers, and proppant beads were used in various samples collected during the study. Other types of chemical products include biocides, corrosion inhibitors and corrosion inhibitor intensifiers, oxygen scavengers, scale inhibitors, well casing cleaner, de-foamers, pH control agents, non-emulsifiers, solvents, and acid treatments. Details of these chemical products are provided below:
  - Proppant: This product is composed of sand or ceramic particles (or beads) that are mixed with a fracturing fluid to hold fractures open after a hydraulic fracturing treatment. Proppant was only used in TCW Category III fluids; two products were used: “Proppant 1” and “Proppant 2.” Both products are composed of ceramic.
  - Polymers and Cross-linkers (Gels) are only used in TCW Category III fluids. Polymers such as guar gum and xanthan gum are used to form gels. Cross-linkers, e.g., ammonium chloride, potassium hydroxide and borate salts, also create a gel-like fluid consistency and were present in TCW fluids. Gel samples were YO64, YU91, and OD76. Representative photographs of gels, including a sample with embedded proppant beads, are provided in **Figure A2**.

- Biocides are used to control bacterial consumption of polymers present in TCW Category III gels, and to minimize microbiological fouling and or corrosion in piping and other infrastructure. The chemical products “Biocide 2” and “Biocide 4” are examples of biocide products used in this study. Common components of these biocides include glutaraldehyde and didecyldimethylammonium chloride (DDAC). Biocides are often, but not always, used in hydraulic fracturing fluid treatments (Kahrilas et al., 2015) and other fluids containing polymers.
- Corrosion inhibitors and corrosion inhibitor intensifiers: Corrosion protection is necessary to ensure safe well operations. “Corrosion Inhibitor 1” is one product that was used as a corrosion inhibitor in TCW Category III fluids and consists of reducing agents, alcohols, and acids. “Intensifier 1” was used to extend the inhibitor upper temperature limits and protect piping, e.g., drill pipe or casing. This product contained potassium iodide.
- Oxygen scavengers: Oxygen scavengers remove soluble oxygen from water-based drilling and completion fluids. “Oxygen Scavenger 1” is a product used for corrosion control; this product is a liquid oxygen scavenger containing the inorganic reducing agent ammonium bisulfite.
- Scale inhibitors: One anti-scaling product commonly used during the study was “Scale Inhibitor 2”, which is comprised of ethylene glycol and sodium molybdate.
- Well casing cleaner: TCW effluent samples containing well casing cleaner were observed. One well-cleaner used in study samples was “Well Cleaner 1”, which is comprised of surfactants and solvents used in fluid displacement and cleanup operations.
- “Fluid additive 1” was another well cleaner product used during the study that contains surfactants, solvents, and water-wetting agents. In one instance, a soap pill was used in a workover well operation to scour and remove debris from the well hole. An example of a cleaning pill used during the study was comprised of a mixture of NaBr and $CaBr_2$ brines and a well cleaning product (“Surfactant 2”).
- De-foamers: “Defoamer 2” was one product used as an antifoam agent; it is composed of the neutral organic chemicals kerosene, naphthalene, and ethylbenzene. “Defoamer 3” was another product used as a de-foamer in TCW Category III fluids.
- pH Control: pH control consists of the addition of sodium hydroxide. An example of a pH control product used was “pH Control 3.”
- Non-emulsifiers: A cationic polymer in solution (“Non-emulsifier 2”) was used in TCW Category III discharges as a non-emulsifier.
- Solvents were also present in TCW Category III effluents. “Solvent 1” contains acetic acid and the neutral organics xylene and 2-butoxyethanol.
- Acidification: In two instances, a treatment with acetic and hydrofluoric acids was observed for a treatment well operation.
- Activator: This product (“Activator 1”) was identified in a single TCW effluent. The product contains cobalt acetate (5% w/w); this was the only composition information provided in the SDS.

- Breakers: Drilling fluids are commonly emulsified such that cuttings are carried back to the surface. A breaker was used to reduce the viscosity of a fluid. One commonly used product in TCW Category I fluids was "Breaker 1".
- Surfactant: Surfactants are used to lower the surface tension between a fluid and a solid. Two surfactant products were observed in TCW Category I fluids ("Surfactant 1" and "Surfactant 2").
- Viscosifiers: Four products were observed in TCW Category III fluids ("Viscosifier 1, "Viscosifier 2", "Viscosifier 3", and "Viscosifier 4"). The viscosifiers were used to increase the viscosity of low weight brines.
- Well casing cleaner: One TCW effluent sample containing well casing cleaner was observed. The product used was "Well Cleaner 1", which is comprised of surfactants and solvents used in fluid displacement and cleanup operations.
- Clay stabilizer: This additive is used in stimulation treatments to prevent the migration or swelling of clay particles. Three clay stabilizer products were used in TCW Category III fluids ("Clay Stabilizer 1", "Clay Stabilizer 2", and "Clay Stabilizer 3").
- Iron control: If iron is not controlled, it can precipitate insoluble products such as ferric hydroxide and ferrous sulfide, which will damage the formation. Chelating agents associate with iron to form soluble complexes. Two iron control products were used in TCW Category III fluids ("Iron Control 1" and "Iron Control 2").
- Synthetic mud casing scrubber: Casing scrubbers are used to remove mud from wells drilled with water-based or non-aqueous fluids. A single product was used in TCW Category III fluids during the study ("Synthetic Mud Casing Scrubber 1").

3.3 Discharge of TCW Effluents to GOM Surface Waters

This section describes discharge configuration, duration, and volume of TCW Category I and TCW Category III effluents. This information illustrates how the discharge of TCW effluents to GOM surface waters is managed.

3.3.1 Discharge Configuration

Most of the selected structures were situated in deep waters (defined by the Bureau of Ocean Energy Management [BOEM] as >304.8 m), with three discharges located in shallow water. Arithmetic mean water column depth at the discharge structures was 1,278 meters (m), with a maximum of 2,913 m. The discharge of TCW effluents typically occurred through a pipe or hose on the structure ranging in diameter from 5 to 46 centimeters (cm). One discharge outfall was near the seafloor at an approximate depth of 2,913 m. The remaining outfalls were located between 27 m above to 46 m below the sea surface. Four structures discharged TCW effluents through a multiport diffuser.

3.3.2 Duration of Sampled Discharges

TCW effluent discharges were intermittent and of short duration. Discharges of TCW Category III effluents occurred over a shorter duration than TCW Category I discharges (**Figure 2**):

- **TCW Category I effluents**: The median discharge duration was 1.1 h, with a range of 0.03 – 96 h. The longest discharge duration was associated with a long-term completion (flow-back) well operation. TCW effluents in that case were discharged over a 96-h period at the beginning of the 31-day flow-back period.
- **TCW Category III effluents**: The median duration of TCW Category III discharges was 1 h, with a range of 0.2 - 3.4 h.

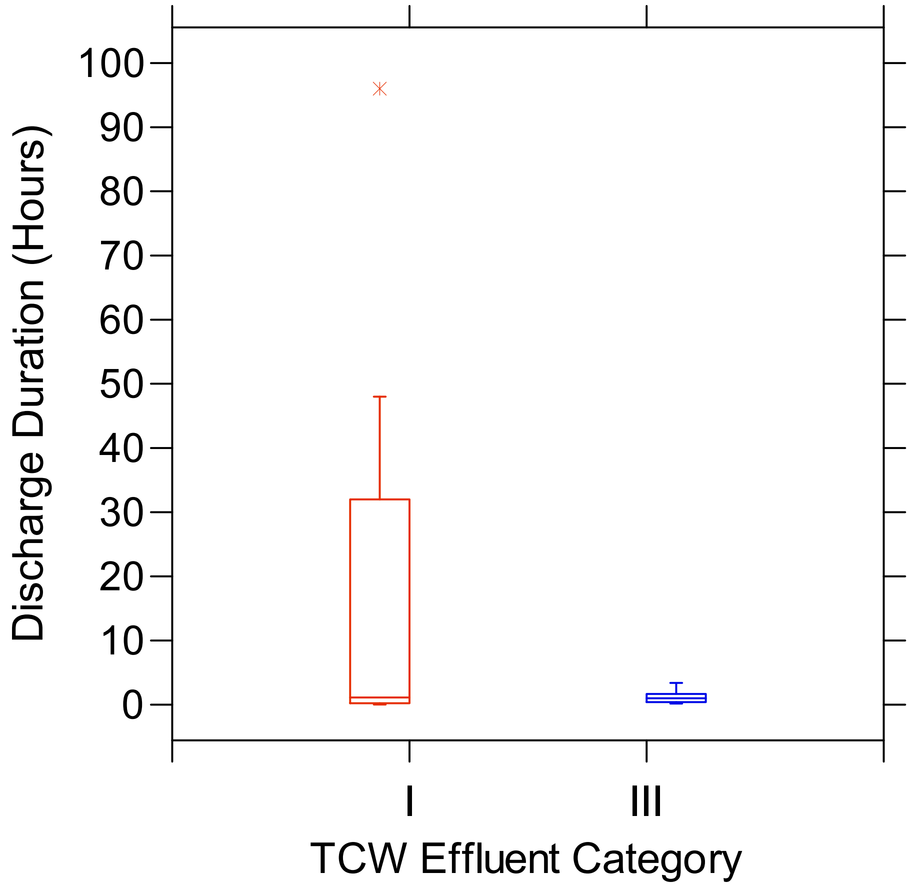


Figure 2. Boxplot of discharge duration (hours) for TCW Category I (n=12) and TCW Category III effluents (n=13). The center line marks the median. Box edges are at the first and third quartiles. Whiskers show the range of observed values that fall within 1.5x of the interquartile range of the box edges. Outliers are determined by the software where outside values, i.e., values between the inner and outer fences are plotted with asterisks (*). Additional details on boxplots are provided in **Appendix C**.

3.3.3 Discharge Volume

Typical TCW effluent discharge volumes (barrel [bbl]) depend on the type of well and the specific well operation being performed. The median volume of discharged TCW Category I effluents was lower than that reported for TCW Category III (**Figure 3)**. The median volume of TCW Category I discharges was 460 bbl, with a range of 10 - 2,534 bbl. The median volume of TCW Category III discharges was 473 bbl with a range of 118 - 2,818 bbl.

An order-of-magnitude estimate of the volume of all TCW effluent discharges to the GOM was obtained from the median volume of TCW discharges sampled for this study and an estimate of the total number of TCW discharges to the GOM during the study period. The total number of TCW discharges was estimated from the number (n=252) of oil-and-grease determinations on discharged TCW fluids done by two major commercial laboratories. The number of oil-and-grease measurements is used as an order-of-magnitude surrogate for the total number of discharges because a monthly laboratory oil-and-grease measurement is required for TCW discharges, regardless of whether the operator is a JIP study participant. BOEM approved 543 TCW jobs during the time period of interest but it is not known how many of these jobs resulted in discharges. Accordingly, an order-of-magnitude estimate of the volume of all TCW effluents discharged to the GOM in 2019-2020, based on the number of oil and grease tests, was 0.1 million barrels [Mbbl]). This estimated volume accounts for 0.01% of the PW discharge volume during the same period (**Table 5**).

Table 5. Comparison of GOM TCW Effluent and Produced Water Discharge Volumes

Effluent Discharge Type	Discharge Volume (Mbbl)	Notes
TCW Effluents (Estimated GOM 2019-2020)	0.1	252 discharges * median JIP Study TCW discharge volume of 473 bbl.
Total GOM PW Production (2019-2020)	825	The data were obtained from the BOEM online database Production Data Online Query (boem.gov).

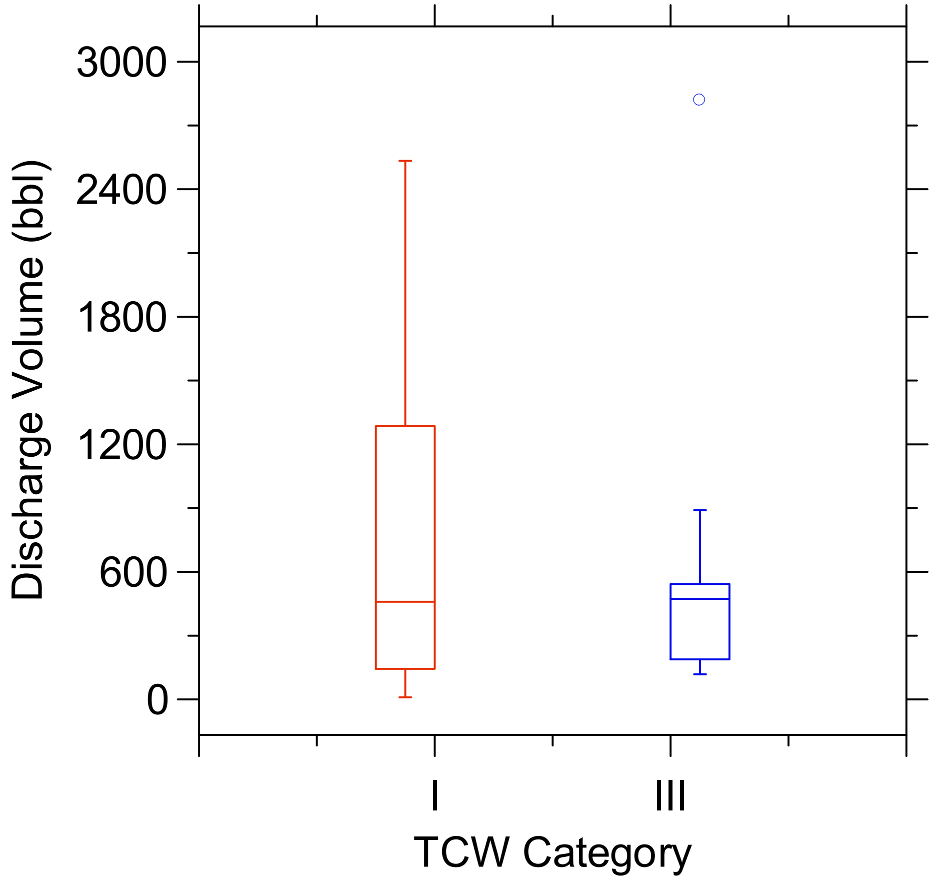


Figure 3. Boxplot of discharge volume (bbl) for TCW Category I (n=12) and TCW Category III effluents (n=13). The center line marks the median. Box edges are at the first and third quartiles. Whiskers show the range of observed values that fall within 1.5x of the interquartile range of the box edges. Outliers are determined by the software. Values beyond the outer fences, i.e., far outside values, are plotted with empty circles (°). Additional details on boxplots are provided in **Appendix C**.

3.4 Treatment of TCW Effluents

End-of-pipe treatment of TCW effluent varied among the structures where samples were collected. In some instances, treatment was used to neutralize pH before the effluents are discharged. More advanced treatment of TCW effluents was observed at three discharge structures (samples ZG57, EP57, TR84, and JH68). For samples ZG57, EP57, and TR84, the well operation was completion (flow-back). The treatment package for these structures included surge tanks, a weir box, solids filters, absorption media, and granular activated carbon (GAC) vessels. For sample JH68, GAC and solids filters for total suspended solids (TSS) were applied to effluents before discharge to GOM surface water. GAC can be used to polish discharges for residual organics and dissolved oil removal via carbon adsorption (Igwe, et al., 2013).

3.5 Summary

Section 3.0 identifies the characteristics of sampled TCW effluent discharges. Based on the information provided, the JIP study questions identified at the beginning of Section 3.0 can be addressed as follows:

- **What substances are currently used in TCW fluids?** TCW fluids are comprised of brines and chemical products. Chloride and bromide brines were used during the study period. Chemical products are largely comprised of organic substances. Chemical products were not always present in TCW Category I fluids but were always used in TCW Category III fluids.
- **How are TCW discharges typically handled and their discharge to GOM surface waters managed?** TCW effluents were discharged through a pipe or hose in most cases. In four instances, the discharge occurred through a submerged diffuser. TCW discharges to GOM surface waters occur intermittently with a median discharge duration of 1h. TCW Category I discharges lasted longer than TCW Category III discharges. In some cases, there was an end-of-pipe treatment of TCW effluents for organics and TSS. The range of TCW discharge volumes was 10 - 2,534 bbl. The discharge volume of TCW Category I discharges was greater than that of TCW Category III discharges. The estimated volume of all discharged TCW effluents during 2019-2020 was approximately equal to 0.01% of the PW discharge volume to the GOM during the same time period.

4.0 TCW Effluent Composition and Variability

This section describes TCW effluent composition and variability and addresses the following JIP study questions:

- *What are the concentrations of substances in GOM surface waters at the critical effluent dilution, i.e., the concentration predicted to exist in the effluent plume at the edge of the 100-m mixing zone?*
- *What is the typical chemical composition of discharged TCW effluents?*
- *How variable are the concentrations of substances over the duration of the discharge?*

4.1 Analytical Laboratories

Three analytical laboratories were used to support the chemical analysis of TCW effluent samples. Environmental Enterprises USA, Inc. (EEUSA; Slidell, LA) conducted the analysis of water quality parameters on samples of undiluted (100%) effluent, prepared samples for chemical analysis at the CD by dilution with laboratory control seawater (LCSW) and shipped the prepared samples to Element Materials Technology Lafayette (Element; Lafayette, LA). Element conducted the analysis of selected analytical parameters. Element subcontracted ALS Environmental (ALS; Kelso, WA) to conduct total and dissolved mercury analysis. Laboratory analytical reports that have been redacted to maintain confidentiality are provided in **Appendix D**.

4.2 Laboratory Control Seawater

The concentrations of 59 analytical parameters were measured in three samples of synthetic LCSW used to prepare the TCW effluent samples at the CD. Laboratory chemical analysis was conducted to understand how LCSW potentially contributes to diluted TCW effluent analytical results. The coefficient of variation (CV) was used to characterize variability in chemical composition. Laboratory analytical parameters are provided in **Table A4.**

4.2.1 Approach

The synthetic LCSW was prepared by EEUSA with hw-MARINEMIX + Bio-elements, Crystal Sea Marinemix Bioassay Laboratory Formula sea salts (80:20), and deionized water. This mixture was adjusted to a salinity of 25 parts per thousand (ppt). Laboratory analytical parameters measured in LCSW are summarized below:

- **Water quality parameters**: Dissolved organic carbon (DOC) and total organic carbon (TOC); alkalinity, total; alkalinity, bicarbonate (estimated as 1.22 * total alkalinity); hardness, total (as $CaCO_3$); TSS; nitrogen, ammonia (as N); and chemical oxygen demand (COD). The parameters DOC, TOC, and COD were used to indicate the presence of organic substances.
- **Metals**: 11 total and dissolved Priority Pollutant (PP) metals, basic cations, and basic anions were analyzed.
- **Organics**: The 16 PP polycyclic aromatic hydrocarbons (PAHs).

The CV (%) was used as a descriptive measure of variability for analytical parameters. The CV is the ratio of the standard deviation (SD) (σ) to the arithmetic mean $(\bar{x})$. The ratio was converted to a percentage. A CV of 100% indicates that σ and $\bar{x}$ are equal. A CV greater than 100% indicates that the parameter of interest was highly variable among the samples tested.

4.2.2 Composition of Laboratory Control Seawater

Three samples of LCSW were collected and analyzed; descriptive statistics are provided below in **Table 6**. Detailed results are presented by sample in **Table A5**.

Table 6. Descriptive Statistics for Analytical Parameters Measured in Synthetic Laboratory Control Seawater.

Parameter	No. of Samples	No. of Detects	Freq. of Detection (%)	Max. of Detects (mg/L)	Mean[1] of Detects (mg/L)	SD[1] of Detects (mg/L)	CV[1] of Detects (%)
Water Quality Parameters (Total)							
Hardness (as CaCO3)	3	3	100	4,430	4,280	141	3
Alkalinity, Total (As CaCO3)	3	3	100	93	74	19	25
HCO_3^- (Estimated as 1.22 * Total Alk.)	3	3	100	113	90	23	25
Total Suspended Solids (Residue, Non-Filterable)	3	1	33	27	--	--	--
Nitrogen, Ammonia (As N)	3	0	0	--	--	--	--
Chemical Oxygen Demand	3	0	0	--	--	--	--
Organic Carbon, Total	3	1	33	1.6	--	--	--
Sulfide	3	2	67	0.03	0.03	0.0007	2
Specific Gravity	3	1	33	1.02	--	--	--
Water Quality Parameters (Dissolved)							
Total Dissolved Solids (Residue, Filterable)	3	3	100	24,400	22,633	2,108	9
Dissolved Organic Carbon	3	0	0	--	--	--	--
Metals (Total)							
As	3	0	0	--	--	--	--
Ba	3	1	33	0.022	--	--	--
Cd	3	2	67	0.013	0.008	0.008	104
Ca	3	3	100	277	270	8	3
Cr	3	0	0	--	--	--	--
Cu	3	2	67	0.03	0.02	0.009	39
Pb	3	0	0	--	--	--	--
Mg	3	3	100	910	875	32	4
Hg	3	3	100	0.0000039	0.000002	0.000002	85
Ni	3	1	33	0.019	--	--	--
K	3	3	100	283	281	2	1
Se	3	3	100	0.31	0.16	0.13	79
Na	3	3	100	7,130	6,773	311	5
Tl	3	0	0	--	--	--	--
Zn	3	2	67	0.024	0.018	0.008	47
Metals (Dissolved)							
As	3	0	0	--	--	--	--
Ba	3	1	33	0.024	--	--	--
Cd	3	2	67	0.007	0.005	0.003	73
Ca	3	3	100	290	268	19	7
Cr	3	0	0	--	--	--	--
Cu	3	2	67	0.024	0.019	0.008	42
Pb	3	0	0	--	--	--	--
Mg	3	3	100	920	868	45	5
Hg	3	2	67	0.0000011	0.0000011	0	0
Ni	3	0	0	--	--	--	--
K	3	3	100	293	271	26	9
Se	3	1	33	0.15	--	--	--
Na	3	3	100	7,430	6,973	398	6
Tl	3	2	67	0.12	0.07	0.08	126
Zn	3	1	33	0.02	--	--	--
Inorganic Anions (Total)							
Br	3	3	100	38	36	3	10
Cl	3	3	100	15,500	14,067	1,290	9
SO_4^{2-}	3	3	100	2,430	2,110	302	14
Polycyclic Aromatic Hydrocarbons (PAHs)							
PAHs	3	0	0	--	--	--	--

Notes: [1] Mean denotes the arithmetic mean; SD denotes standard deviation; and CV denotes the coefficient of variation.

The composition of LCSW and composition variabilities are summarized below:

- **Substances not detected** above the laboratory reporting limit (RL) in LCSW were nitrogen, ammonia, COD, DOC, total metals (As, Cr, Pb, and Tl); dissolved metals (As, Cr, Pb, and Ni); and 16 PAHs.

- **Substances with 100% detection frequency** were hardness; alkalinity (total and bicarbonate); total dissolved solids (TDS); total metals (Ca, Mg, Hg, K, Se, Na); dissolved metals (Ca, Mg, K, Na, Tl); and inorganic anions (Br^-, Cl^-, and sulfate [$SO_4^{(2-)}$]). Total and dissolved Hg were typically detected near the laboratory method reporting limit.
- **Variability in analytical parameters**: Consistent with the laboratory protocol for preparing LCSW, most parameters exhibited little variability in concentration. Detected analytical parameters with a CV greater than 100% included total Cd (104%) and dissolved Tl (126%).

4.3 Effluent Composition at the Critical Effluent Dilution

The concentrations of 59 analytical parameters were measured at the CD, to improve environmental relevance, in TCW effluent samples. This data was used as an estimate of the concentrations that might be observed at the edge of the 100-m mixing zone. As discussed above, the samples were prepared with LCSW. The CV was used to characterize variability in chemical composition at the CD.

4.3.1 Approach

Laboratory analytical parameters were measured at the CD concentration consistent with the study plan:

- **Estimation of the CD**: Estimated CDs were provided to EEUSA so that samples for chemical analysis could be prepared. The CD was estimated by scaling the observed discharge volume (bbl) to a daily discharge rate (bbl/day) using discharge durations provided by JIP Study participants. This information was combined with discharge pipe diameter (inches) and the depth difference between end-of-pipe and seafloor (meters) to obtain the CD. Consistent with the study plan, CDs were obtained from the PW critical effluent dilution tables provided in Appendix D of the Region 6 general permit (USEPA, 2017a). All the samples collected in the JIP study were from discharges occurring in Region 6 waters.
- **Laboratory analytical parameters**: The same suite of analytical parameters evaluated for LCSW (**Table 6**) was evaluated in the TCW effluent samples. Due to the nature of the discharge and mixing of toxicity test samples during sample preparation, the loss of volatile organic compounds (VOCs) through volatilization may occur. Hence, VOCs were not analyzed in TCW effluent samples.
- **Samples not analyzed**: Samples IH80 and BT52 were not subjected to chemical analysis. Sample IH80 formed two phases when mixed with laboratory control seawater and was not submitted for analysis. After further investigation, it was later determined that this fluid had not been discharged (**Table 2**, **Appendix E**). Insufficient sample volume for laboratory analysis was collected in the field to analyze BT52.
- **Coefficient of variation (CV)**: The CV (%) was used as a descriptive measure of variability for analytical parameters as described above for LCSW. Elevated variability in TCW effluents can potentially result from well operation type, type of brine and chemical products, and other factors, e.g., formation rock type.

4.3.2 TCW Category I Effluent Composition

TCW Category I effluents at the CD (average CD = 0.41% effluent) were comprised of inorganics and organic chemical products. Descriptive statistics are provided below in **Table 7**. Detailed results are presented by sample in **Table A5**. The composition of Category I effluents and composition variabilities are summarized below:

- **Substances not detected** above the laboratory RL were nitrogen, ammonia; dissolved As; total Pb; total and dissolved Cr and Ni; and 16 PAHs.
- **Substances with 100% detection frequency** were: hardness; alkalinity (total and bicarbonate); TDS; total metals (Ca^{2+}, Mg^{2+}, Hg, K^{+}, and Na^{+}), dissolved metals (Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}); and inorganic anions (Br^{-}, Cl^{-}, and sulfate [$SO_4^{(2-)}$]). Total Hg was typically detected near the method reporting limit (0.0000005 mg/L). The mean Hg level in effluents at the CD was less than the mean level in LCSW.
- **Variability in analytical parameters**: Detected analytical parameters with a CV greater than 100% included Br^{-}, DOC, TOC, total zinc, total and dissolved thallium (Tl), and total and dissolved barium. The higher variability in TOC and DOC of TCW Category I effluents may reflect the unique makeup of each treatment. For example, TOC and DOC concentrations below the RL were associated with effluent samples that did not have any chemical products present (HV63 and XP62). TOC and DOC were also not detected in effluents where GAC treatment was present (ZG57, EP57, and TR84). The variability of cation and anion concentrations was low.
- **Maximum concentrations of highly variable substances**: The maximum concentration of Br^{-} (2,630 mg/L) was observed at sample RU61 (completion well operation with a $CaBr_2$ brine and acetic/HCl acid treatment). Maximum TOC (406 mg/L) and DOC (385 mg/L) were also observed at RU61. The elevated DOC and TOC for RU61 may be associated with acetic acid. The maximum concentration of Tl (0.062 mg/L), which is slightly above the laboratory RL (0.06 mg/L), was observed in sample (DO57). The maximum concentration of total copper (0.046 mg/L) was observed for EP57; this sample was collected at the beginning of a completion well operation flow-back. Cu was also detected in the LCSW (arithmetic mean = 0.03 mg/L). The origin of the copper in LCSW has not been determined.

Table 7. Descriptive Statistics for Analytical Parameters Measured in TCW Category I Effluents at the CD.							
Parameter	**No. of Samples**	**No. of Detects**	**Freq. of Detection (%)**	**Max. Detect (mg/L)**	**Mean[1] of Detects (mg/L)**	**SD[1] of Detects (mg/L)**	**CV[1] of Detects (%)**
Water Quality Parameters (Total)							
Hardness (as CaCO3)	12	12	100	5,810	4,617	861	19
Alkalinity, Total (As CaCO3)	12	12	100	98	83	8	10
HCO_3^- (Estimated as 1.22 * Total Alk.)	12	12	100	119	101	10	10
Total Suspended Solids (Residue, Non-Filterable)	12	10	83	19	10	4	43
Nitrogen, Ammonia (As N)	12	0	0	0	--	--	--
Chemical Oxygen Demand	12	4	33	1,420	700	514	0.7
Organic Carbon, Total	12	7	58	406	89	153	173
Sulfide	12	10	83	0.04	0.03	0.007	25
Hardness (as CaCO3)	12	12	100	1.5	1.2	0.2	13
Water Quality Parameters (Dissolved)							
Total Dissolved Solids (Residue, Filterable)	12	12	100	29,700	25,063	2,586	10
Dissolved Organic Carbon	12	7	58	385	82	145	176
Metals (Total)							
As	12	1	8	0.1	0.1	--	--
Ba	12	4	33	0.4	0.13	0.16	126
Cd	12	4	33	0.01	0.004	0.004	100
Ca	12	12	100	834	477	222	47
Cr	12	0	0	0	--	--	--
Cu	12	6	50	0.05	0.02	0.02	76
Pb	12	0	0	0	--	--	--
Mg	12	12	100	935	868	42	5
Hg	12	12	100	0.000002	0.000001	0.0000004	28
Ni	12	0	0	0	--	--	--
K	12	12	100	381	297	41	14
Se	12	6	50	0.5	0.3	0.1	49
Na	12	12	100	7,690	7,039	348	5
Tl	12	3	25	0.062	0.026	0	120
Zn	12	5	42	0.6	0.2	0.2	122
Metals (Dissolved)							
As	12	0	0	0	--	--	--
Ba	12	4	33	0.4	0.2	0.2	117
Cd	12	3	25	0.002	0.002	0.0001	4
Ca	12	12	100	808	472	209	44
Cr	12	0	0	0	--	--	--
Cu	12	5	42	0.05	0.02	0.02	88
Pb	12	1	8	0.034	--	--	--
Mg	12	12	100	931	867	35	4
Hg	12	8	67	0.000002	0.000001	0.0000004	36
Ni	12	0	0	0	--	--	--
K	12	12	100	373	299	27	9
Se	12	6	50	0.4	0.2	0.1	41
Na	12	12	100	7,690	7,120	344	5
Tl	12	2	17	0.1	0.05	0.1	121
Zn	12	4	33	0.5	0.2	0.2	111
Inorganic Anions (Total)							
Br	12	12	100	2,630	415	769	185
Cl	12	12	100	15,700	14,000	988	7
SO_4^{2-}	12	12	100	2,230	2,010	149	7
Polycyclic Aromatic Hydrocarbons (PAHs)							
PAHs	12	0	0	--	--	--	--
Notes: [1] Mean denotes the arithmetic mean; SD denotes standard deviation; and CV denotes the coefficient of variation.							

4.3.3 TCW Category III Effluent Composition

TCW Category III effluents at the CD (average CD = 0.37% effluent) were comprised of inorganics (cations and anions) and organics from chemical products. The CVs for TOC and DOC were lower than reported for TCW Category I effluents because organic chemical products were present in all TCW Category III effluent samples. Descriptive statistics are provided below in **Table 8**; detailed results are presented in **Table A5**. The composition of TCW Category III effluents and composition variabilities are summarized below:

- **Substances not detected** above the RL were total and dissolved metals (Cr, Pb, and Ni); and 16 PAHs.
- **Substances with 100% detection frequency** were hardness; alkalinity (total/bicarbonate); TDS; total Hg; total and dissolved Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}; and anions: Br^{-}, Cl^{-}, and SO_4^{2-}.
- **Variability in analytical parameters**: The anion Br^{-} exhibited the greatest variability (CV = 243%). Other detected analytical parameters with a CV greater than 100% included: dissolved As, DOC, total/dissolved Tl, TOC, and dissolved cadmium.
- **Maximum concentrations of highly variable substances**: The maximum concentration of Br^{-} (2,975 mg/L) was reported for effluent sample TF74 (a well treatment operation/fracturing job reverse-out). The maximum concentration of dissolved As (0.288 mg/L) was reported for RU72 (well treatment operation). RU72 was a sample of a TCW Category III KCl brine “frac-pack” and proppant beads were present in the sample. Maximum detected concentrations of COD (960 mg/L), TOC (70 mg/L), and DOC (126 mg/L) were reported for sample YO64. This TCW Category III gel sample was collected from a treatment well operation. Chemical products containing organics were present in this sample.

Table 8. Descriptive Statistics for Analytical Parameters Measured in TCW Category III Effluents at the CD.							
Parameter	**No. of Samples**	**No. of Detects**	**Freq. of Detection (%)**	**Max. Detect (mg/L)**	**Mean[1] of Detects (mg/L)**	**SD[1] of Detects (mg/L)**	**CV[1] of Detects (%)**
Water Quality Parameters (Total)							
Hardness (as CaCO3)	12	12	100	6,243	4,339	757	17
Alkalinity, Total (As CaCO3)	12	12	100	105	80	13	17
HCO_3^- (Estimated as 1.22 * Total Alk.)	12	12	100	128	96	18	18
Total Suspended Solids (Residue, Non-Filterable)	12	11	92	77	21	19	88
Nitrogen, Ammonia (As N)	12	1	8	1	--	--	--
Chemical Oxygen Demand	12	2	17	960	770	269	35
Organic Carbon, Total	12	7	58	70	23	24	107
Sulfide	12	6	50	0.05	0.03	0.010	37
Water Quality Parameters (Dissolved)							
Total Dissolved Solids (Residue, Filterable)	12	12	100	32,900	25,011	3,688	15
Dissolved Organic Carbon	12	6	50	126	36	46	128
Metals (Total)							
As	12	1	8	0.2	--	--	--
Ba	12	2	17	0.1	0.1	0.1	96
Cd	12	3	25	0.01	0.01	0.004	53
Ca	12	12	100	978	341	209	61
Cr	12	0	0	--	--	--	--
Cu	12	7	58	0.1	0.04	0.01	31
Pb	12	0	0	--	--	--	--
Mg	12	12	100	937	847	93	11
Hg	12	12	100	0.000003	0.000002	0.000001	45
Ni	12	0	0	--	--	--	--
K	12	12	100	499	343	86	25
Se	12	7	58	0.5	0.3	0.1	34
Na	12	12	100	7,650	6,673	741	11
Tl	12	2	17	0.1	0.1	0.1	114
Zn	12	3	25	0.2	0.1	0.1	82
Metals (Dissolved)							
As	12	2	17	0.3	0.2	0.2	128
Ba	12	2	17	0.1	0.1	0.1	89
Cd	12	2	17	0.01	0.01	0.01	102
Ca	12	12	100	909	342	186	55
Cr	12	0	0	--	--	--	--
Cu	12	2	17	0.05	0.033	0.028	85
Pb	12	0	0	--	--	--	--
Mg	12	12	100	930	865	66	8
Hg	12	10	83	0.000002	0.000001	0.000001	36
Ni	12	0	0	--	--	--	--
K	12	12	100	504	344	75	22
Se	12	9	75	0.5	0.3	0.1	27
Na	12	12	100	8,310	7,009	702	10
Tl	12	2	17	0.1	0.1	0.1	127
Zn	12	1	8	0.4	--	--	--
Inorganic Anions (Total)							
Br	12	12	100	2,975	345	839	243
Cl	12	12	100	14,500	13,800	388	3
SO_4^{2-}	12	12	100	2,230	1,949	145	7
Polycyclic Aromatic Hydrocarbons (PAHs)							
PAHs	12	0	0	--	--	--	--
Notes: [1] Mean denotes the arithmetic mean; SD denotes standard deviation; and CV denotes the coefficient of variation.							

4.4 Composition of Undiluted (100%) Effluent

The evaluations presented in this subsection address the chemical concentrations of key water quality parameters in undiluted TCW effluents, i.e., before mixing with LCSW. These analyses were needed to prepare WET test samples, to illustrate changes in effluent composition with fluid type, to explore variability in composition during a discharge event, and to compare effluent compositions to acute toxicity unit values

(TUa). Chemical composition was determined by directly measuring 4 analytical parameters and modeling the concentrations of 10 additional analytical parameters, using analytical results for samples diluted to the CD.

4.4.1 Approach

Analytical parameters were either directly measured or estimated to assess the composition of undiluted effluents:

- **Directly measured parameters**: Analytical parameters directly measured in undiluted effluent (only for non-gel samples) are specific gravity (@4˚C; salinity (parts per thousand [ppt]); alkalinity, as calcium carbonate ($CaCO_3$); and pH. Specific gravity was measured by Element. The water quality parameters were recorded by EEUSA upon sample receipt and are provided in the whole effluent toxicity (WET) test laboratory report.
- **Estimated parameters**: Parameters estimated in undiluted effluent are cations (Na^+, Mg^{2+}, K^+, and Ca^{2+}); anions (HCO_3^-, Cl^-, and Br^-); TOC; DOC; and TSS. The concentrations of these parameters in undiluted 100% effluent (C_{TCW100}) were estimated where: $C_{TCW100} = (C_{sample}-C_{LCSW}*(1-CD/100))/(CD/100)$ and: C_{sample} = concentration at the CD, and C_{LCSW} = concentration in laboratory control seawater. Estimates of C_{TCW100} are not reliable, however, unless $C_{sample} > C_{LCSW}$; in these instances, the LCSW concentration was used. Cation and anion concentrations were converted from mg/L to milliequivalents per liter (meq/L). Non-detect values were reported as 100% of the laboratory RL.

4.4.2 TCW Category I Effluent Composition

Undiluted TCW Category I effluents were, in most cases, denser than seawater due to their elevated salinity and alkaline, with effluents reaching a pH of 10.0:

- **Directly measured parameters**: Undiluted TCW Category I effluents exhibited a specific gravity range of 1.02 (this is the typical density of surface seawater) to 1.45 (hypersaline). They have a median salinity of 278.5 ppt, exhibit an alkalinity range of 20 to >400 mg/L, and are slightly acidic to alkaline (pH range 5.6 to 10) (**Figure 4**). Raw data and descriptive statistics for substances are provided in **Table 9**.

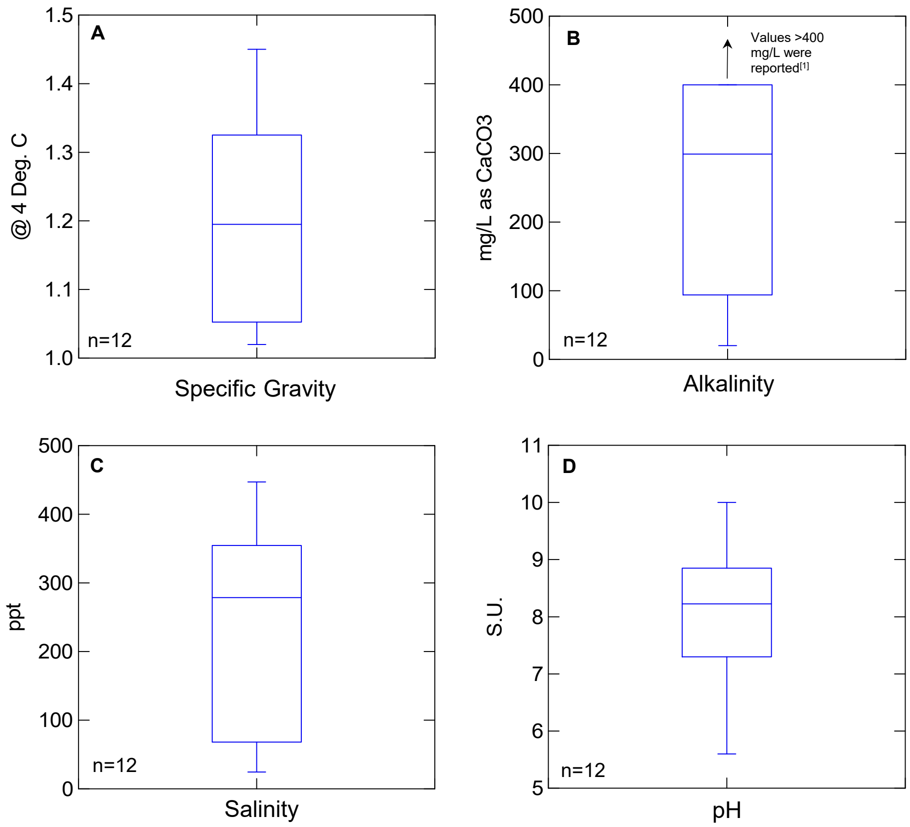


Figure 4. Boxplots for specific gravity, salinity, alkalinity, and pH of undiluted TCW Category I effluents (n=12). The center line marks the median. Box edges are at the first and third quartiles. Whiskers show the range of observed values that fall within 1.5x of the interquartile range of the box edges. Additional details on boxplots are provided in **Appendix C**. Notes: [1]: Values for alkalinity reported as >400 mg/L indicate that the upper range of the instrument was exceeded.

Table 9. Raw Data for Directly Measured Parameters in Undiluted TCW Category I Effluents.				
Sample	**Specific Gravity**	**Alkalinity, as CaCO3 (mg/L)**	**Salinity (ppt)**	**pH**
HV63	1.26	104	358	8.3
RD67	1.24	400	354	10
RU61	1.45	136	295	6.6
XP62	1.3	400	447	9.8
LC54	1.07	72	103	8
AU71	1.15	20	262	8
ZG57	1.02	348	24.5	8.9
CM89[1]	1.06	250	77.6	8.2
QK91	1.05	>400	58.8	8.7
DO57	1.02	>400	53.3	6.1
PO80	1.35	84	335	5.6
UP92	1.42	>400	355	8.8
n	12	12[2]	12	12
Median	1.20	299	278.5	--
Min.	1.02	20	24.5	5.6
Max.	1.45	>400	447	10
Notes: [1]. Sample CM89 is an arithmetic mean of two samples collected at structure No. 18. [2]. Greater than (>) values for alkalinity were defaulted to 400 mg/L when calculating the median.				

- **Estimated dissolved cations and anions**: The arithmetic mean ratio of cations to anions in TCW Category I effluents was 2.8 (range 0.3 - 10.5). TCW effluent sample PO80 (a $CaBr_2$ brine) exhibited the highest combined Na^+ and Ca^{2+} milliequivalents (12,779 meq/L) (**Figure 5A**). In contrast, ZG57 exhibited cation/anion milliequivalents that are lower than observed in the LCSW. The maximum values for K^+ and Cl^- were observed for sample AU71 (NaCl brine) (**Figure 5B**). The maximum milliequivalent for Br^- (5,904 meq/L) was reported for sample RU61 ($CaBr_2$ brine). Estimated concentrations and descriptive statistics for substances in undiluted effluents are provided in **Table 10**.

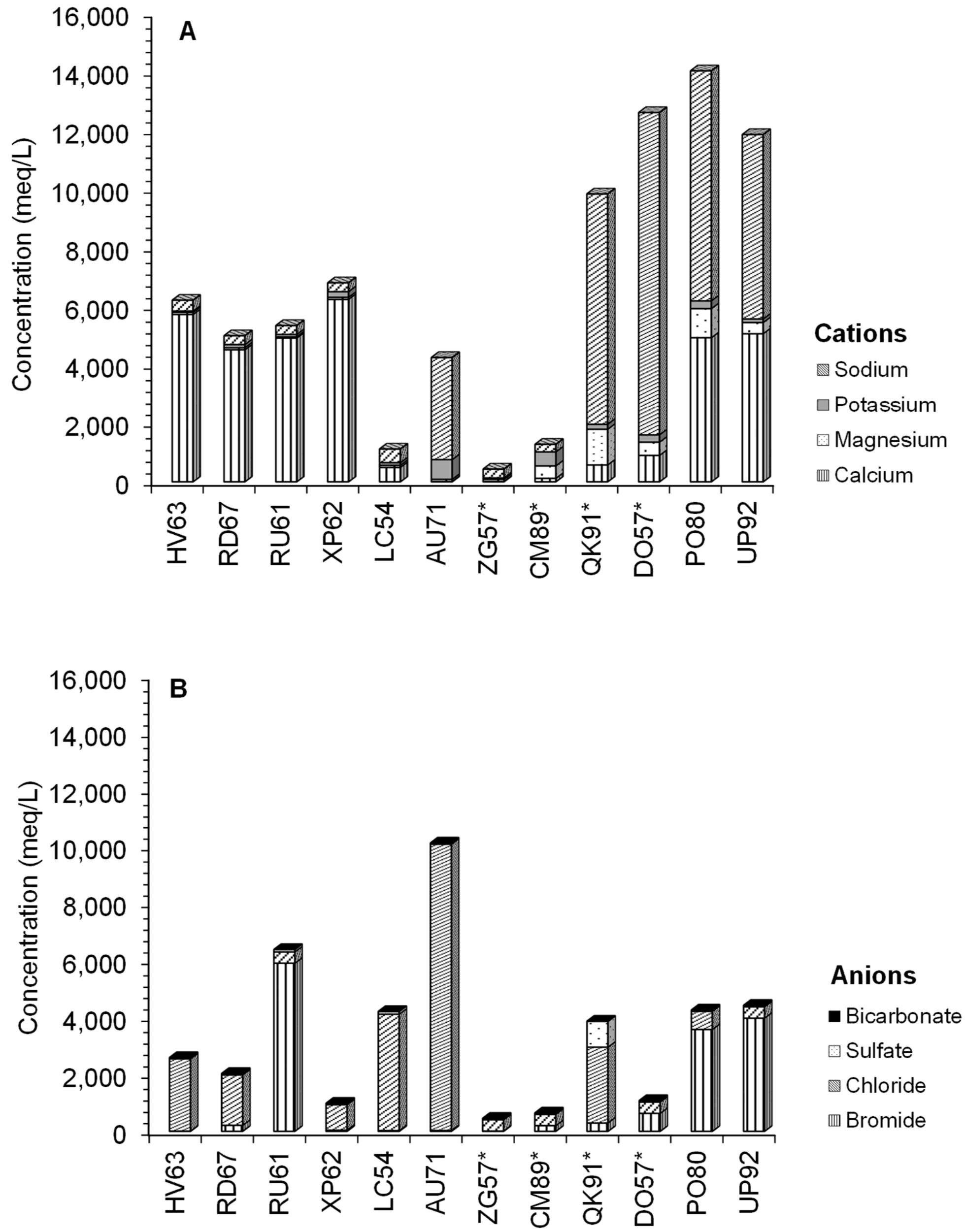


Figure 5. Bar charts of estimated dissolved cations and anions in undiluted TCW Category I effluents. Sample CM89 is an arithmetic mean of two samples collected over a single discharge. Discharges with GAC and filtration (*) and tank storage and filtration (**) are identified.

Table 10. Raw Data and Descriptive Statistics for Estimated Dissolved Ions in Undiluted TCW Category I Effluents.								
Parameter	**Mg^{2+}**	**K^+**	**Na^+**	**Ca^{2+}**	**Br^-**	**Cl^-**	**$SO_4^{(2-)}$**	**HCO_3^-**
Units	meq/L	meq/L	meq/L	meq/L	meq/L	meq/L	meq/L	meq/L
HV63	71	46	369	5,726	8	2,537	44	2
RD67	71	106	303	4,520	210	1,771	44	8
RU61	46	80	303	4,919	5,904	397	82	3
XP62	71	191	303	6,241	41	893	44	8
LC54	71	90	466	492	25	4,089	94	1
AU71	71	674	3,499	13	28	10,055	44	0.4
ZG57	71	48	303	13	9	397	44	7
CM89[1]	426	476	258	118	200	397	44	5
QK91	1,219	171	7,873	575	295	2,662	903	8
DO57	453	250	11,011	901	630	397	44	8
PO80	992	267	7,847	4,932	3,577	639	44	2
UP92	382	121	6,294	5,069	3,976	397	44	8
n	12	12	12	12	12	12	12	12
Median	71	146	417	2,711	205	766	44	6
Min	46	46	258	13	8	397	44	0.4
Max	1,219	674	11,011	6,241	5,904	10,055	903	8
Notes: [1]. Sample CM89 is an arithmetic mean of two samples (EP57 and TR84) collected at one structure.								

- **Estimated TOC and DOC (mg/L)**: Median estimated TOC in TCW Category I effluents was 664 mg/L, with a range of 3 - 73,361 mg/L; samples RU61 and DO57 exhibited the highest concentrations (**Figure 6; Table 11**). TCW effluent samples HV63, XP62, ZG57, CM89, and QK91 had the lowest estimated TOC. The latter three of these samples had end-of-pipe GAC treatment.

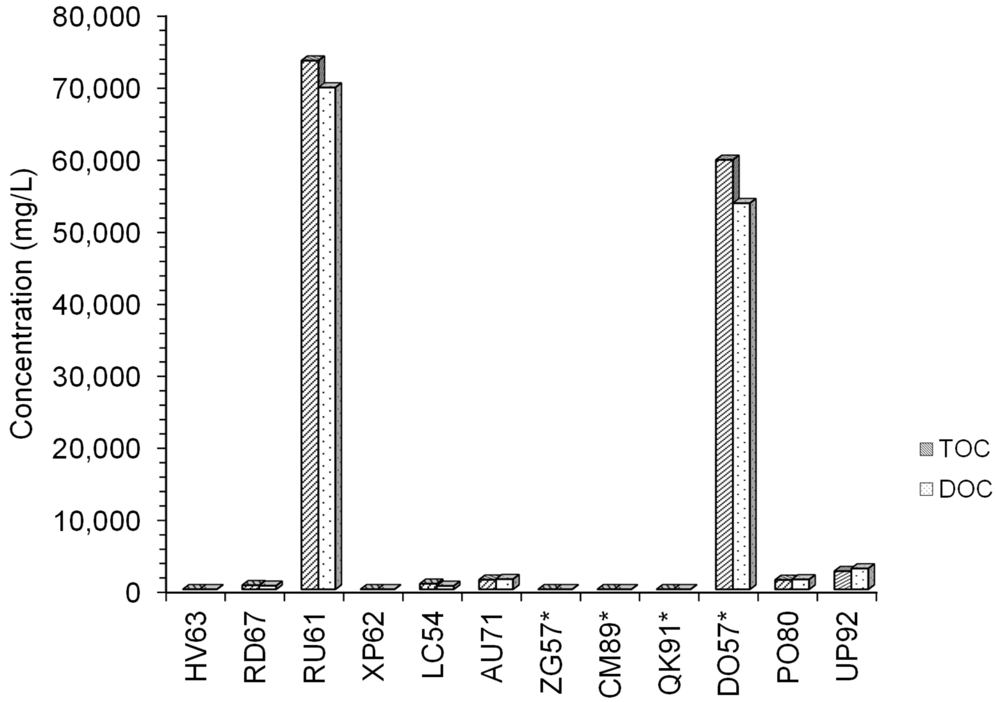


Figure 6. Bar chart of estimated TOC and DOC (mg/L) in undiluted TCW Category I effluents. Sample CM89 is an arithmetic mean of the two samples (EP57 and TR84) collected over a single discharge at one structure. Discharges with GAC and filtration (*) and tank storage and filtration (**) are identified.

- **Estimated TSS (mg/L)**: TSS was only detected above the laboratory RL in two TCW Category I effluent samples. The highest estimated concentration of TSS was reported for AU71 (1,628 mg/L) (**Figure 7**).

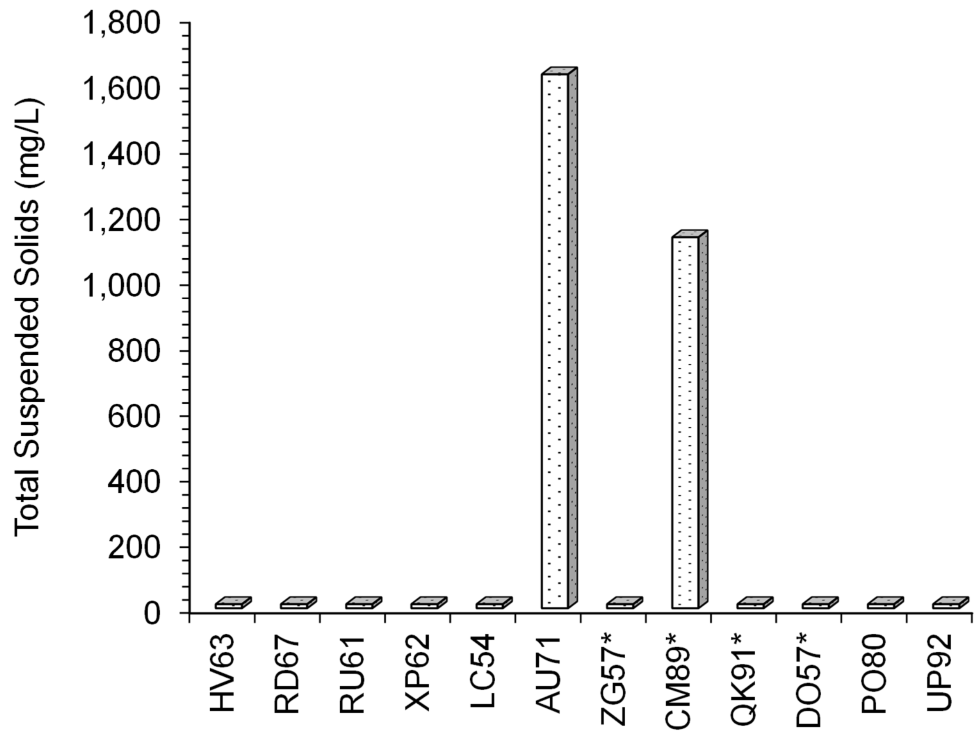


Figure 7. Bar chart of estimated TSS in undiluted TCW Category I effluents. Samples with end-of-pipe treatment are denoted by a * (GAC and filtration) and ** (tank storage, filtration). Sample CM89 is an arithmetic mean of values from samples EP57 and TR84, which were collected at the same structure.

Table 11. Raw Data and Descriptive Statistics for Estimated TSS and TOC in Undiluted TCW Category I Effluents.			
Parameter	**TSS**	**TOC**	**DOC**
Units	mg/L	mg/L	mg/L
HV63	12	3	2
RD67	12	559	490
RU61	12	73,361	69,638
XP62	12	3	2
LC54	12	768	466
AU71	1,628	1,329	1,407
ZG57	12	3	2
CM89[1]	1,131	3	2
QK91	12	3	2
DO57	12	59,615	53,610
PO80	12	1,303	1,361
UP92	12	2,518	2,889
n	12	12	12
Median	12	664	478
Min	12	3	2
Max	1,628	73,361	69,638
Notes: [1]. Sample CM89 is an arithmetic mean of three samples collected at structure No. 18.			

4.4.3 TCW Category III Effluent Composition

Category III effluents are less saline and possess higher TOC and TSS than Category I effluents:

- **Directly measured parameters**: TCW Category III effluents exhibited a specific gravity range of 1.01 to 1.49, a median salinity of 63 ppt, and an alkalinity range of 80 to >400 mg/L, and have a circumneutral to alkaline pH (range 6.7 to 9.9) (**Figure 8**). Raw data and descriptive statistics are provided below in **Table 12.**

Table 12. Raw Data and Descriptive Statistics for Directly Measured Parameters in Undiluted TCW Category III Effluents.				
Sample	**Specific Gravity**	**Alkalinity, as CaCO3 (mg/L)**	**Salinity (ppt)**	**pH**
JK70	1.03	148	57.8	7.7
NY50	1.12	292	175	7.9
YO64	Frac. gel; unable to analyze	Frac. gel; unable to analyze	Frac. gel; unable to analyze	Frac. gel; unable to analyze
FP89	1.04	120	64.5	7.6
GQ67	1.49	>400[1]	390	9.1
YU91	Frac. gel; unable to analyze	Frac. gel; unable to analyze	Frac. gel; unable to analyze	Frac. gel; unable to analyze
LX98	1.01	80	23.7	7.7
IS88	1.03	144	34.6	7.6
RU72	1.04	>400[1]	58.5	9.8
BT52	Insufficient sample volume	>400[1]	58.5	9.9
SH87	1.05	356	80	9.9
NZ96[2]	1.34	300	261.5	9.6
JH68	1.04	>400[1]	63	6.7
n	10	11	11	11
Median	1.04	300	63	7.9
Min.	1.01	80	23.7	6.7
Max.	1.49	>400	390	9.9
Notes: [1]. Greater than (>) values for alkalinity were defaulted to 400 mg/L when calculating the median; [2] Sample NZ96 is an arithmetic mean of three samples of a single discharge collected at structure No. 19.				

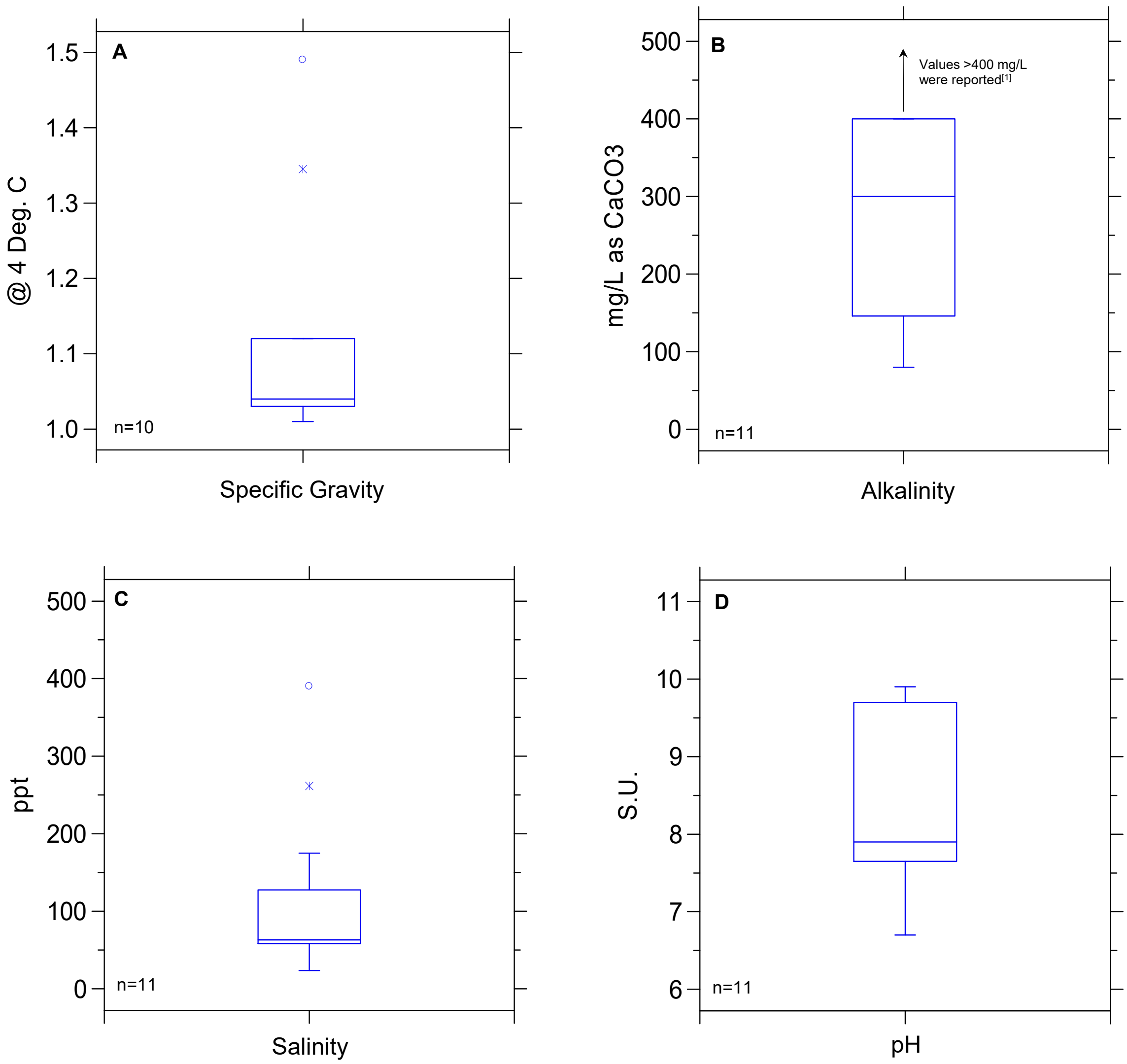
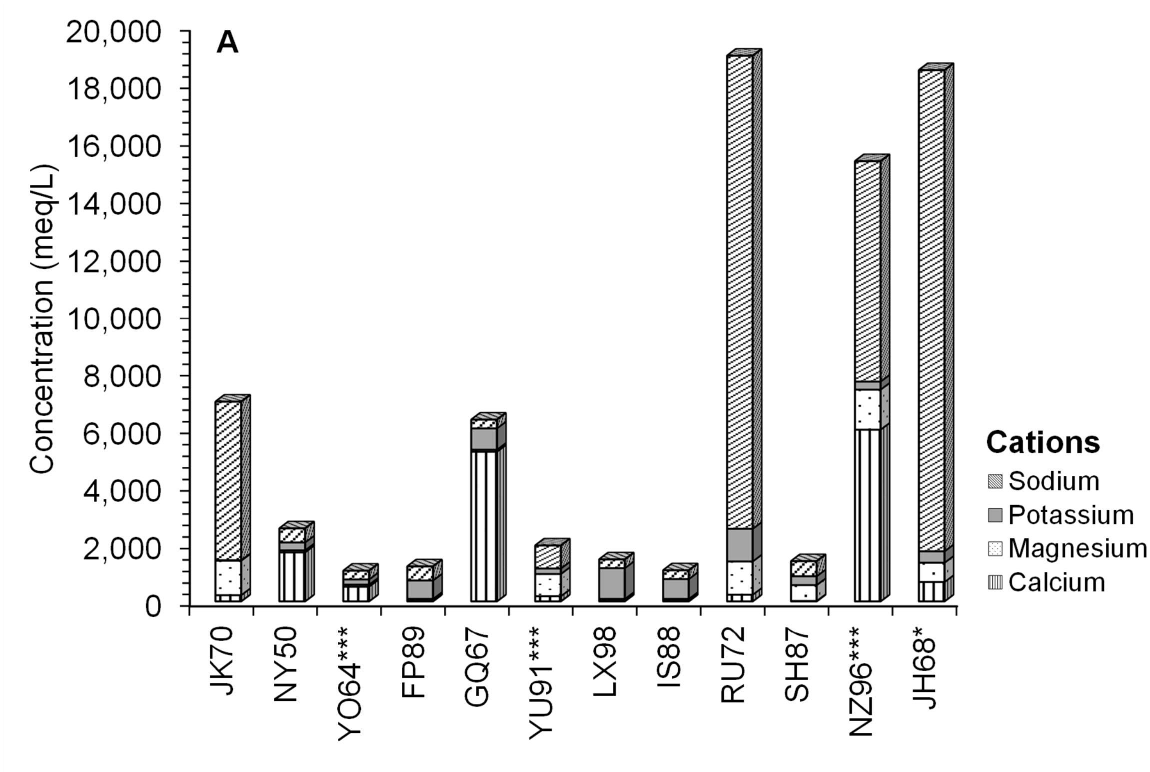


Figure 8. Boxplots for specific gravity, salinity, alkalinity, and pH of undiluted TCW Category III effluents. The center line marks the median. Box edges are at the first and third quartiles. Whiskers show the range of observed values that fall within 1.5x of the interquartile range of the box edges. Outliers are determined by the software. Outside values, i.e., values between the inner and outer fences are plotted with asterisks (*). Values beyond the outer fences, i.e., far outside values, are plotted with empty circles (°). Additional details on boxplots are provided in **Appendix C**. Notes: [1]: Values for alkalinity reported as >400 mg/L indicate that the upper range of the instrument was exceeded.

- **Estimated dissolved cations/anions**: The arithmetic mean ratio of cations to anions in TCW Category III effluents was 7.8 (range 0.3 – 32.1). For most of the samples, Na^+ was the dominant cation; Ca^{2+} concentrations were highest in samples GQ67 and NZ96 (**Figure 9A**). The concentration of the Cl^- anion was highest in sample FP89; Br^- concentrations were highest in sample GQ67 and NZ96 (**Figure 9B**). A table of estimated concentrations and descriptive statistics for detected substances are provided below in **Table 13**.



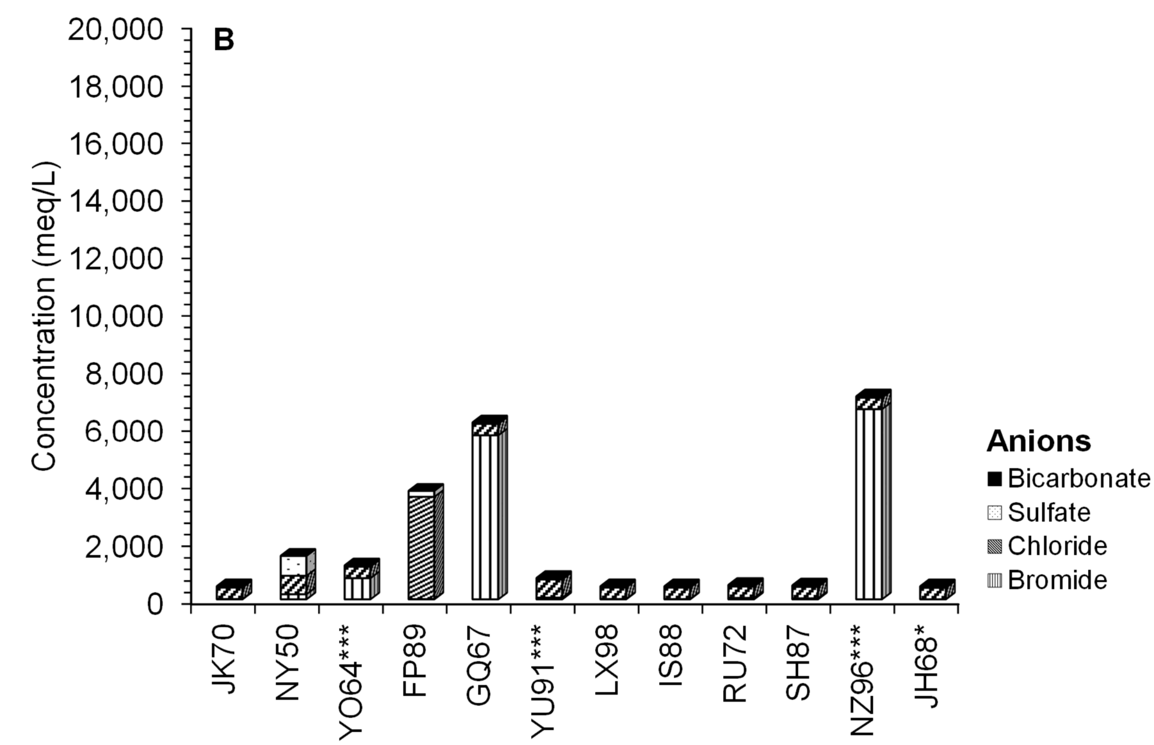


Figure 9. Bar charts of estimated dissolved cations and anions in undiluted TCW Category III effluents. Samples with end-of-pipe treatment (GAC and filtration) are denoted by (*) and gel samples are denoted by (***). Sample NZ96 is an arithmetic mean of three samples (RC74, OD76, and TF74) collected at a single structure.

Table 13. Raw Data and Descriptive Statistics for Estimated Dissolved Ions in TCW Category III Effluents.								
Parameter	**Mg^{2+}**	**K^+**	**Na^+**	**Ca^{2+}**	**Br^-**	**Cl^-**	**$SO_4^{(2-)}$**	**HCO_3^-**
Units	meq/L	meq/L	meq/L	meq/L	meq/L	meq/L	meq/L	meq/L
JK70	1,198	18	5,506	214	8	397	44	3
NY50	71	274	489	1,701	175	639	685	6
YO64	71	182	303	509	730	397	44	2
FP89	71	641	489	13	8	3,536	204	2
GQ67	71	740	303	5,197	5,688	397	44	8
YU91	771	192	798	180	59	627	44	8
LX98	71	1,070	303	13	9	397	44	2
IS88	71	690	303	13	6	397	44	3
RU72	1,156	1,134	16,447	231	47	397	44	8
SH87	552	307	523	13	33	397	44	7
NZ96[1]	1,390	280	7,671	5,964	6,595	397	44	6
JH68	669	398	16,728	673	0.4	397	44	8
n	12	12	12	12	12	12	12	12
Median	312	352	506	223	40	397	44	6
Min.	71	18	303	13	0.4	397	44	2
Max.	1,390	1,134	16,728	5,964	6,595	3,536	685	8
Notes: [1]. Sample NZ96 is an arithmetic mean of three samples collected at structure No. 19.								

- **Estimated TOC (mg/L)**: The median TOC for Category III effluents was 513 mg/L, with a maximum of 17,380 mg/L for YO64 (**Figure 10; Table 14**). TOC was not detected about the laboratory RL in 5 samples.

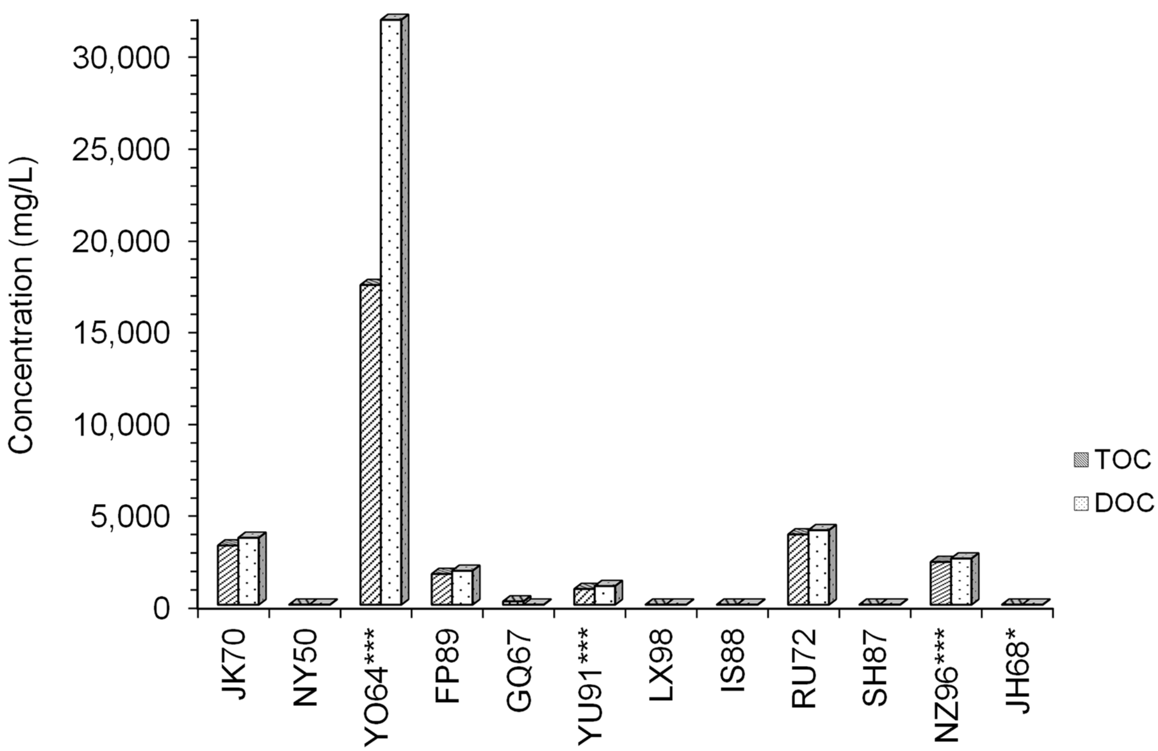


Figure 10. Bar chart of estimated TOC and DOC in undiluted TCW Category III effluents. Samples with end-of-pipe treatment (GAC and filtration) are denoted by (*) and gel samples are denoted by (***). Sample NZ96 is an arithmetic mean of three samples (RC74, OD76, and TF74) collected at a single structure.

- **Estimated TSS (mg/L)**: Median estimated TSS was 1,243 mg/L, with a range of 12 - 16,499 mg/L. The highest estimated concentration of TSS was reported for YO64 (**Figure 11**).

Table 14. Raw Estimates and Descriptive Statistics for Estimated TSS and TOC in TCW Category III Effluents.

Parameter	**TOC**	**DOC**	**TSS**
Units	mg/L	mg/L	mg/L
JK70	3,201	3,617	1,730
NY50	3	2	1,064
YO64	17,380	31,797	16,499
FP89	1,662	1,833	1,423
GQ67	176	2	12
YU91	850	1,007	2,573
LX98	3	2	566
IS88	3	2	274
RU72	3,801	4,030	1,873
SH87	3	2	12
NZ96[1]	2,310	2,496	5,404
JH68	3	2	12
n	12	12	12
Median	513	504	1,243
Min.	3	2	12
Max.	17,380	31,797	16,499

Notes: [1]. Sample NZ96 is an arithmetic mean of three samples (RC74, OD76, and TF74) collected at a single structure.

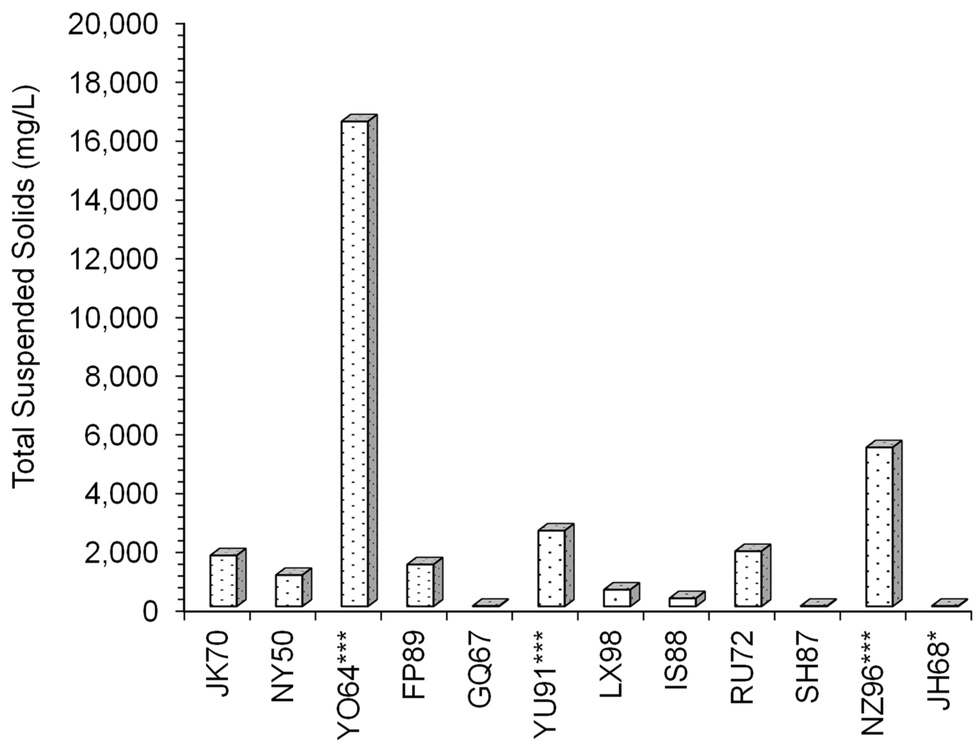


Figure 11. Bar chart of estimated TSS in undiluted TCW Category III effluents. Samples with end-of-pipe treatment (GAC and filtration) are denoted by (*) and gel samples are denoted by (***). Sample NZ96 is an arithmetic mean of three samples (RC74, OD76, and TF74) collected at a single structure.

4.5 Variability in Effluent Composition During a Single Discharge

Variability in effluent chemical composition during a single discharge was evaluated for select structures. Samples prepared at the CD and undiluted samples were used in the evaluation. The purpose of this evaluation is to address the question posed by USEPA Region 4 and Region 6 "*Does effluent composition change during the discharge?*"

4.5.1 Approach

Samples selected for the evaluation were collected from a 40-h completion operation: EP57 (begin) and TR84 (end); and a 2.76-h treatment operation: RC74 (begin), OD76 (middle), and TF74 (end). Effluent parameters selected for evaluation were HCO_3^-, TOC, salinity, DOC, major cations (Ca^{2+}, Mg^{+2}, K^+, and Na^+) and major anions (Br^-, Cl^-, and SO_4^{2-}). The change in concentration of salinity, major cations and anions, TOC, and DOC over the discharge was expressed as a ratio. Non-detect values were represented by 100% of the laboratory RL when calculating the ratio. For this discussion, effluent parameters that exhibit an increase with a ratio $\geq$2.0 (greater than a 100% increase), or a decrease with a ratio $\leq$0.5 (greater than a 50% decrease) are emphasized.

4.5.2 Variability Evaluation Results

Assessment results indicate there was some variability in effluent composition when measured over the duration of a single discharge. Not all samples and parameters, however, were equally variable. The ratios of component concentrations between samples taken at different times during a discharge (**Table 15**) reveal which component concentrations vary during a discharge. A ratio near 1.0 indicates a component whose concentration is not changing appreciably; results are summarized below:

- **EP57 and TR84:** The samples were collected during a single discharge, lasting 40 h, at one structure (**Table A2**). The concentrations of the selected parameters were largely unchanged over the discharge. Sample EP57 was collected at the beginning of the discharge, and TR84 was collected at the end of the discharge, when the well stopped producing. This discharge structure had end-of pipe treatment, e.g., filtration and GAC.
- **RC74, OD76, and TF74**: The samples were collected during a single discharge, lasting 2.76 h, at one structure from a well treatment operation (**Table A2**). Effluents discharged included a Category III gel followed by a $CaCl_2$ brine with a small amount of ceramic proppant. Sample RC74 was collected at the beginning of the discharge, OD76 was collected in the middle, and sample TF74 was collected at the end of the discharge. Except for a decrease in salinity, differences in effluent composition between the beginning and the middle of the discharge were not pronounced. Substantial differences in effluent composition, however, were observed between the beginning and end of the discharge, and the middle and end of the discharge. The most noticeable changes were an increase in Br^-, total and dissolved Ca^{2+}, and salinity. The increases in Ca^{2+} and salinity likely reflect the shift to a $CaCl_2$ brine at the end of the discharge.

Table 15. Change in Analytical Parameters at Different Times in the Discharge Expressed as a Ratio (End:Begin)[1].				
Parameters	**Ratios**			
	TR84 (End): EP57 (Begin)	**OD76 (Middle): RC74 (Begin)**	**TF74 (End): RC74 (Begin)**	**TF74 (End): OD76 (Middle)**
Water Quality Parameters				
HCO_3^- (Estimated as 1.22 * Total Alk.)	1.0	1.0	1.1	1.0
Organic Carbon, Total	1.0	1.0	1.0	1.0
Salinity (100% Effluent)	1.4	**0.3**	**6.3**	**18.1**
Dissolved Organic Carbon	1.0	1.0	1.1	1.1
Metals (Total)				
Ca	1.0	0.9	**8.0**	**8.9**
Mg	1.0	0.9	0.9	1.1
K	1.0	1.0	1.0	1.0
Na	1.0	0.9	1.0	1.0
Metals (Dissolved)				
Ca	1.0	1.1	**7.8**	**6.8**
Mg	1.0	1.1	0.9	0.8
K	1.0	1.0	1.0	0.9
Na	1.0	1.1	0.9	0.8
Inorganic Anions (Total)				
Br^-	1.4	0.9	**228.1**	**241.1**
Cl^-	1.0	1.0	1.0	1.0
$SO_4^{(2-)}$	0.9	1.1	1.0	0.9
Notes: [1]. Ratios >2.0 or <0.5 are boldfaced for clarity.				

4.6 Summary

Section 4.0 characterized TCW effluent composition for well treatment, completion, and workover well operations. Based on the information provided, the JIP study questions identified at the beginning of Section 4.0 can be addressed as follows:

- *What are the concentrations of substances in GOM surface waters at the critical effluent dilution, i.e., the concentration predicted to exist in the effluent plume at the edge of the 100-m mixing zone?*
    - TCW Category I and III effluents at the CD are comprised of metals, cations and anions, and organics. Due to low critical dilution concentrations, ionic concentrations at the CD are largely consistent with the concentrations in laboratory control seawater.
    - Some priority pollutant metals were detected at low concentrations in some effluent samples diluted to the CD and in laboratory control seawater. The origins of these metals were not clear but review of operator-provided SDSs did not reveal any products that were described as containing priority pollutant metals. This indicates that these metals were not known to be in products used to formulate TCW fluids. No priority pollutant organics were detected in any effluent sample diluted to the CD.
    - Concentrations of some substances were highly variable, reflecting changes in TCW fluid composition needed to achieve well operational objectives:
        - Detected analytical parameters in TCW Category I effluents with a CV greater than 100% included Br^-, DOC, TOC, total Zn, total and dissolved Tl, and total and dissolved Ba.
        - In TCW Category III effluents, the anion Br^- exhibited the greatest variability (CV = 243%). Other detected analytical parameters with a CV

greater than 100% included: dissolved As, DOC, total/dissolved Tl, TOC, and dissolved Cd.

- *What is the typical chemical composition of discharged TCW effluents?*
  - Undiluted TCW Category I effluents ranged in specific gravity from 1.01 to 1.45. They ranged in pH from 5.6 – 10.0. TCW Category III effluents ranged in specific gravity from 1.01 to 1.66, were less saline than TCW Category III effluents, and ranged in pH from 6.7 to 9.9. TCW Category III effluents exhibited higher TOC and TSS than TCW Category I effluents.
  - Variability in effluent chemical composition was observed when evaluated over the duration of a 2.76-h and 40-h discharge for salinity, calcium, and bromide. The evaluations indicate that effluent composition is influenced by the type of well operation. Additional factors that may have influenced the results include changes in use of chemical products and brine type during an operation.

5.0 Acute Aquatic Hazard of Added Chemical Products

This section describes the acute aquatic hazard of added chemical products as proposed in the study plan. The evaluations presented address the JIP study question "*What are the general aquatic hazard characteristics of the substances currently used in TCW fluids?"*

Participants reported 75 unique chemical products with 31 product functionalities that were used in formulating TCW fluids pumped into the wells and could potentially have been present in TCW effluents discharged to GOM surface water and sampled during this study. These products were typically mixtures and contained inorganic and organic substances that could potentially contribute, in addition to substances picked up while downhole, to the observed acute whole effluent toxicity. Examples of chemical classes used in products include aldehydes, aliphatic amines, amides, cellulose ethers, phosphate esters, inorganic salts, neutral acids, neutral organics, and thiols/mercaptans.

The use of chemical products in the GOM by the oil and gas industry has been studied extensively. For example, the 2001 *Deepwater Program: Literature Review, Environmental Risk of Chemicals used in Gulf of Mexico Deepwater Oil and Gas Operations* study (Boehm et al., 2001) assessed risk to the aquatic environment associated with releases of chemical products. The study included an inventory of chemical products, and a summary of hazardous chemicals defined in 40 CFR 116 (Boehm et al., 2001). Five samples in the present JIP study were evaluated by Boehm et al. (2001).

5.1 Hazard Assessment Approach

A simplified approach was used to qualitatively describe the aquatic hazard of chemical products. The manufacturer SDSs provided by JIP study participants were used as the source of information for aquatic hazard. Concentrations of organic and inorganic substances in chemical products were not measured in the laboratory or available to be provided by JIP participants due to the proprietary nature of purchased products.

5.1.1 GHS Acute Aquatic Toxicity Classification

SDSs for a minority of chemical products used in TCW fluids provided aquatic hazard information. For these products, an aquatic hazard assessment was conducted consistent with the United Nations (2019) guidance *A Guide to The Globally Harmonized System of Classification and Labeling of Chemicals (GHS) 8th Edition*. The GHS classification system provides an internationally recognized and standardized framework for assessing the level (or category) of aquatic toxicity hazard posed by a chemical product.

The acute GHS aquatic toxicity classification for a chemical product mixture was identified from SDS "*Section 2. Hazards Identification.*" The provision of GHS hazard classification data in SDS Section 2 is voluntary in the United States. For chemical products where GHS classification information was not provided in SDS Section 2, no aquatic hazard assessment could be made, and thus no conclusion about potential for aquatic toxicity is implied. These products were identified as "Not Assessed."

The GHS classification system for acute aquatic toxicity was applied to chemical products as follows (United Nations, 2019), where L(E)C50 refers to 50% lethal or non-lethal effect concentrations:

- **GHS Acute Category 1**: L(E)C50 ≤1.0 mg/L. Product is very toxic to aquatic life.
- **GHS Acute Category 2**: L(E)C50 >1.0 mg/L but ≤10 mg/L. Product is toxic to aquatic life.
- **GHS Acute Category 3**: L(E)C50 >10 mg/L but ≤100 mg/L. Product is harmful to aquatic life.

Where available, the Chemical Abstracts Service (CAS) number and descriptive information on product composition presented in SDS *Section 3.* "*Composition and Information on Ingredients"* were used as a complement to the GHS acute aquatic toxicity category. Composition of individual substances is presented in % w/w.

5.2 TCW Category I Effluents

Twenty-three distinct chemical products were identified as potentially being present in TCW Category I effluent samples. Chemical products are present in all but three TCW Category I effluent samples (HV63, XP62, and PO80) (**Table A6**). The most frequently used product functionalities were defoamers (n=7), oxygen scavengers (n=5), and corrosion inhibitors (n=5). Nineteen products used in TCW Category I effluent samples were identified as "Not Assessed." Four chemical products were assigned an acute GHS aquatic toxicity classification of 1-3 based on the description provided in SDS Section 2. These products account for 17% of the total number of chemical products used. The products functioned as biocides, defoamers, and non-emulsifiers.

5.2.1 GHS Acute Category 1

The single product with a GHS Acute Category 1 classification is "Biocide 1" and was potentially present in sample LC54. This product was used as an electrophilic biocide and is comprised of glutaraldehyde (CAS No.111-30-8; 10-30% w/w) and methanol (CAS No. 67-56-1; 0.1-1 % w/w).

5.2.2 GHS Acute Category 2

Chemical products with a GHS Acute Category 2 classification are a defoamer and a non-emulsifier:

- **"Defoamer 1"**: The product was potentially present in sample RD67 and is used to prevent or eliminate existing foam in water-based drilling fluids and brines. The product contains 30-60% w/w of an alkyl phosphate (tributyl phosphate or "TBP"; CAS No. 126-73-8).

- **"Non-emulsifier 1"**: This product was potentially present in samples RD67, RU61, LC54, and AU71. "Non-emulsifier 1" is used to prevent the formation of emulsions between calcium-based completion brines ($CaBr_2$ and $CaCl_2$) and crude oil. The product contains 30-60% w/w isopropanol (CAS No. 67-63-0), 5-10% w/w of ethylene glycol monobutyl ether (CAS No. 111-76-2), 5-10% w/w of a proprietary ammonium salt (CAS No. not provided), 1-5% w/w of proprietary quaternary ammonium compounds (QACs) (CAS No. not provided), 1-5% w/w of xylene (CAS No. 1330-20-7), and 0.1-1% w/w of methanol (CAS No. 67-56-1).

5.2.3 GHS Acute Category 3

The single product with a GHS Acute Category 3 classification is the lytic biocide "Biocide 4." This chemical product was potentially present in sample AU71. "Biocide 4" is a cationic surfactant that contains 50% w/w of the QAC didecyldimethylammonium chloride (DDAC) CAS No. 7173-51-5, and two alcohols (ethyl [0-10% w/w; CAS No. 64-17-5] and methyl [30-40% w/w; CAS No. 67-56-1]).

5.3 TCW Category III Effluents

In total, 57 distinct chemical products are potentially present in Category III effluent samples. Chemical products were present in all TCW Category III effluent samples (**Table A7**). Most products present in Category III effluent samples were identified as "Not Assessed" (n=47). A single product ("Oil Tracer 1") had a chronic aquatic toxicity classification only. The most frequently used product functionalities were fluid additives (n=9), defoamers (n=5), pH control (n=5), clay stabilizers (n=4), and viscosifiers (n=4).

There were more chemical products with the potential to contribute to aquatic toxicity than were observed for Category I effluents. Ten chemical products were observed with an acute aquatic toxicity GHS classification. These products account for 18% of the total number of chemical products used. These chemical products functioned as activators, biocides, breakers, corrosion inhibitors, non-emulsifiers, oxygen scavengers, and solvents.

5.3.1 GHS Acute Category 1

Two biocides and a corrosion inhibitor have a GHS Acute Category 1 classification:

- **"Biocide 2"**: This product was potentially present in samples FP89 and is used as a water-based, non-oxidizing biocide in hydraulic fracturing treatment well operations to minimize bacterial contamination. The product contains 1-5% w/w of the quaternary phosphonium biocide tributyl tetradecyl phosphonium chloride (TTPC) CAS No. 81741-28-8. This was the only substance identified in the SDS.
- **"Biocide 3"**: This product was potentially present in sample FP89 as an electrophilic biocide to control bacterial growth. "Biocide 3" contains 60-100% w/w of the quaternary phosphonium compound tetrakis (hydroxymethyl) phosphonium sulphate (THPS) (2:1) (CAS No. 55566-30-8).
- **"Corrosion Inhibitor 3"**: This product was potentially present in sample JH68 and is used as a corrosion inhibitor. Substances identified in the SDS are 30 to 60% w/w methanol (CAS No. 67-56-1); 10 to 30% w/w ethoxylated alcohols (CAS No. Proprietary); 10 to 30% w/w modified thiourea polymer (CAS No. Proprietary); and 5 to 10% w/w propargyl alcohol (CAS No. 107-19-7). The product prevents acid from damaging piping and other infrastructure.

5.3.2 GHS Acute Category 2

Chemical products with a GHS Acute Category 2 classification are a non-emulsifier, a corrosion inhibitor, a breaker, a solvent, and an activator:

- **"Non-emulsifier 1"**: This non-emulsifier was potentially present in samples NY50 and YO64. See discussion provided in Section 5.2.2 for this chemical product.
- **"Breaker 1"**: The product was potentially present in effluent samples RC74, OD76, and TF74 (three samples from a single discharge event. This product is used as an emulsion breaker and contains sodium chloride (10-30% w/w; CAS No. 7647-14-5) and chlorous acid, sodium salt (5-10% w/w; CAS No. 7758-19-2). These were the only substances identified on the SDS.
- **"Solvent 4"**: This product was potentially present in effluent sample JH68. This product consists of aromatic hydrocarbons used as a solvent: 60 - 100% w/w xylene (CAS No. 1330-20-7), 10 - 30% w/w ethyl benzene (CAS No. 100-41-4), and 0.1 - 1% w/w toluene (CAS No. 108-88-3).
- **"Activator 1"**: This product was potentially present in effluent sample SH87. This product consists of cobalt acetate (CAS No. 71-48-7; 5-10% w/w); this was the only substance identified by the SDS.

5.3.3 GHS Acute Category 3

Chemical products with a GHS Acute Category 3 classification are a lytic biocide and an oxygen scavenger:

- **"Biocide 4"**: This product was potentially present in samples YO64 and IS88. See discussion provided in Section 5.2.3 for this chemical product.
- **"Oxygen Scavenger 1"**: This product was used as a liquid oxygen scavenger for corrosion control of water-based fluids in TCW effluent samples LX98 and IS88. The product contains ammonium bisulfite (30-60%; CAS No. 10192-30-0); this is the only substance identified on the SDS.

5.4 Summary

The chemical hazard assessment qualitatively described acute aquatic hazard characteristics for chemical products. Performing more comprehensive evaluations would require proprietary information on the concentrations of individual substances in chemical products. The study question of "*What are the general aquatic hazard characteristics of the substances currently used in TCW fluids?*" can be addressed as follows:

- In total, 75 chemical products were potentially present in sampled TCW effluents. Approximately 81% of these chemical products were identified as "Not Assessed." For chemical products where GHS classification information was not provided in SDS Section 2, no aquatic hazard assessment could be made, and no conclusion about the potential for aquatic toxicity is implied.
- The most frequently used chemical products in TCW Category I effluents were defoamers, oxygen scavengers, and corrosion inhibitors. In TCW Category III effluents, the most frequently used products were fluid additives, defoamers, pH control, clay stabilizers, and viscosifiers.

- Among the chemical products whose SDS presented GHS classifications, there were products in each of the three GHS acute aquatic toxicity categories: GHS Category 1 – Very toxic; GHS Category 2 – Toxic; and GHS Category 3 – Harmful.
- TCW Category III effluents contained more added chemical products than did TCW Category I effluents. The product functionalities in TCW Category III effluents are electrophilic and lytic biocides, cationic and non-ionic surfactants, breakers, corrosion inhibitors, non-emulsifiers, defoamers, solvents, and an activator.
- TCW chemical products contain primarily organic substances that could potentially contribute to aquatic toxicity in the TCW effluent samples.

6.0 Acute Aquatic Toxicity of Discharged TCW Effluents

This section describes the acute whole effluent toxicity of TCW Category I and TCW Category III effluent samples. The evaluations presented address the JIP study question "*How toxic are TCW effluents towards marine biota?"* Topics discussed are acute 48-h static renewal WET test procedures, preparation of TCW Category III gel samples for WET testing, acute WET test results for TCW Category I effluents, WET test results for Category III effluents, differences in the acute toxicity of TCW Category I and III effluents, and supplemental WET tests evaluating the effect of short exposure durations..

6.1 Acute 48-h Static Renewal WET Test

Acute, static renewal 48-h WET testing was conducted consistent with the study plan, the general permits, and the USEPA (2002) guidance on WET methods. The WET test was used to evaluate the aggregate toxicity resulting from the mixture of all substances contained in the effluent, and aquatic hazard. Acute 48-h WET test laboratory reports that have been redacted to maintain confidentiality are provided in **Appendix F**.

6.1.1 WET Test Procedures

WET testing was conducted by EEUSA. WET test procedures are summarized below:

- **Test duration**: WET test organisms were exposed to the test medium for 48 hours (48-h).
- **Effluent dilution series**: Consistent with the study plan, the tested effluent dilutions were a laboratory control (0%); 0.1%; 0.3%; 0.8%; 2%; 6%; 18%; and 50%. The range of dilutions was chosen because historical WET testing of GOM PW samples indicates (anecdotally) that complete mortality occurs at 100% effluent. The 0.1% effluent dilution reflects the anticipated lower limit of the critical effluent dilution. See Section 4.0 for a discussion on how the CD was calculated.
- **Test species and number of replicates**: The WET test species were *Americamysis bahia* (Mysid) and *Menidia beryllina* (Inland silverside minnow). A minimum of five replicates with eight organisms per replicate were used in the laboratory control and in each effluent dilution.
- **WET test endpoints:** Acute survival was evaluated. Test endpoints were a 48-h no observed effect concentration (NOEC) and a lowest observed effect concentration (LOEC). Two supplemental test endpoints were a 25% lethal concentration (LC25) and a 50% median lethal concentration (LC50).
- **WET test acceptability criteria (TAC)** are consistent with the GPs and USEPA (2002).
- **WET test holding time compliance:** WET test sample holding time was 36 hours from the time the TCW effluent sample is collected in the field, to the time of WET test setup at EEUSA. Sample holding times for three samples were exceeded due to transport delays (RU72; 122 hours), and the need to prepare difficult-to-analyze TCW Category III gel samples (YO64 [1,320 hours] and YU91 [100 hours]). Consistent with the study plan, samples exceeding the hold times were analyzed and reported, but the limitations of using such data were noted in

the laboratory report. For more information on potential impacts to toxicity from sample aging see Section 6.2.2.

6.1.2 Preparation of TCW Category III Gel Samples

Gel samples YO64, YU91, and OD76 required sample mixing because a homogeneous aqueous solution is required to conduct WET testing. USEPA approved the adoption of the mixing approach as a departure from the original study plan via email on November 18, 2020. The gel samples were mixed by EEUSA with LCSW at 320 revolutions per minute for 5 h on magnetic stirrers using ½ inch diameter by 3-inch-long stir bars. Photographs of the mixing apparatus and an example of the aqueous solution after mixing the gel sample are presented in **Figure A3**.

6.1.3 Aquatic Toxicity of TCW Category I Effluents

The aquatic toxicity of Category I effluents was variable with CV for the LC50 of 140% and 180% for the Inland silverside minnow and Mysid, respectively (**Figure 12**). Possible sources of variability include differences in well operation, the application of end-of-pipe treatment (for samples ZG57, EP57, TR84, and QK19), and downhole conditions:

- **Inland silverside minnow**: The geometric mean LC50 for the Inland silverside minnow was 4.4% effluent, with LC50s ranging from 0.2% to >50% effluent (**Table 16**). The most toxic TCW Category I effluent sample was UP92, which is a workover brine that contained several chemical products e.g., fluid stabilizers, viscosifiers, defoamers, surfactants, and a hydrogen sulfide scavenger. The least toxic sample was ZG57; this long-term flowback effluent was treated with GAC and filtration before discharge.
- **Mysid**: The geometric mean LC50 for the Mysid was 1.6% effluent, with LC50s ranging from 0.19% to 35.2% effluent. The most toxic sample was sample UP92 and the least toxic sample was ZG57.

Table 16. Acute 48-h Whole Effluent Toxicity of TCW Category I Effluents.								
Sample	WET Test Endpoint (% Effluent)							
	Inland silverside minnow				Mysid			
	NOEC	LC25	LOEC	LC50	NOEC	LC25	LOEC	LC50
HV63	2	3.05	6	4.11	0.3	0.42	0.8	0.54
RD67	2	3	6	4	0.3	0.46	0.8	0.61
RU61	0.8	1.51	2	2.54	0.3	0.44	0.8	0.57
XP62	2	2.92	6	3.95	0.3	0.44	0.8	0.57
LC54	2	3	6	4	2	2.94	6	4.12
AU71	0.3	0.45	0.8	0.6	0.3	0.46	0.8	0.66
ZG57	50	>50	>50	>50	18	26.5	50	35.2
EP57-Begin (Structure 18)	6	13.5	18	23.3	18	21.8	50	31.2
TR84-Middle (Structure 18)	6	11	18	16	2	6	6	10
CM89 (Geometric Mean Structure 18)	6	12	18	19	6	11	17	18
QK91	18	26	50	34	6	4.18	18	8.4
DO57	2	3.3	6	5.2	0.8	1.19	2	1.61
PO80	2	2.67	6	3.78	0.3	0.36	0.8	0.51
UP92	0.1	0.15	0.3	0.21	0.1	0.13	0.3	0.19
n[1]	12	12	12	12	12	12	12	12
Geometric Mean[2]	2.1	3.2	5.6	4.4	0.8	1.1	2.2	1.6
Min[2]	0.1	0.15	0.3	0.2	0.1	0.13	0.3	0.19
Max[2]	50.0	>50	>50	>50	18.0	26.5	>50	35.2
Notes: [1] Excludes samples EP57 and TR84; [2] Values >50% were defaulted to 50.								

6.1.4 Aquatic Toxicity of TCW Category III Effluents

The acute toxicity of TCW Category III effluents was variable with a CV of 130% and 140% for the Inland silverside minnow and Mysid LC50s respectively (**Figure 12**). In general, TCW Category III gel samples exhibited higher toxicity than other types of TCW fluids. Sample IH80 was found after collection not to have been discharged so its toxicity is reported in Appendix E. Details for TCW Category III effluents are provided below by WET test organism:

- **Inland silverside minnow**: The geometric mean LC50 for the Inland silverside minnow was 3.8% effluent, with LC50s ranging from 0.2% to 38.7% effluent (**Table 17**). The most toxic samples were YO64, which is a gel that contained a biocide (GHS Acute 3) and a non-emulsifier (GHS Acute 2), and sample FP89. Sample FP89 was from a well treatment fracturing job. This effluent contained two biocides with a GHS acute category of 1. The least toxic sample was JH68, which was an acid treatment effluent that received end-of-pipe treatment with GAC and filtration before discharge to GOM surface water.
- **Mysid**: The geometric mean LC50 for the Mysid was 1.1% effluent, with LC50s ranging from 0.05% to 13.1% effluent (**Table 17**). The most toxic sample was YO64, and the least toxic sample was SH87. Effluent sample SH87 was a well treatment operation in which chemical products, including a breaker (GHS Acute 2) were used.

Table 17. Acute 48-H Whole Effluent Toxicity of TCW Category III Effluents.

Sample	Difficult to Analyze Sample?	WET Test Endpoint (% Effluent)							
		Inland silverside minnow				Mysid			
		NOEC	LC25	LOEC	LC50	NOEC	LC25	LOEC	LC50
JK70	No	0.8	2.3	2.6	3.57	0.8	1.24	2.6	1.69
NY50	No	6	9	18	12	2	3	6	4
YO64	Yes[1]	0.1	0.14	0.3	0.2	<0.1	0.03	0.1	0.05
FP89	No	0.3	0.41	0.8	0.54	<0.1	0.06	0.1	0.13
GQ67	No	0.8	1.05	2	1.37	0.3	0.43	0.8	0.56
YU91	Yes[1]	6	9.64	18	13.3	0.1	0.15	0.3	0.2
LX98	No	2	3	6	4	0.8	1.1	2	1.4
IS88	No	0.8	1.1	2	1.4	0.3	0.55	0.8	0.8
RU72	Yes[2]	0.3	0.45	0.8	0.6	0.8	1.08	2	1.39
BT52	No	18	25.4	50	33.6	6	9.08	18	12.2
SH87	No	18	26	50	34	6	9.53	50	13.1
RC74-Begin (Structure 19)	No	6	9	18	12	6	8.82	18	12.4
OD76-Middle (Structure 19)	Yes[1]	6	8.77	18	11.9	<0.1	0.07	0.1	0.15
TF74-End (Structure 19)	No	0.1	0.15	0.3	0.2	0.1	0.14	0.3	0.2
NZ96 (Geo. Mean Structure 19)	--	1.5	2.3	4.6	3.1	0.4	0.4	0.8	0.7
JH68	No	18	27.2	50	38.7	2	3.13	6	4.25
n[3]		13	13	13	13	13	13	13	13
Geometric Mean[4]	--	1.8	2.8	5.2	3.8	0.9	0.8	1.6	1.1
Min[4]	--	0.1	0.1	0.3	0.2	<0.1	0.03	0.1	0.05
Max[4]	--	18	27.2	50	38.7	6.0	9.5	50	13.1

Notes: [1]. Fracturing gel; a homogeneous mixture suitable for WET testing was achieved after mixing (see Section 5.1.2 and Figure A3); [2] Sample contained proppant beads. The beads were removed before WET testing; [3] Excludes samples RC74, OD76, and TF74; [2] Values <0.1% were defaulted to 0.1.

6.1.5 Variability in Effluent Toxicity During a Single Discharge

Variability in effluent toxicity during a single discharge was evaluated for samples collected from a completion operation: EP57 (start) and TR84 (end); and a treatment operation: RC74 (start), OD76 (middle), and TF74 (end). The change in the 48-h LC50 was expressed as a ratio. LC50s that exhibited an increase with a ratio ≥2.0, or a decrease with a ratio ≤0.5 are emphasized to call attention to the largest variations in toxicity.

Increases in toxicity were observed over the course of a single discharge (**Table 18**). Mysid toxicity increased for all samples, with the most pronounced increase observed for the end and beginning of the treatment operation. The most substantial increases in Inland silverside minnow toxicity were also observed for the treatment operation.

Table 18. Change in acute toxicity (LC50) at Different Times in the Discharge for Well Completion and Treatment Operations Expressed as a Ratio[1].

Test Organism	Ratios			
	Completion Operation	Treatment Operation		
	TR84 (End): EP57(start)	OD76 (Middle): RC74 (start)	TF74 (End): OD76 (Middle)	TF74 (End): RC74 (start)
Minnow	0.69	**0.15**	0.73	**0.11**
Mysid	**0.3**	**0.19**	**0.32**	**0.06**

Notes: [1]. Ratios ≥2.0 or ≤0.5 are boldfaced to highlight larger variations in toxicity.

6.1.6 Comparison of TCW Category I and III Effluents

Differences in Mysid and Inland silverside minnow 48-h LC50s for TCW Category I and TCW Category III effluents were compared with a non-parametric Wilcoxon rank sum (WRS) test. A single LC50 reported as >50% effluent was defaulted to 50% effluent, and the geometric mean LC50 was used to represent discharge structures with multiple samples. Statistically significant differences in 48-h LC50s are reported where $p \leq 0.05$.

Statistically significant differences were not observed between TCW Category I and TCW Category III effluents for either species, indicating that TCW Category I and TCW Category III effluents are equally toxic (**Figure 12**). The Mysid was, however, more sensitive to both TCW Category I (p=0.008) and TCW Category III (p=0.004) effluents than the Inland silverside minnow (**Table 19**).

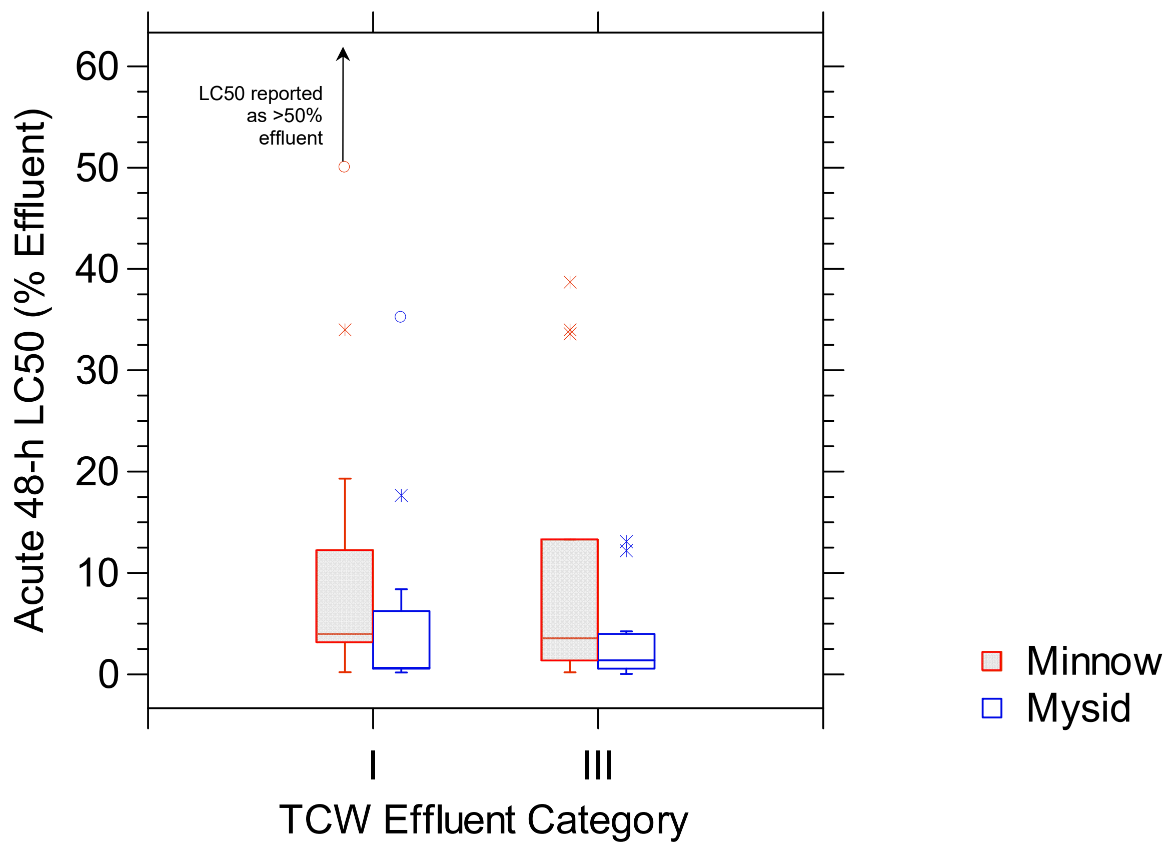


Figure 12. Boxplots for Mysid and Inland Silverside Minnow 48-h LC50s for TCW Category I (n=12) and TCW Category III effluents (n=13). The center line marks the median. Box edges are at the first and third quartiles. Whiskers show the range of observed values that fall within 1.5x of the interquartile range. Outliers are determined by the software where outside values, i.e., values between the inner and outer fences are plotted with asterisks (*). Values beyond the outer fences, i.e., far outside values, are plotted with empty circles (°). Additional details on boxplots are provided in **Appendix C**.

Table 19. WRS Test Two-Sided Probabilities for Comparison of 48-H LC50 Data (% Effluent)[1].				
	TCW Cat. I Minnow LC50	TCW Cat. I Mysid LC50	TCW Cat. III Minnow LC50	TCW Cat. III Mysid LC50
TCW Cat. I Minnow LC50	--			
TCW Cat. I Mysid LC50	**0.008**	--		
TCW Cat. III Minnow LC50	0.814	0.53	--	
TCW Cat. III Mysid LC50	0.155	0.695	**0.004**	--
Notes: [1]. Boldfaced values are statistically significant ($p \leq 0.05$).				

6.1.7 Comparison with Produced Water Effluents

Unlike TCW discharges, PW discharges have been well characterized for over 30 years through routine and compliance WET testing under NPDES discharge permit (Hughes et al., 2021). TCW Category I and TCW Category III acute toxicity data were compared to available acute PW toxicity data and the PW CDs presented in the GOM GPs. The purpose of the comparison was to (1) place the toxicity of TCW discharges into context, and (2) assess whether the PW CDs can be used to evaluate the toxicity of TCW effluents, respectively:

- **Data used in the evaluation**: Acute toxicity data are limited compared to the availability of chronic toxicity data, the collection of which is required by the GOM NPDES Permit. Historical PW acute toxicity from the 1990s and 48-h LC50s calculated from an acute WET test dataset from 2020 (n=5) were used (**Table A8**). Produced water 24-h to 168-h L(EC)50 data were reported for three species: Mysid, Inland silverside minnow, and Sheepshead minnow (*Cyprinodon variegatus*). The data were presented as either an arithmetic mean or single concentration (% effluent):
  - Louisiana Department of Environmental Quality (LDEQ). Avanti Corporation 1993. Raw 96-h LC50 data for the Mysid.
  - Meinhold, A.F., Holtzman, S., and DePhillips, M.P. 1996. PW discharges to the Gulf of Mexico: Background Information for Ecological Risk Assessment Gulf of Mexico. The study presented 96-h LC50s for Mysid and Sheepshead minnow obtained from LDEQ discharge monitoring report data (Avanti Corporation, 1992).
  - Sauer, T.C., Costa, H.J., Brown, J.S., and Ward, T.J. 1997. Toxicity Identification Evaluations of Produced-Water Effluents. Environmental Toxicology and Chemistry, Vol. 16, No. 10, pp. 2020–2028. The study reported 24-h LC50s for the Mysid.
  - Neff, J.M. 2002. Bioaccumulation in Marine Organisms. Effects of Contaminants from Oil Well PW. Elsevier Science Publishers, Amsterdam. 452 pp. Data collected from the GOM (near Louisiana) were evaluated. Acute WET test endpoints were 96-h LC50s for Mysid and Sheepshead minnow.
  - EEUSA. 2021: EEUSA reviewed routine 7-day chronic tests conducted in 2020 for Inland silverside minnow (USEPA Method 1006) and Mysid (USEPA Method 1007) exposed to PW effluents. The review identified 5 samples with reported 48-h survival data. The 48-h LC50s were calculated with two approaches (1) an Inhibition Concentration (ICp), which is a point estimate approach, and (2) survival data that exhibited an “all or nothing response”

(USEPA, 2000), i.e., 100% survival at one test dilution followed by 100% mortality at the next test dilution, were calculated with the Binomial or Graphical method.

- **Data analysis**: The Mysid was selected for evaluation because sample size was sufficient to conduct a statistical comparison. Mysids have also been found in this study to be more sensitive to TCW effluents. Published studies (Hughes, et al., 2021) found that Mysids are more sensitive to PW than are Inland silverside minnows. The total Mysid sample size was 255; of these data, 241 are 96-h LC50s (LDEQ, 1992), with the remainder comprised of 24 - 168-h L(E)C50s. Neither the Inland silverside minnow (n=2) nor Sheepshead minnow (n=5) PW toxicity data were evaluated. All data are, however, provided in **Table A-8**. A non-parametric WRS test was used to compare differences in Mysid L(E)C50s across effluent types. Statistically significant differences are reported where $p \leq 0.05$.
- **Comparison results:** TCW effluents are not more (or less) toxic than PW effluents (WRS $p>0.05$) (**Figure 13**). Geometric mean LC50s range from 1.1 (TCW Category III) to 7.2 for PW, with 75% of PW LC50s at concentrations of ≤12% effluent. For all three datasets, outliers occur from 10-35% effluent, with extreme outliers at concentrations >35% effluent.

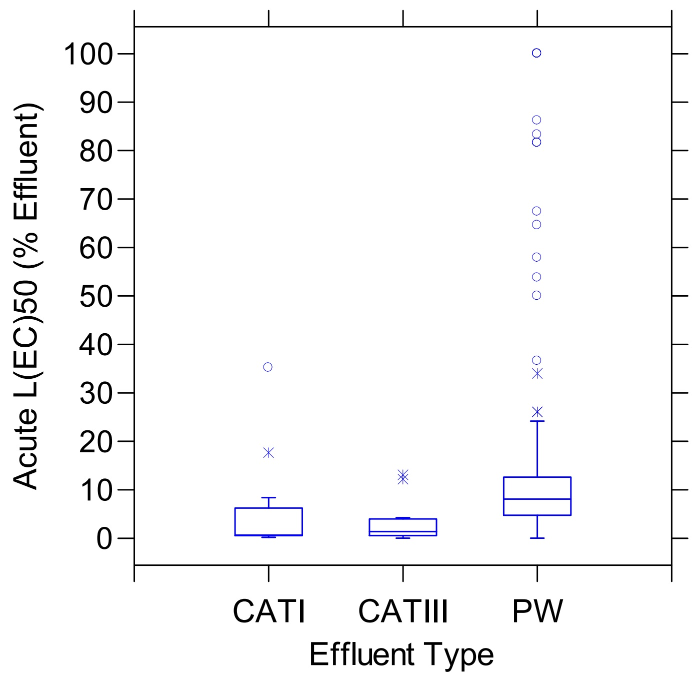


Figure 13. Boxplots of Mysid acute aquatic toxicity data for TCW Category I effluents (CATI) (48-h LC50; n=12), TCW Category III effluents (CATIII) (48-h LC50; n=13) and PW effluents (PW) (24 to 168-h L[E]C50; n=255). The center line marks the median. Box edges are at the first and third quartiles. Whiskers show the range of observed values that fall within 1.5x of the interquartile range. Outliers are determined by the software where outside values, i.e., values between the inner and outer fences are plotted with asterisks (*). Values beyond the outer fences, i.e., far outside values, are plotted with empty circles (°). Additional details on boxplots are provided in **Appendix C**.

- **Comparison of the TCW NOEC with the PW CD:** A comparison of the chronic NOEC with the PW CD was performed as it is an environmental benchmark for evaluating PW chronic toxicity. For TCW effluents, the lowest acute NOEC observed in 48-h WET tests was above the PW CD for a majority of both TCW Category I (seven of 13 samples) and TCW Category III (nine of 15 samples). It was not known, however, if the GP PW CDs are appropriate for evaluating the risk of TCW effluents. TCW effluents display specific gravities ranging from 1.01 to 1.66 and effluent density impacts critical dilution concentrations predicted by the Cornell Mixing Zone Expert System (CORMIX) used by USEPA. USEPA assumed a PW specific gravity of 1.07 in calculating the GP CD tables. To determine whether the PW CDs are appropriate for use when evaluating the acute toxicity of TCW effluents, a series of CORMIX simulations was performed using measured TCW effluent specific gravities (**Appendix G**). It was found that the calculated TCW CDs were a function of effluent specific gravity and that the median ratio of the TCW CD predicted with effluent specific gravity to the PW CD was 0.7. This indicates that the use of the PW CDs did not introduce a strong bias in the comparison of the NOEC with the CD and are appropriate for evaluating the acute toxicity of TCW effluents.

6.2 Supplemental WET Testing

Because the median duration of a typical TCW discharge is 1 h, standardized 48-h WET tests may overestimate the actual aquatic hazard of TCW effluents. Hence, supplemental WET testing, using 2-h exposure times, was used to assess an exposure scenario representative of short-duration TCW effluent discharges. The supplemental testing also provided some insight on toxicity persistence and uptake rate of potential toxicants.

6.2.1 Approach

The supplemental WET testing was conducted as a slight modification of the acute WET test procedures described in USEPA (2002) from a 48-h exposure to a 2-h exposure. This modification has been followed previously for the evaluation of pulse exposures (Angel et al., 2018)) and episodic exposures (Gordon et al., 2012). Two types of supplemental WET tests were conducted on effluent samples previously evaluated with a 48-h static-renewal WET test (**Figure 14**). Details of the laboratory procedure are provided in **Appendix H,** and supplemental WET test laboratory reports that have been redacted to maintain confidentiality are provided in **Appendix I**:

- **Test 1: Re-test of initial 48-h acute test**: The 48-h retest of previously tested samples provided insight into how sample toxicity may have changed during storage and a baseline for comparison with the results of a 2-h exposure test.
- **Test 2**: **2-h exposure**: This test consisted of a 2-h exposure with subsequent transfer to laboratory control seawater for the remaining 46-h of the 48-h test. This approach is consistent with evaluations of 2-h exposures of marine organisms to GOM PW effluents (Gissi, et al., 2021). A 2-h exposure to TCW testing seemed appropriate since 75% of the 23 TCW discharges sampled in 2019, 2020, and 2021 were $\leq$2-h in duration. **Appendix J** provides further discussion of the rationale for a 2-h exposure in these tests.

Test 1	48-h Exposure to TCW Effluent	
Test 2	2-h Exposure to TCW Effluent	46-h Exposure to Laboratory Control Seawater

Figure 14. Study design for supplemental WET testing. Dark grey coloration indicates exposure to TCW effluents; light grey coloration indicates transfer to laboratory control seawater.

In 2020, both tests were run in parallel on aged TCW effluents. The tests were conducted on samples where the NOEC of the most sensitive WET test organism(s) was less than the CD. A laboratory control and three effluent dilutions were run, whereby two effluent dilutions bracketed the critical effluent dilution. Survival count data were recorded at the following intervals: 0.5-h, 1-h, 1.5-h, 2-h, 24-h, and 48-h. Differences in the proportions of surviving organisms were evaluated with a Test of Equal Proportions (Wilson, 1927); sample IS88 was not evaluated because the laboratory inadvertently used an incorrect CD for Test 1. Statistically significant differences were reported where $p \leq 0.05$. In 2021, only Test 2 was conducted for Mysid and Inland silverside minnow exposed to non-aged TCW effluents. The test series bracketed the NOEC. The data were compared with the CD.

6.2.2 Aged Effluent Samples

Six effluent samples ranging in age from 4 to 134 days ($\bar{x}$ = 64 days) and with a median discharge duration of 0.7-h were evaluated (**Table 20**).

Table 20. Characteristics of Aged Effluent Samples Evaluated with Supplemental WET Testing.			
Sample	**TCW Effluent Category**	**Discharge Duration (h)**	**Sample Age when Tested (days)**
HV63	I	1.25	103
RD67	I	1.5	134
RU61	I	0.08	96
AU71	I	0.4	24
FP89	III	1.0	21
IS88	III	0.18	4

For most of the aged samples, toxicity was persistent but reducing the exposure duration to 2-h did result in lower toxicity to both the Mysid and Inland silverside (**Table 21**):

- **Test 1**: Sample aging had a minimal effect on reducing toxicity after a 48-h exposure.
- **Test 2**: Reducing the exposure duration to 2 h was beneficial, i.e. the NOEC increased in most cases.

Table 21. Supplemental WET Testing Results for Aged TCW Effluents.				
Sample	Species	NOEC (% Effluent)		
		Initial 48-h Test	Test 1 (48-h Retest)	Test 2 (2-h Exposure)
HV63	Mysid	0.3	0.44	0.8
RD67	Mysid	0.3	0.48	0.8
RU61	Mysid	0.3	0.55	0.8
AU71	Mysid	0.3	0.8	0.8
	Minnow	0.3	0.39	0.39
FP89	Mysid	<0.1	<0.3	<0.3
	Minnow	0.3	0.3	0.8
IS88	Mysid	0.3	0.3	0.8

The concentration response curves (**Figure 15**) show that in all but one case (AU71 – Mysid) the 2-h exposure resulted in less mortality across the range of concentrations tested than either the initial 48-h test or the 48-h retest (Test 1). This suggests that a shorter exposure, more reflective of field conditions, tends to reduce the potential for toxicity.

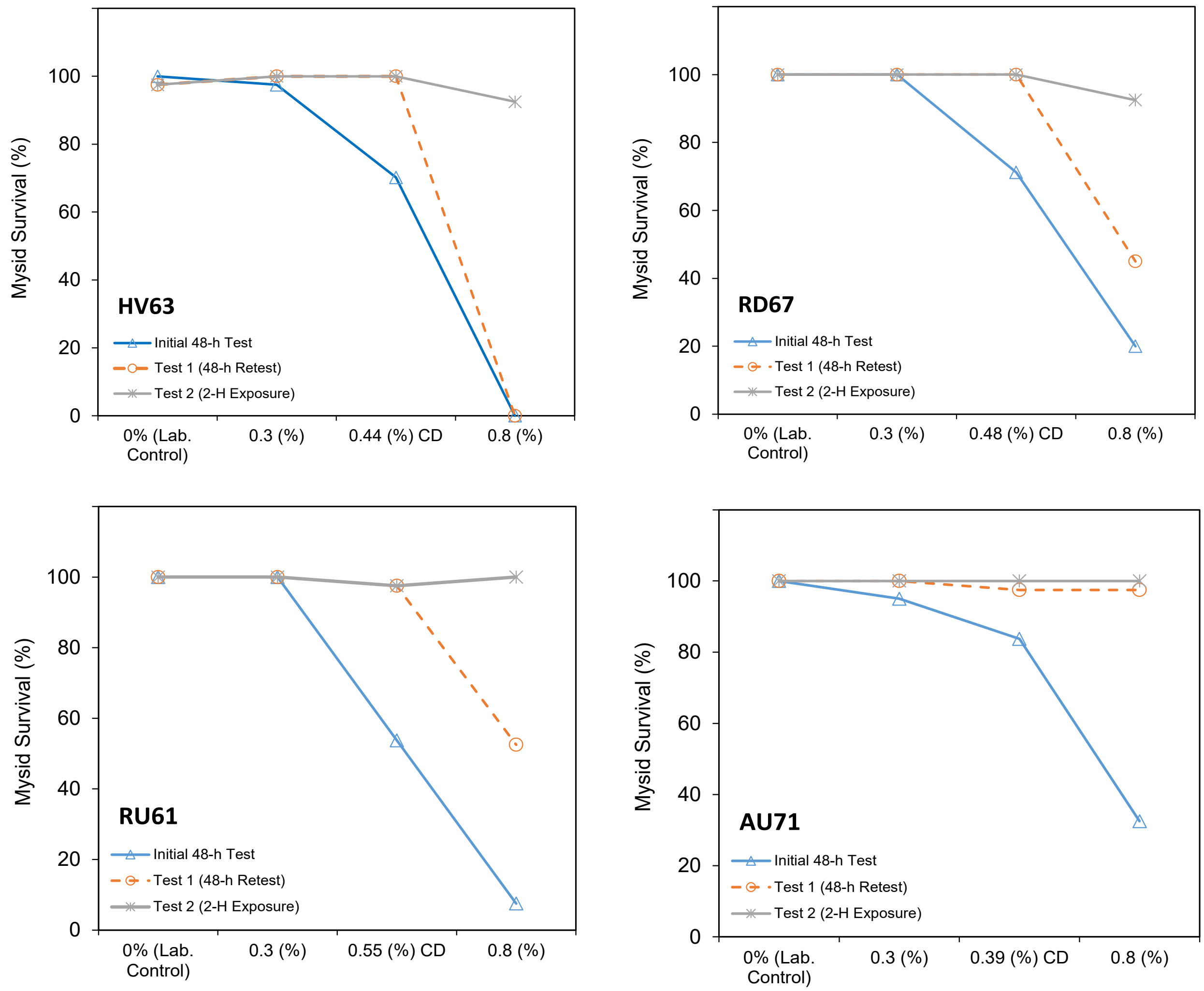


Figure 15. Influence of exposure duration on toxicity. Initial 48-h toxicity results (collected and tested within hold time) are compared with retests of 2-h or 48-h exposure to an aged sample effluent.

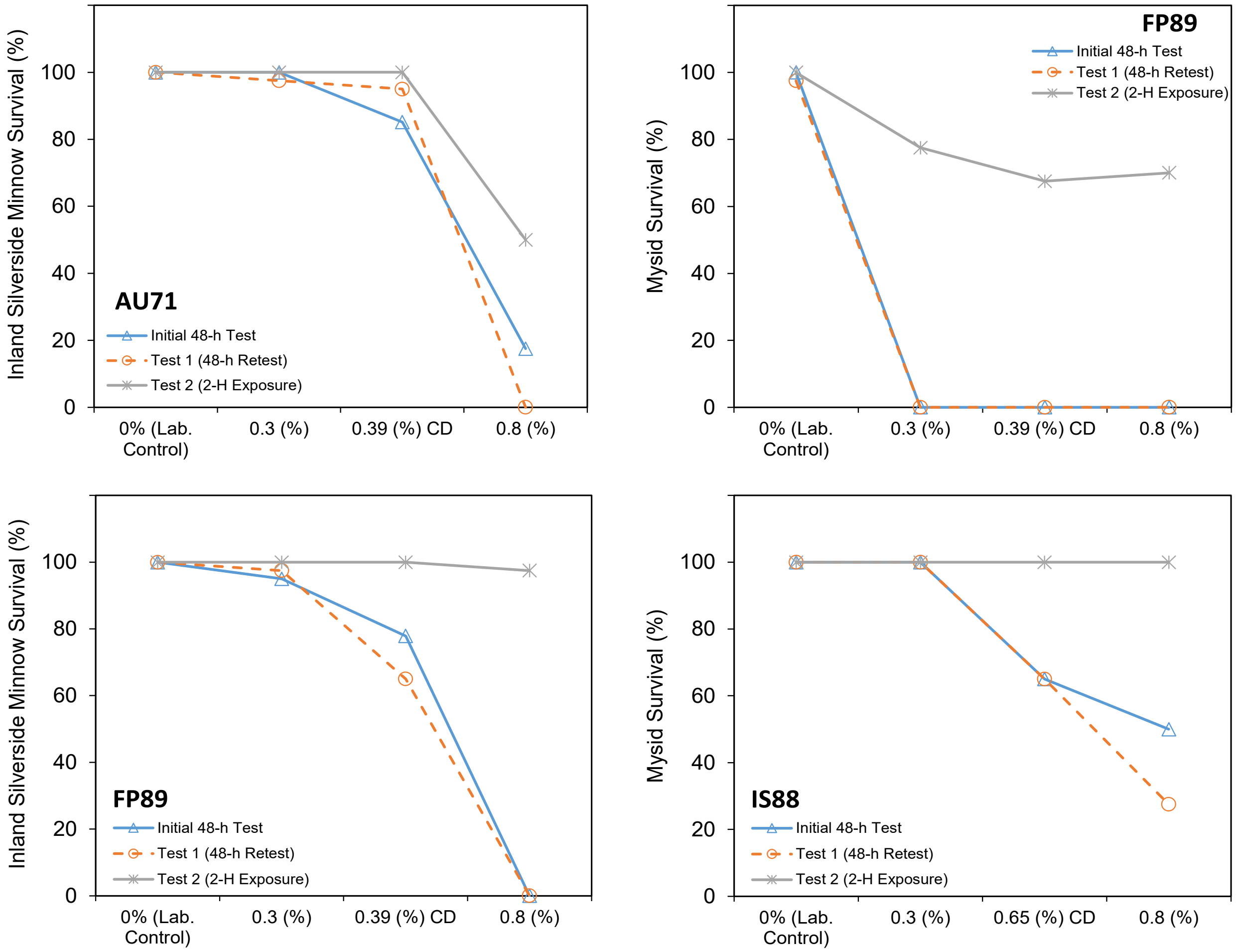


Figure 15 (cont.). Influence of exposure duration on toxicity. Initial 48-h toxicity results (collected and tested within hold time) are compared with retests of 2-h or 48-h exposure to an aged sample effluent.

A statistical test of equal proportions goes beyond a comparison of the NOEC to test for significant differences in the concentration response curves. Test results (**Table 22**) show that, apart from sample AU71, there was a significant difference between 2-h and 48-h exposures, i.e. a decrease in toxicity, in every sample.

Table 22. Test of Equal Proportions p-Values for Mysid and Inland Silverside Survival in Aged TCW Effluents[1].		
Mysid		
Sample	**Initial 48-h Test vs. Test 1**	**Test 1 vs. Test 2**
HV63	0.16	**<0.001**
RD67	**0.01**	**<0.001**
RU61	**<0.001**	**<0.001**
AU71	**<0.001**	0.48
FP89	0.13	**<0.001**
Inland silverside minnow		
Sample	**Initial 48-h Test vs. Test 1**	**Test 1 vs. Test 2**
AU71	1.0	**0.002**
FP89	1.0	**<0.001**
Notes: [1]. This table shows p-values for each comparison evaluated. Boldfaced values indicate a statistically significant difference in survival (p<0.05)		

6.2.3 Non-aged Effluent Samples

Three non-aged effluent samples from discharges with a median duration of 0.8-h were evaluated with the Test 2 protocol, which was initiated at the end of the 48-h test (**Table 23**).

Table 23. Characteristics of Non-Aged Effluent Samples Evaluated with Test 2: 2-H Exposure.		
Sample	**TCW Effluent Category**	**Discharge Duration (h)**
PO80	I	0.5
JH68	III	0.67
UP92	I	1.0

For every case except sample PO80 for the Inland silverside minnow, apparent toxicity decreased, i.e. the NOEC increased (**Table 24**, **Figure 16**). This indicates that a shorter exposure time, more reflective of field conditions, would result in reduced potential for toxicity.

Table 24. Supplemental WET Testing Results for Non-Aged Effluents.			
Sample	**Species**	**NOEC (% Effluent)**	
		Initial 48-h Test	**Test 2 (2-h Exposure)**
PO80	Mysid	0.3	0.8
	Inland silverside minnow	2	2
JH68	Mysid	2	6
	Inland silverside minnow	18	50
UP92	Mysid	0.1	0.3
	Inland silverside minnow	0.1	0.3

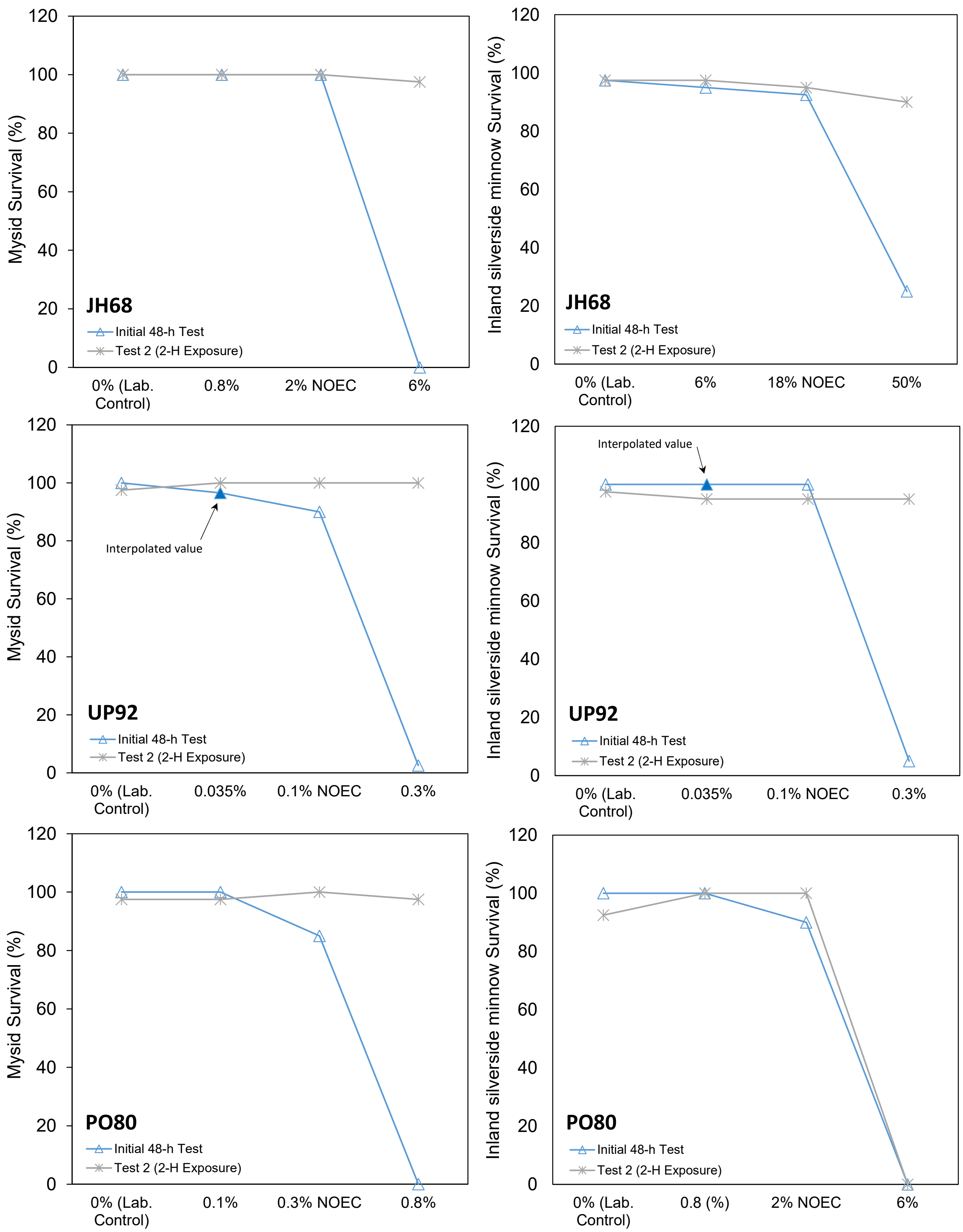


Figure 16. Mysid and Inland silverside minnow survival relative to the laboratory control when exposed to non-aged TCW effluents for 2-h and 48-h. For the purposes of plotting the UP92 data, percent survival at an effluent dilution of 0.035% was estimated with linear interpolation.

6.3 Summary

The evaluations presented in this section address the study question “How toxic are TCW effluents to exposed marine biota?”. The results can be summarized as follows:

- TCW effluents exhibited a wide range of aquatic toxicity. This variability appears to be influenced by well operation, stage in the discharge, and substances used in the fluids, and the application of end-of-pipe treatment.
- The Mysid was more sensitive to both TCW Category I and TCW Category III effluents than was the Inland silverside minnow, and the difference was statistically significant.
- The acute toxicity of TCW effluents towards the Mysid is comparable to the toxicity of PW effluents. The PW CDs presented in the GOM general permits are appropriate for evaluating the acute toxicity of TCW effluents.
- The supplemental WET test results indicated that 2-h exposures lead to reduced mortality compared with 48-h exposure. Since 75% of the sampled TCW discharges are ≤2-h in duration, this result suggests that a 48-h WET test is a conservative metric for assessing the potential for aquatic toxicity.

7.0 Potential Causes of Acute Aquatic Toxicity

The evaluations presented in this section are used to address the study questions of "*Can general toxicity-composition connections be made?*" and "*What substances could potentially be associated with acute aquatic toxicity at the CD*?" Multiple lines of evidence were considered when assessing potential causes of acute aquatic toxicity. Evaluations were conducted to assess the potential causes of acute aquatic toxicity were toxicity-composition connection evaluations, a statistical assessment of patterns in acute aquatic toxicity, and an acute aquatic toxicity screening at the critical effluent dilution.

7.1 Toxicity-Composition Connections

The toxicity-composition connections addressed the potential for aquatic hazard by addressing the following questions:

- *Do inorganic and organic substances potentially contribute to toxicity? Do Mysids and Inland silverside minnows respond differently to these substances?*
- *Are the observed toxicity-composition connections biologically plausible? Are they consistent with the current scientific literature?*

7.1.1 Approach

The data evaluations assessed the contribution of inorganic and organic substances to the observed acute aquatic toxicity. The evaluations were conducted for TCW Category I and TCW Category III effluents. The approach consisted of selecting substances for evaluation, estimating concentrations of substances in 100% effluent, and data analysis. Details are provided below:

- **Acute toxic unit (TUa)**: The 48-h LC50s for Inland silverside minnow and Mysid were converted to an acute toxic unit (TUa) for 25 effluent samples evaluated with 48-h WET testing. This approach normalized the LC50 to the whole effluent. The TU is defined by the USEPA (2010) as "*a measure of toxicity in an effluent as determined by the acute toxicity units (TUa) measured. The larger the TU, the greater the toxicity.*" The USEPA (2010) calculates the TUa as "*100 times the reciprocal of the effluent concentration that causes 50 percent of the organisms to die in an acute toxicity test where TUa = 100/LC50.*"
- **Substances selected for evaluation and rationale**: Substances were selected for evaluation based on their likely presence in effluents, potential toxicity towards the Mysid and Inland silverside minnow, and their ability to act as a surrogate for organic toxicants. The substances selected are major cations and anions, TOC, and DOC. The rationale for their selection is presented below:
  - Dissolved cations and anions: The cations evaluated are Ca^{2+}, K^+, Na^+, and Mg^{2+}. The anions evaluated are HCO_3^-, Cl^-, and Br^-. Base brines of various densities are present in all effluent samples. As previously discussed, base brines used during the study are chloride brines: ($CaCl_2$, NaCl, and KCl), and bromide brines ($CaBr_2$ and NaBr).

    Toxicity towards marine organisms can result from an ion imbalance due to both ion deficiency and excess. Because TCW effluents may be hypersaline, toxicity can be caused by an ion excess. Individual ions including K^+, Ca^{2+}, Mg^{2+}, and HCO_3^- have been shown to cause toxicity towards marine WET test organisms based on molarity models (Pillard et al., 2000). The Inland silverside minnow is more tolerant of ion-related toxicity than is the Mysid (Pillard et al., 2000).

Ion-related toxicity towards aquatic organisms can occur from exposure to individual ions, or an ion mixture. An ion imbalance can adversely affect osmoregulation. Although adverse effects may be associated with osmoregulation, individual ions can also adversely affect specific physiological functions, which may be of greater significance (Pillard et al., 2000). For example, Ca^{2+} has been shown to be an important ion influencing Mysid toxicity (Kline and Stekoll, 2000), and in some cases was the primary cause of wastewater toxicity (Dorn and Rodgers, 1989; in Pillard et al., 2000). The ratio of Ca^{2+} to Mg^{2+} is also toxicologically relevant.

- TOC and DOC: Organic substances may contribute to the observed toxicity. Because specific organic substances were not measured in sampled effluents, the water quality parameters TOC and DOC were selected as a surrogate for the level of organic substances in the effluent. Potential sources of DOC and TOC in TCW effluents include organic substances in chemical products, organic acids, hydrocarbons added to TCW fluids or picked up downhole, and bacterial biomass.
- TSS: The composition of TSS and substances bound to TSS can influence bioavailability and toxicity. For example, a non-polar organic sorbed to bacterial cells might be available to Mysids. TSS could also potentially reduce the bioavailability of certain metals.

- **Estimated concentrations of substances in 100% effluent (C_{TCW100}):** The laboratory analytical data measured at the CD were scaled to 100% effluent as previously discussed (Section 4.4) so that the analytical data could be related to the TUa.
- **Data analysis**: Correlation and regression analyses were conducted. The laboratory control was included in analyses with a default TUa of 1.0. Concentrations of substances reported below the RL were assigned a concentration equal to 100% of the RL. An arithmetic mean for substances and a geometric mean for the TUa were used for structures with multiple samples for a single discharge. Details are provided below:
  - Correlation: Due to issues of non-normality, non-parametric Spearman rank-order correlation was used to associate estimated concentrations of dissolved Ca^{2+} and total Mg^{+2}, Na^{+}, Br^{-}, Cl^{-}, and HCO_3^{-} in 100% effluent with the TUa (reported as Spearman's Rank correlation coefficient, R_s). Statistically significant associations are reported where $p \leq 0.05$ consistent with Zar (1984) (see **Appendix C** for details).
  - Regression: Non-linear best-fit regression was used to characterize the association of the TUa with estimated concentrations of dissolved Ca^{2+}, TSS, DOC, and TOC in 100% effluent.

7.1.2 Acute Toxic Unit

The TUa is presented by sample in **Figure 17**. The sample with the highest Mysid TUa was the TCW Category III gel sample YO64. The highest Inland silverside minnow TUa were observed for samples YO64 and UP92. The TUa was generally lowest for TCW Category I and III TCW effluents with end-of-pipe treatment.

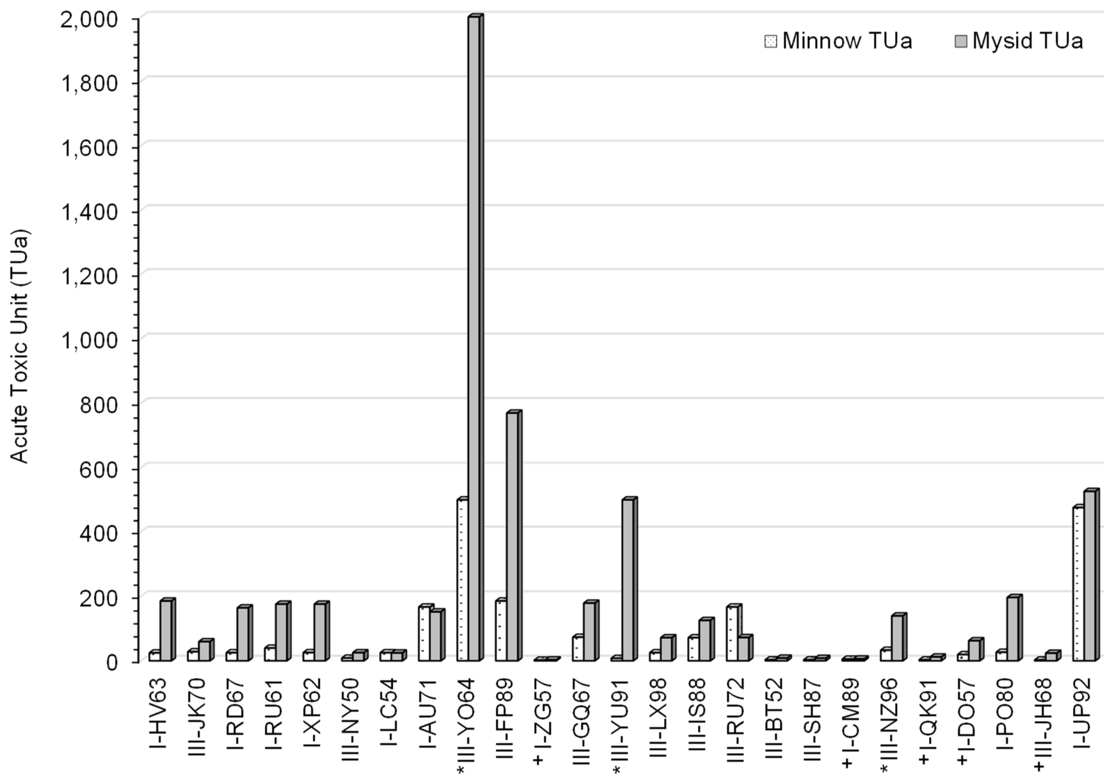


Figure 17. Acute toxic unit (TUa) by TCW effluent sample. The vertical bars represent the acute toxic unit where TUa = 100/LC50. A TUa of 2 indicates that the LC50 was 50% TCW effluent, whereas a TUa of 2,000 indicates that the LC50 was 0.05% TCW effluent. TCW Category I effluent samples are denoted by a "I", TCW Category III effluent samples are denoted by a "III", and TCW Category III gel samples are denoted by a (*). The (+) indicates samples that received end-of-pipe treatment (GAC and filtration). The TUa for CM89 (samples EP57 and TR84) and NZ96 (samples RC74, OD76, and TF74) was calculated from the geometric mean LC50s.

7.1.3 TCW Category I Effluents

The cation Ca^{2+} was correlated with Mysid toxicity in TCW Category I effluents. Toxicity to the Inland silverside minnow was not as strongly influenced by Ca^{2+}. Of the ions evaluated, dissolved Ca^{2+} was the only substance that had a statistically significant positive association with the Mysid TUa (**Table 25**). The identified association with Ca^{2+} is supported by the literature (Kline and Stekoll, 2000; Dorn and Rodgers, 1989; Pillard et al., 2000). Except for a weakly significant (p=0.051) association with Br^-, the Inland silverside minnow TUa is not associated with dissolved ion concentrations. The greater tolerance of the Inland silverside minnow to ion imbalance has been reported previously (Pillard et al., 2000).

Table 25. Spearman rank-order Correlation of TUa with Estimated Dissolved Ion Milliequivalents and the ratio of Ca:Mg in undiluted TCW Category I Effluents.			
Dissolved Ion (meq/L)	**Sample Size[1]**	**Mysid R_s**	**Minnow R_s**
Ca^{2+}	13	**0.852; p=0.0002**	0.501
Mg^{2+}	13	-0.006	-0.179
Ratio Ca:Mg	13	**0.722; p=0.005**	0.515
K	13	0.168	0.377
Na	13	0.306	0.226
Br	13	0.531	0.55; p=0.051[2]
Cl	13	0.12	0.217
$SO_4^{(2-)}$	13	-0.162	-0.035
HCO_3^-	13	0.144	-0.082
Notes: TUa; acute toxic unit where TUa = 100/LC50. Boldfaced R_s values indicate statistical significance ($p \leq 0.05$). Other Rs values are not statistically significant ($p>0.05$); [1] represents all TCW Category I samples and the laboratory control; [2] weakly significant p-value.			

The association between the Mysid TUa and the ratio of dissolved Ca^{2+}: Mg^{2+} is also statistically significant. The regression indicated that there was a moderate association between the Mysid TUa and dissolved Ca^{2+} (meq/L) (R^2 = 0.6) (**Figure 18**). Most of the samples are clumped together, except for samples AU71 and UP92. The regression was strongly influenced by sample AU71, which had low dissolved Ca^{2+}, but high toxicity. Sample UP92 was among the most toxic samples collected; although Ca^{2+} was elevated, UP92 contained several chemical additives.

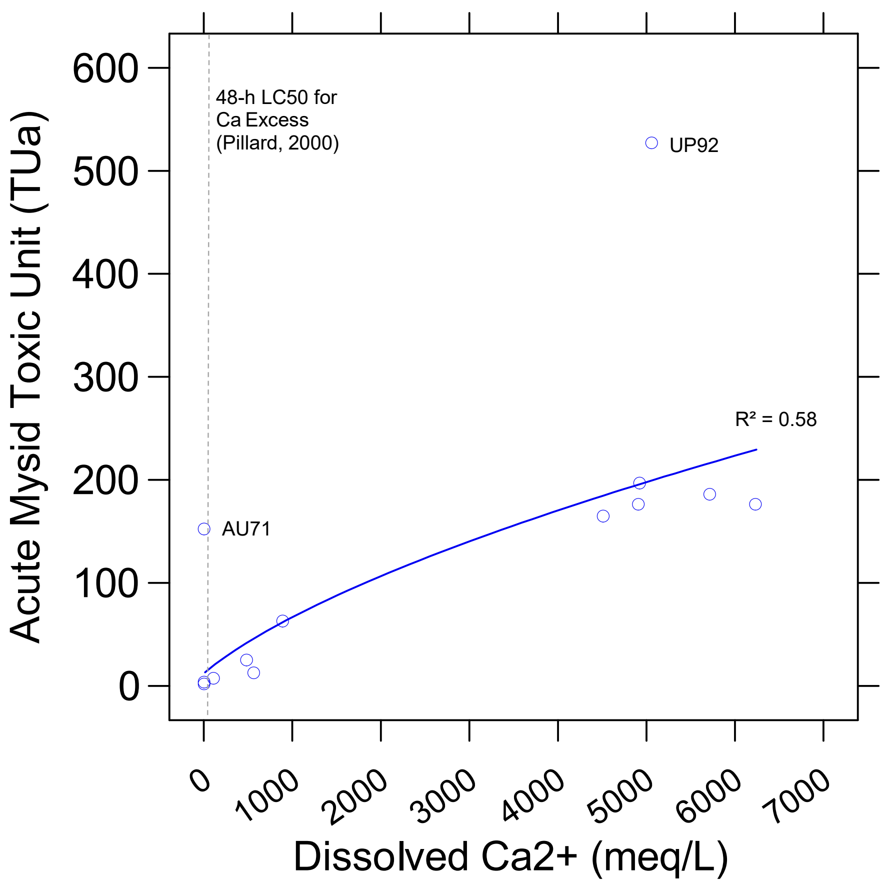


Figure 18. Power regression of the Mysid TUa with estimated dissolved calcium in undiluted TCW Category I effluents (n=13).

There was a statistically significant positive association between the Minnow TUa, TOC, and DOC for TCW Category I effluents (**Table 26**). TSS was not associated with either the Mysid or Inland silverside minnow TUa.

Table 26. Spearman rank-order Correlation of TUa with Estimated TOC, DOC, and TSS in undiluted TCW Category I Effluents.

Water Quality Parameter (mg/L)	Sample Size[1]	Mysid R_s	Minnow R_s
TOC	13	0.476	**0.689; p=0.009**
DOC	13	0.493	**0.689; p=0.009**
TSS	13	-0.21	0.149

Notes: TUa; acute toxic unit where TUa = 100/LC50. Boldfaced R_s values indicate statistical significance ($p \leq 0.05$). Other Rs values are not statistically significant ($p>0.05$); [1] Represents all TCW Category I samples and the laboratory control.

7.1.4 TCW Category III Effluents

Individual ions were not associated with TUa in TCW Category III effluents (**Table 27**). The Mysid and Inland silverside minnow TUa, however, are associated with DOC, TOC, and TSS in TCW Category III effluents (**Table 28**).

Table 27. Spearman rank-order Correlation of TUa with Estimated Dissolved Ion Milliequivalents and the ratio of Ca:Mg in undiluted TCW Category III Effluents.

Ion (meq/L)	Sample Size[1]	Mysid R_s	Minnow R_s
Ca^{2+}	13	0.198	-0.085
Mg^{2+}	13	-0.084	-0.352
Ratio Ca^{+2}:Mg^{+2}	13	0.398	0.039
K^{+1}	13	0.165	-0.033
Na^{+1}	13	-0.181	-0.328
Br^{-1}	13	0.521	0.355
Cl^{-1}	13	0.297	0.360
$SO_4^{(2-)}$	13	0.079	0.472
HCO_3^-	13	0.022	-0.219

Notes: TUa; acute toxic unit where TUa = 100/LC50. Notes: [1] Represents all TCW Category I samples and the laboratory control.

Table 28. Spearman rank-order Correlation of TUa with Estimated TOC, DOC, and TSS in undiluted TCW Category III Effluents.

Water Quality Parameter (mg/L)	Sample Size[1]	Mysid R_s	Minnow R_s
TOC	13	**0.642; p=0.018**	**0.705; p=0.003**
DOC	13	**0.556; p=0.048**	**0.627; p=0.02**
TSS	13	**0.646; p=0.016**	0.540; p=0.056[2]

Notes: TUa; acute toxic unit where TUa = 100/LC50. Boldfaced R_s values indicate statistical significance ($p<0.05$). The remaining correlations are not statistically significant ($p>0.05$). Notes: [1] represents all TCW Category I samples and the laboratory control; [2] weakly significant p-value.

A regression of Inland silverside minnow TUa indicated an association with DOC and TOC (R^2=0.86) (**Figure 19A**). Similar associations were observed for the Mysid TUa with DOC (R^2=0.84) and TOC (R^2=0.83) (**Figure 19B**). The regressions for both species are driven by a single extreme data point. This suggests that while organic substances may contribute to Mysid toxicity in TCW Category III effluents, toxicity likely involves more than one type of potential toxicant.

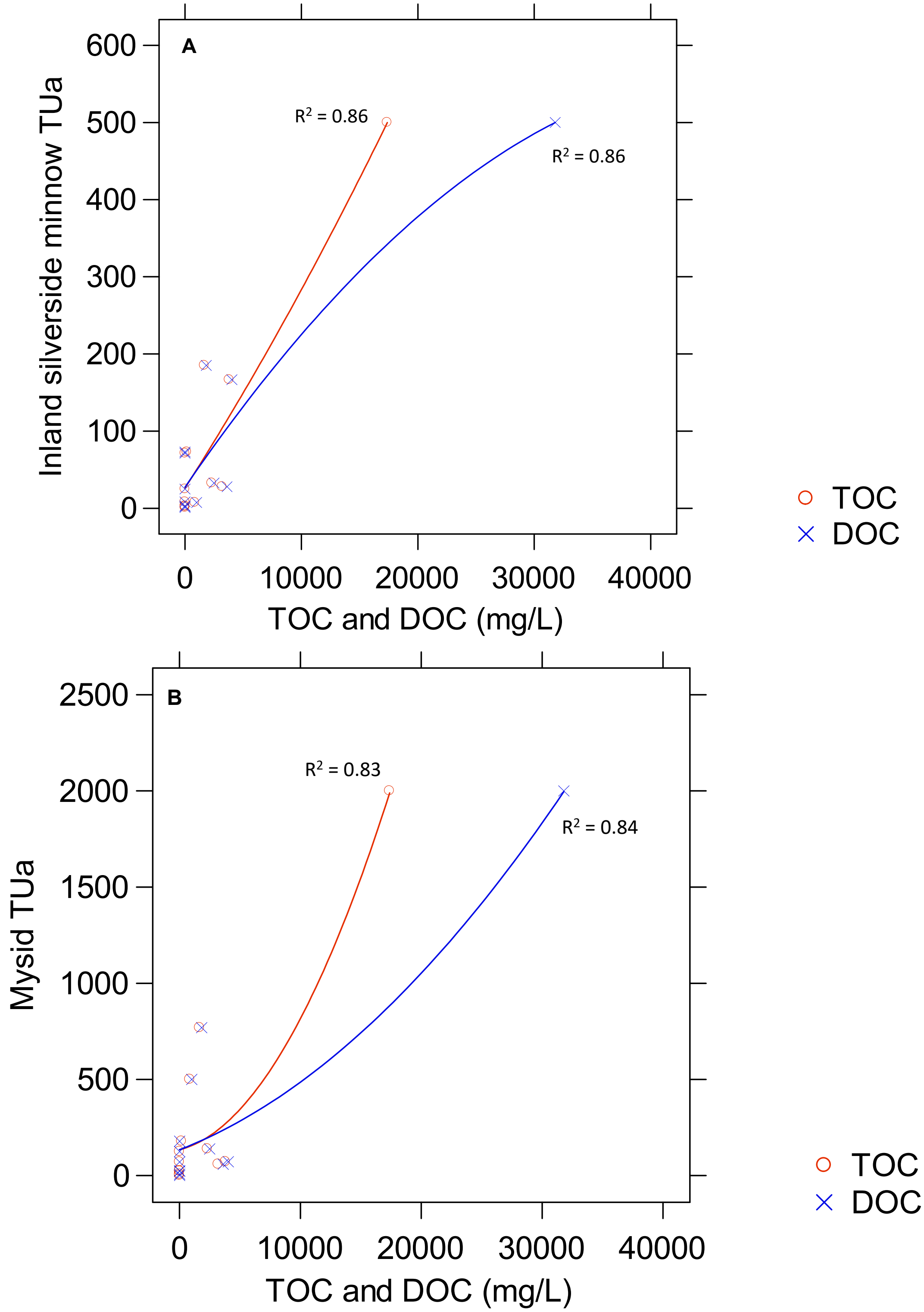


Figure 19. 2nd-order Polynomial regression of the Inland silverside minnow and Mysid acute toxic unit (TUa) with estimated DOC and TOC in undiluted TCW Category III effluents (n=13). The TUa for structures where multiple samples were taken were presented as a geometric mean.

TSS was also positively associated with the Inland silverside minnow (R^2=0.79) and Mysid (R^2=0.84) TUa (**Figure 20**); both regressions were influenced by a single data point. TSS was strongly associated with TOC (R^2 = 0.94), suggesting that potential toxicants could be bound with suspended particulates.

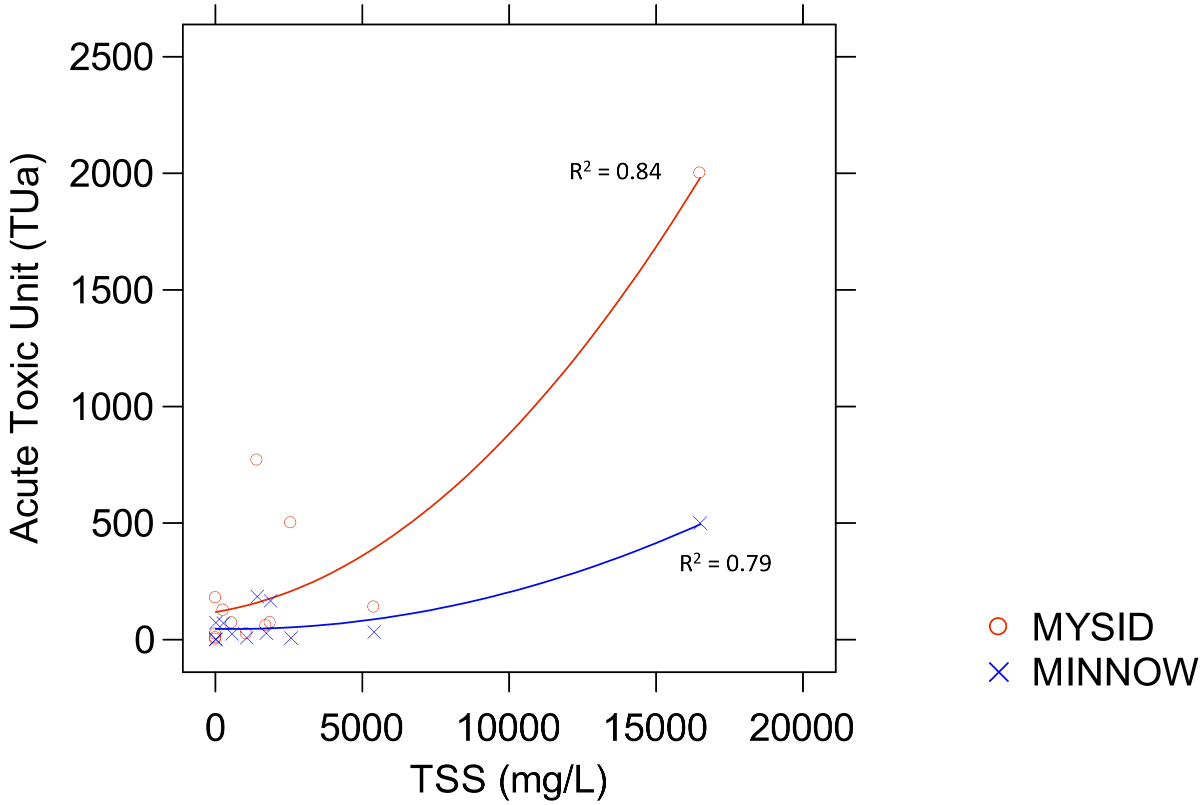


Figure 20. 2nd-order Polynomial regression of the Mysid and Inland silverside minnow acute toxic unit (TUa) with estimated TSS in undiluted TCW Category III effluents.

7.2 Patterns in Acute Aquatic Toxicity

Patterns in acute toxicity were characterized by applying multivariate ordination to the WET test endpoint data for the Mysid and Inland silverside minnow. The purpose of the ordination was to assess potential differences and similarities in the acute toxicity of TCW Category I and TCW Category III effluents that could be used to support the toxicity-composition evaluations for both species. The ordination also identified effluents with the greatest potential for aquatic hazard based on consideration of all the toxicity endpoints.

7.2.1 Approach

Each Mysid and Inland silverside minnow WET test endpoint (NOEC, LOEC, LC25, and LC50), i.e., the "toxicity fingerprint", was ordinated with hierarchical and agglomerative cluster analysis. This approach addressed the relative sensitivity of the WET test species to substances in the TCW effluents. Details of the ordination and a separate ordination for the Mysid, which was the more sensitive WET test organism in this study, are provided in **Appendix C**.

Cluster analysis is a multivariate procedure that was used to identify natural groupings in the individual WET test endpoint data. The cluster analysis yielded a dendrogram that grouped the TCW effluent samples according to similarity in WET test endpoints. The dendrogram was “cut” subjectively to yield meaningful clusters that reflect well operation, presence and absence of chemical products, and TCW effluent chemistry. For the ordination, a default value of 0.035% effluent was assigned to WET test endpoints <0.1% effluent. WET test endpoints >50% effluent were defaulted to a value of 100% effluent.

7.2.2 Ordination Results

Samples were clustered based on the similarity of the Inland silverside minnow and Mysid WET test endpoints (**Figure 21**). The dendrogram indicates that TCW Category I and TCW Category III effluents did not ordinate into two separate groups, and that patterns in acute toxicity are driven by a set of factors more complex than TCW effluent category. Eight clusters of effluent samples were identified that occur along an effluent toxicity gradient. Cluster 1 includes the least toxic sample, which is a TCW Category I effluent with end-of-pipe treatment. Cluster 8 contains the most toxic samples including a TCW Category III gel and a TCW Category I brine with several chemical additives.

Details of the dendrogram are provided below by cluster:

- **Clusters 1 through 5:** The TCW Category I and TCW Category III effluent samples in clusters 1 through 5 were the least toxic samples observed (the geometric mean Mysid TUa = 8, and the Inland silverside minnow TUa = 3) (**Table 29**). The pre-discharge treatment of GAC and filtration were present for the samples in clusters 1, 3, 4, and 5; the samples were collected at the beginning of a long-term flowback and a Category III well treatment operation.
- **Cluster 6:** This cluster consisted of two TCW Category III effluent samples, one of which was a gel sample. Based on the LC50, the Mysid was approximately 14 times more sensitive to substances in the tested effluents than the Inland silverside minnow. Sample NY50 contained chemical products with a GHS Acute Category 2 classification.
- **Cluster 7:** Most (67%) of the samples in this cluster are TCW Category I effluents. The Mysid was 4 times more sensitive than the Inland silverside minnow to the effluent samples in this cluster. The most toxic samples are NZ96 and JK70.
- **Cluster 8**: Most (63%) of the samples in this cluster are TCW Category III effluents. This cluster contains eight of the most toxic TCW effluent samples observed. Based on the LC50, the effluents were 2 times more toxic to the Mysid than the Inland silverside minnow. The two most toxic samples were UP92 and YO64. Sample UP92 represented a well abandonment operation and was collected from a holding tank on the structure before being discharged near the seafloor. UP92 contained several chemical additives that may have contributed to the observed toxicity. Sample YO64 was a TCW Category III gel sample that potentially contained chemical products that are toxic to aquatic biota. These products are “Non-emulsifier 1” (GHS Acute 2) and the lytic biocide “Biocide 4” (GHS Acute 3), which both contain QACs.

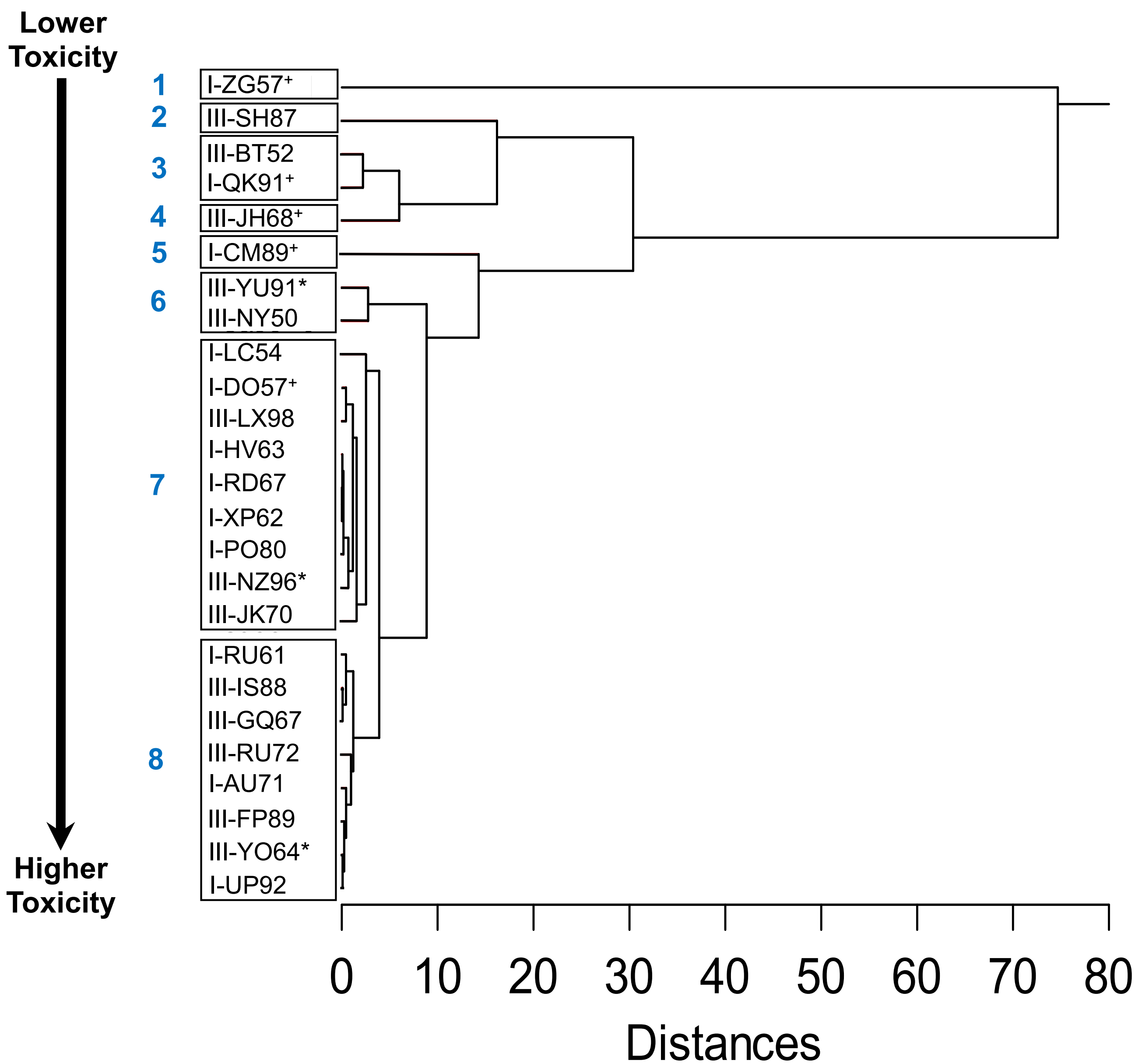


Figure 21. Cluster analysis dendrogram of the Inland silverside minnow and Mysid acute WET test endpoints (NOEC, LC25, LOEC, LC50). TCW Category I effluent samples are denoted by a "I", TCW Category III effluent samples are denoted by a "III", and TCW Category III gel samples are denoted by a (*). The (+) indicates samples that received end-of-pipe treatment (GAC and filtration). The arrow illustrates a whole effluent toxicity gradient. Background information on cluster analysis and details of the ordination are provided in **Appendix C**.

Table 29. Inland Silverside Minnow and Mysid Acute WET Test Endpoint by Cluster Analysis Grouping.										
Cluster	Sample Size	Inland silverside minnow (% Effluent)				Mysid (% Effluent)				Ratio Inland silverside Minnow:Mysid LC50
		NOEC	LC25	LOEC	LC50	NOEC	LC25	LOEC	LC50	
1	1	50.0	100.0	100.0	100.0	18.0	26.5	100.0	35.2	2.8
2	1	18.0	26.0	50.0	34.0	6.0	9.5	50.0	13.1	2.6
3	2	18.0	25.7	50.0	33.8	6.0	6.2	18.0	10.1	3.3
4	1	18.0	27.2	50.0	38.7	2.0	3.1	6.0	4.3	9.1
5	1	6.0	12.2	18.0	19.3	6.0	11.4	17.3	17.7	1.1
6	2	6.0	9.3	18.0	12.6	0.4	0.7	1.3	0.9	14.1
7	9	1.8	2.8	5.3	3.9	0.5	0.7	1.4	1.0	3.9
8	8	0.3	0.5	0.9	0.7	0.2	0.2	0.5	0.4	1.9

Notes: A geometric mean is presented where n>1 and "n" represents the number of samples in the cluster. Endpoints >50% effluent were defaulted to 100%; endpoints <0.1 effluent were defaulted to 0.035%.

As discussed in **Appendix C**, the separate Mysid-data-only dendrogram also indicates that TCW Category I and TCW Category III effluents did not ordinate into two separate groups. Seven clusters of effluent samples were identified (Clusters 1-7) that occur along an effluent toxicity gradient. Cluster 1 includes the least toxic sample, which is a Category I effluent with end of pipe treatment (GAC and filtration). Cluster 7 contains the most toxic TCW effluent samples (n=13), which are a mixture of TCW Category I and TCW Category III effluents, including gel samples.

7.2.3 Key Substances and Acute Toxicity

The cluster analysis identified patterns in acute toxicity that may be explained by specific substances in the effluent. These substances are likely to be cations and anions from brines, and organics from chemical products and substances from down-hole. The cluster analysis also highlighted the ability of end-of-pipe treatment to reduce aquatic toxicity.

Clusters 1-5 comprise the "lower toxicity" effluents and clusters 6-8 comprise the "higher toxicity" effluents. Ca^{2+} appeared to be associated with Mysid toxicity in the "lower toxicity" effluents, whereas a mixture of Ca^{2+}, DOC, TOC, and TSS influence the "higher toxicity" effluents (**Figure 22**). End-of-pipe treatment that removed DOC, TOC, and TSS also removed some of the acute toxicity. For example, 80% of the lower toxicity effluents had end-of-pipe treatment that targeted organics (GAC) and suspended solids (filtration). These types of treatments are not, however, effective at removing ions, e.g. Ca^{2+}.

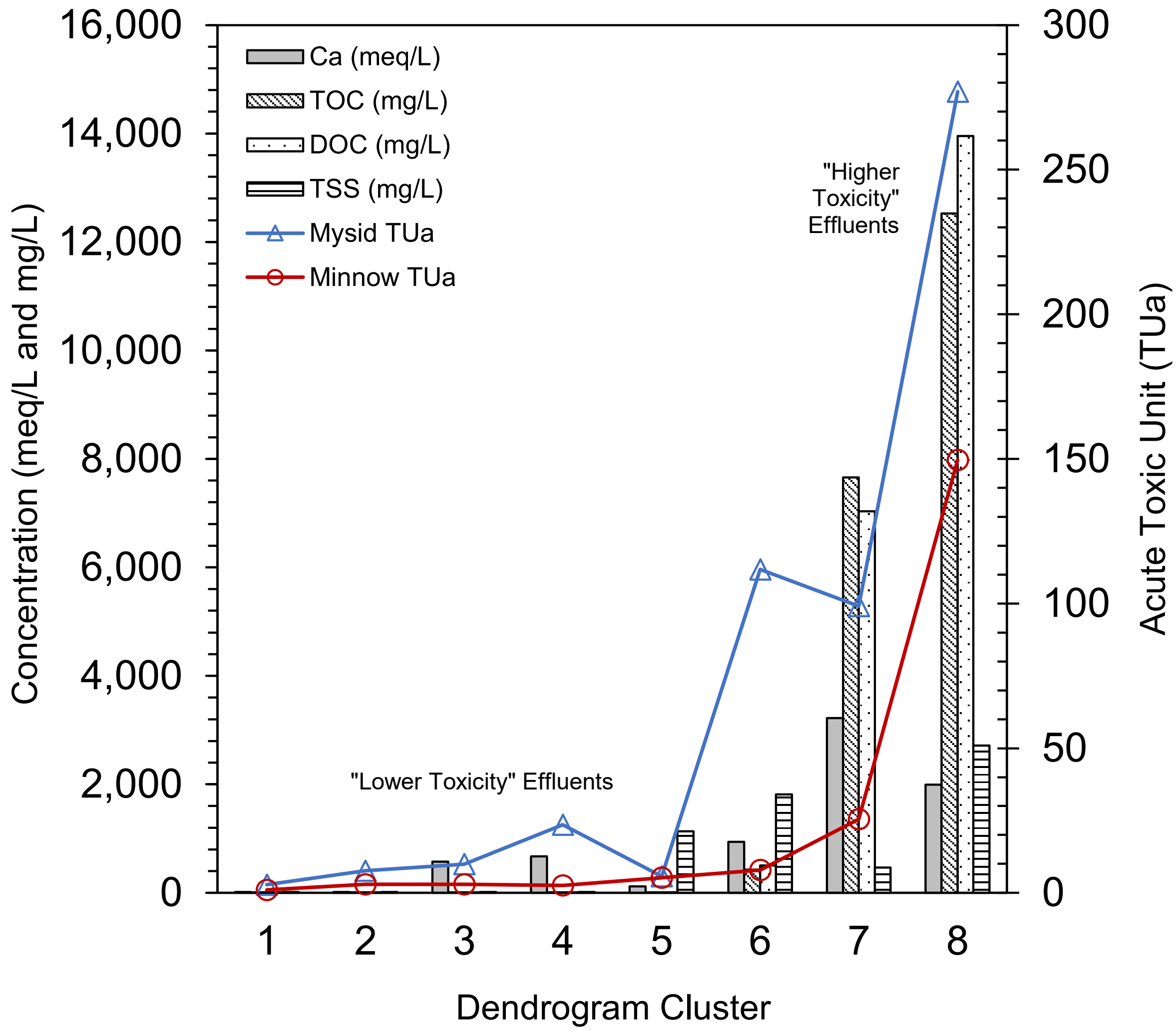


Figure 22. Combined bar chart and line graph of estimated Ca, TOC, DOC, TSS, and the acute toxic unit (TUa) for each dendrogram cluster. Clusters 1-5 consist of "lower toxicity" samples, whereas clusters 6-8 consist of "higher toxicity" samples.

7.3 Evaluation of Acute Toxicity at the CD

The study question "*What substances could potentially be associated with acute aquatic toxicity at the CD*?" was addressed by means of an ecological benchmark screening that aimed at identifying substances with the potential to contribute to toxicity at the CD. The ecological benchmark screening was conducted in two tiers. Tier 1 used conservative assumptions to identify substances present in TCW effluents with the potential to contribute to observed toxicity at the CD. Such substances may have been used in formulating TCW fluids or were picked up during downhole circulation. Tier 2 applied additional filters to the Tier 1 substances to further refine the list of potential substances and facilitate interpretation.

7.3.1 Tier 1 Ecological Benchmark Screening

Tier 1 of the ecological benchmark screening involved comparing exposure point concentrations (EPCs) for substances detected above the laboratory RL to established USEPA acute water quality criteria for saltwater (**Table A9**). The Tier 1 EPC was calculated as the maximum concentration of a substance (across all 27 samples evaluated), minus the arithmetic mean concentration in the LCSW samples for a given substance.

Substances with a USEPA published species-specific acute saltwater effects benchmark and/or aquatic life criterion were evaluated. Preferred ESVs were obtained from published literature data. Published acute saltwater aquatic life criteria were only used if reliable, species-specific effects benchmarks were not identified. The hierarchy of ESVs, listed in order of decreasing priority, was as follows:

1. Pillard et. al., 2000. Predicting the Toxicity of Major Ions in Seawater to Mysid Shrimp (*Mysidopsis bahia*), Sheepshead Minnow (*Cyprinodon variegatus*), and Inland Silverside Minnow (*Menidia beryllina*). The 48-h LC50s reported for Mysid and Inland silverside minnow were used.
2. USEPA. 2018a. National Recommended Water Quality Criteria - Aquatic Life Criteria Table: Saltwater Criterion Maximum Concentration (CMC) (Acute).
3. USEPA. 2018b. Region 4 Surface Water Screening Values for Hazardous Waste Sites: Saltwater (Acute).

The Toxicity Quotient (TQ) was used to assess the association between the EPC and the potential for acute toxicity at the CD. The TQ was calculated by: $TQ = \frac{EPC}{ESV}$. For substances where TQ<1.0 for species-specific ESVs, acute aquatic toxicity to Mysid and Inland silverside minnow is not probable. If there are no species-specific acute aquatic toxicity data, but the EPC is below the aquatic life criterion, then it may be concluded that the substance is likely not associated with acute toxicity to Mysid and Inland silverside minnow. Substances with a TQ≥1.0 pose the potential for adverse effects to aquatic biota at the CD and were carried forward for the Tier 2 refinement step.

Table 30 presents the results of the Tier 1 screening by listing substances with TQ≥1 and indicating the sample with the maximum EPC and the frequency at which that substance was detected. Eleven exceedances of the acute ESVs were observed. Specific substances include the bromide anion and several total and dissolved metals: As, Ca^{2+}, Cu, Se, and Zn. Samples containing substances with TQs ≥1.0 are nearly all TCW Category III effluents, including two gel samples. Sample TF74 accounts for 36% of the 11 exceedances identified. TQs range from 1.1 (Br) to 11.1 (dissolved Cu). It is important to note that Cu (and Se) were detected above the ESV in the LCSW.

Table 30. Tier 1 Acute Toxicity Screening at the Critical Effluent Dilution									
Substance	**TCW Effluent Max. (mg/L)**	**Mean LCSW (mg/L)**	**Tier 1 EPC (mg/L)**	**TCW Sample with Max.**	**Frequency of Detection**	**ESV (mg/L)**	**Number of TCW Samples > ESV**	**Detected Conc. in LCSW≥ESV?**	**Toxicity Quotient (Tier 1 EPC/ESV)**
As,T	0.181	0.07	0.111	III-SH87	2/27	0.069	2	No	1.6
Ca,T	2,370	270	2,099	III-TF74	27/27	Mysid=1,100	1	No	1.9
	2,370	270				Minnow=4,610			
Cu,T	0.0550	0.0257	0.0293	III-TF74	14/27	0.0056	14	**Yes**	5.2
Se,T	0.4730	0.1643	0.3087	III-YU91	15/27	0.29	9	**Yes**	1.1
Zn,T	0.608	0.018	0.59	I-PO80	8/27	0.092	5	No	6.4
As,D	0.288	0.07	0.218	*III-RU72	2/27	0.069	1	No	3.2
Ca,D	2,140	268	1,872	III-TF74	27/27	Mysid=1,100	1	No	1.7
	2,140	268				Minnow=4,610			
Cu,D	0.0532	0.0290	0.0242	III-JH68	7/27	0.0048	7	**Yes**	5.0
Se,D	0.47	0.18	0.28	*III-RU72	17/27	0.29	9	No	1.0
Zn,D	0.51	0.04	0.47	I-PO80	5/27	0.09	3	No	5.2
Br,T	8,850	36	8,814	III-TF74	27/27	7,990	1	No	1.1
Notes: TCW Category I effluent samples are denoted by a "I." TCW Category III samples are denoted by a "III." TCW Category III gel samples are denoted by a (*). "T" indicates total; "D" indicates dissolved.									

7.3.2 Tier 2 Refinement and Ecological Benchmark Screening

Tier 2 of the ecological benchmark screening refined the list of Tier 1 substances by estimating the upper confidence limit (UCL) of the mean for each substance across all samples. The USEPA software ProUCL (Ver. 5.1.002) was used to calculate the UCL; raw output is provided in **Appendix K**. The arithmetic mean concentration in LCSW was subtracted from the UCL to generate the refined Tier 2 EPC. A negative value indicates that the concentration in the sample was less than the arithmetic mean concentration in the LCSW samples. In this case, the EPC was represented by the concentration in the sample.

The Tier 2 refinements eliminated all substances with TQs ≥1.0 (**Table 31**). This suggests that there is low potential or adverse ecological effects at the CD, i.e., the edge of the 100-m mixing zone.

Table 31. Tier 2 Refinements of the Acute Toxicity Screening at the Critical Effluent Dilution.							
Substance	Units	C_{sample} (UCL)	UCL Type	Mean LCSW	Tier 2 EPC (UCL - Mean LCSW)[1]	ESV (mg/L)	Toxicity Quotient (Tier 2 EPC/ESV)
As, T	mg/L	0.021	KM H-UCL	0.07	-0.049	0.069	<1
Ca,T	mg/L	801.8	95% Chebyshev (Mean, Sd) UCL	270	531	1,100	<1
Br,T	mg/L	2,021	95% Chebyshev (Mean, Sd) UCL	36	1,985	7,990	<1
Cu,T	mg/L	0.0277	95% KM (t) UCL	0.026	0.002	0.0056	<1
Se,T	mg/L	0.268	95% KM (t) UCL	0.164	0.10	0.29	<1
Zn,T	mg/L	0.095	95% KM (t) UCL	0.018	0.077	0.092	<1
As,D	mg/L	0.11	97.5% KM (Chebyshev) UCL	0.07	0.04	0.069	<1
Ca,D	mg/L	757	95% Chebyshev (Mean, Sd) UCL	268	488	1,100	<1
Cu,D	mg/L	0.0315	95% KM (t) UCL	0.029	0.0025	0.0048	<1
Se,D	mg/L	0.29	95% KM (t) UCL	0.18	0.11	0.29	<1
Zn,D	mg/L	0.12	95% KM (t) UCL	0.04	0.08	0.09	<1
Notes: [1] The arithmetic mean concentration in LCSW was subtracted from the UCL to generate the refined EPC. A negative value indicates that Csample<CLCSW; in this case the Tier 2 EPC was defaulted to C_{sample}. [2] UCLs are computed across all TCW effluent samples. "T" indicates total; "D" indicates dissolved.							

7.3.3 Summary

The toxicity-composition connection evaluations presented in this section assessed whether patterns in acute toxicity are present, what some of the potential causes of toxicity are, and screened for substances that could potentially contribute to acute aquatic toxicity at the CD. The evaluations can be summarized as follows:

- TCW Category III effluents and a subset of TCW Category I effluents were the most toxic effluents sampled:
  - The ordination (**Figure 21**) suggests that patterns in the acute aquatic toxicity of TCW effluents are complex and cannot be reduced to a single factor, e.g., TCW Category I effluent versus TCW Category III effluent. Effluent toxicity may be partially attributable to organic substances in chemical products,
  - The cation Ca^{2+} appears to contribute to Mysid toxicity in TCW Category I effluents, whereas there is no association of Ca^{2+} with toxicity to the Inland silverside minnow.
- In TCW Category III effluents, DOC, TOC, and TSS appear to contribute to Mysid and Inland silverside minnow toxicity. Although organics are potentially influencing Mysid toxicity, the association with TOC and DOC is not as clear and other toxicants are likely playing a role.
- Patterns in aquatic toxicity reflected the varying influence of organics and inorganics, i.e., mixture toxicity. This also raises the possibility that synergistic or antagonistic interactions might occur between toxicants with a different toxicological mode of action.
- The lower toxicity effluents included TCW Category I and Category III brines. Eighty percent of these effluents had end-of-pipe treatment. Higher toxicity effluents were TCW Category III gels and TCW Category I and III effluents containing chemical additives. Ca^{2+} appears to be a primary determinant of Mysid

toxicity in the “lower toxicity” effluents, whereas Ca^{2+}, DOC, TOC, and TSS influence the “higher toxicity” effluents.

- None of the substances analyzed in the samples had concentrations that were found to be above available water quality criteria at the critical dilution. This suggests that the potential for toxicity at the CD from analyzed substances in the sampled TCW effluents is low.

8.0 Risk Assessment

This section considers the potential hazard and risk associated with TCW effluent discharges to the GOM aquatic environment. This section brings the individual lines of evidence together and discusses (1) potential causes and sources of aquatic toxicity, (2) patterns in acute aquatic toxicity, (3) discharge duration, and (4) potential for risk in the receiving water. The purpose of this discussion is to place the potential aquatic hazard and risk of TCW effluents into context. Where applicable, study limitations and their potential effect on the assessment are noted.

8.1 Potential Toxicants and Sources of Aquatic Hazard

This sub-section addresses potential toxicants in TCW effluents and sources of these toxicants. General fate processes are discussed where they may support the observed associations between toxicants and acute toxicity.

8.1.1 Potential Toxicants in TCW Effluents

The JIP study evaluations suggest that TCW effluents are complex and that a mixture of inorganic and organic substances is potentially contributing to aquatic hazard. Because exposures of Mysid and the Inland silverside minnow to TCW effluents involve more than one type of potential toxicant, there is the possibility that synergistic or antagonistic interactions might have occurred. The net result of these interactions was reflected in the WET testing results.

Potential toxicants identified in TCW effluents were Ca^{2+}, DOC, TOC, and TSS. Apparent Ca^{2+}- related effects towards the Mysid were observed in TCW Category I effluents and “lower toxicity” TCW effluents that received end-of-pipe treatment. The effects of Ca^{2+} towards the Mysid may, however, be obscured in the “higher toxicity” TCW Category I and III effluents containing elevated DOC, TOC, and TSS. The Inland silverside minnow appears to be more tolerant of ions than the Mysid. Potential toxicants for the Inland silverside minnow are TOC, DOC, and TSS.

Other substances may have also contributed to aquatic toxicity. For example, the loss of 48-h toxicity to the Mysid in the aged TCW effluent sample AU71 after 24 days suggests that the potential toxicant was either a volatile component, biodegraded, or precipitated from solution (**Table 20, Figure 15**). The loss of acute Mysid toxicity is also observed in PW effluents for reasons potentially related to volatilization or precipitation (Sauer et al., 1997). Organic cationic surfactants such as the QACs may also be present in TCW effluents and could act as potential toxicants. The QACs will sorb with a wide range of suspended matter in wastewater, e.g., biomass and inorganic matter; sorption is likely the most important fate process for the QACs in aerobic environments (Ying, 1999). Assuming QACs were contributing to toxicity, sorption may partially account for the observed association between TSS and acute toxicity.

8.1.2 Potential Sources of Toxicants

The primary sources of potential toxicants in TCW effluents are brines containing Ca^{2+}, e.g., $CaCl_2$, $CaBr_2$, and chemical additives that contain organic substances. Products that contain these organic substances are used as cationic surfactants, lytic biocides, and non-emulsifiers. Contributions to toxicity from substances picked up downhole cannot be excluded.

8.2 Patterns in Acute Aquatic Toxicity

The JIP study evaluations characterized differences in species sensitivity, variability in acute toxicity, and compared the toxicity of TCW and PW effluents.

8.2.1 Species Sensitivity

There were no differences between the 48-h LC50s reported for TCW Category I and TCW Category III effluents. Hence, the aquatic hazard of both effluent types is deemed to be equal. The Mysid was, however, more sensitive than the Inland silverside minnow to both TCW Category I and TCW Category III effluents. The greater sensitivity of the Mysid has also been observed in ecotoxicological evaluations of onshore and offshore oil and gas facility effluents (Hughes et al., 2021) and offshore PW effluents (Sauer et al., 1997). It is possible that the greater sensitivity of the Mysid is due to the presence of ions and biocides in the effluent. Anecdotally, Mysids are more sensitive to effluents containing metals and biocides, whereas Minnows are more sensitive to surfactants (EEUSA, personal communication, 2020).

8.2.2 Variability in Acute Toxicity and Potential Causes

The acute toxicity of TCW effluents was highly variable, with acute LC50s ranging from 0.2 to >50% effluent for the Inland silverside minnow and from 0.05 to 35% effluent for the Mysid. This variability appears to be influenced by end-of-pipe treatment, well operation type, stage of the discharge, brine type, and the chemical additives used for each well operation. The end-of-pipe treatment of organics and suspended particulates improved effluent quality, especially for the Inland silverside minnow. Most of the least toxic effluents were associated with long-term completion flow-back operations with end of pipe treatment, whereas the most toxic effluents were associated with well treatment and workover operations. The higher toxicity effluents were gels and effluents containing several chemical additives.

8.2.3 Comparison with Produced Water

Based on the results of this study and literature data on produced water toxicity, the toxicity of TCW effluents was not significantly different than the toxicity of GOM PW to Mysids (**Figure 13**). Both TCW and PW effluents displayed a wide variability in toxicity to Mysids, e.g., outliers occur from 10-35% effluent, with extreme outliers at concentrations >35% effluent. As previously discussed, the estimated total volume of TCW discharges during 2019-2020 was 0.01% of the volume of produced water discharges (**Table 4**) during that period.

Karman and Smit (2019) discuss the use of discharge volume and WET data in assessing the risk of produced water discharges. They conclude that environmental risk from a low-volume produced water discharge has a high probability of being adequately controlled. Considering the low volume of individual TCW discharges, and the small collective volume of TCW discharges compared to produced water discharges, it is not unreasonable to conclude that TCW effluents are unlikely to present a greater risk to the receiving environment than PW effluents. As pointed out by Karman and Smit (2019), studies have indicated that there is a low risk of widespread ecological impacts from produced water discharges, which suggests that that TCW discharges, being smaller in volume than, and similar in toxicity to produced water discharges, represent a low environmental risk.

8.3 Effects of Discharge Duration

Since most (75%) of the TCW effluent discharges sampled were ≤2-h in duration, a 48-h WET test exposure may overestimate the potential for toxicity. The supplemental WET test results demonstrated how exposure duration can influence acute toxicity. As discussed by Gissi et al. (2021), a relevant exposure duration will better inform assessments of aquatic hazard associated with oil and gas effluents in offshore marine habitats.

Similar to the Gissi et al. (2021) study, the supplemental WET test results suggested that the potential for toxicity is a function of the exposure duration. For most of the TCW effluents tested, acute Inland silverside minnow and Mysid toxicity was reduced by shortening the exposure duration to 2-h. This indicated that substances with an uptake rate >2-h are influencing toxicity. In a few instances, no improvement in toxicity with a 2-h exposure was observed, suggesting that exposure to toxicants taken up quickly contributed to acute toxicity.

As discussed by Gissi et al. (2021), short-duration toxicity tests are appropriate to evaluate the aquatic hazard of PW effluents in offshore marine waters. Data comparing differences between continuous 48-h and short-term 2-h exposures of marine organisms to offshore PW effluents are, however, limited. Hence, the lack of comparable data is a limitation of the supplemental WET testing conducted as part of the JIP study.

8.4 Potential for Acute Toxicity in the Receiving Water

There are concerns that the discharge of hydraulic fracturing−flowback and produced water effluents may adversely affect marine habitats (Zhong et al., 2021). Based on the JIP study results and studies of PW effluents (Gissi et al., 2021), the potential for adverse effects in the receiving water is influenced by exposure duration, type of potential toxicant and concentration, end-of-pipe treatment, and the processes of mixing and assimilation. These factors work to limit the potential for aquatic toxicity. An ecological benchmark screening analysis based on measured concentrations showed that none of the substances analyzed would pose potential hazard to aquatic biota at the edge of the mixing zone.

9.0 Conclusions

This study characterized 28 TCW samples and assessed the potential for TCW effluent characteristics to contribute to acute whole effluent toxicity. The study provides a better understanding of how TCW discharges to the GOM are managed and of TCW effluent characteristics, their aquatic toxicity, and substances that potentially contribute to this toxicity. Study conclusions are summarized below, organized by the study questions posed in the Introduction section:

- **How are TCW discharges typically handled and their discharge to GOM surface waters managed?** TCW discharges were generally made through a pipe or hose. Exceptions to this practice included four cases where the discharge was made through a diffuser. Some effluents were subjected to end-of-pipe treatments such as granular activated carbon (GAC) or filtration. One discharge outfall was at the seafloor. The remaining outfalls were located between 27 m above to 46 m below the sea surface. The median discharge duration and volume were 1 hour and 473 bbl, respectively.

  TCW discharges represent a small input to the GOM. An order-of-magnitude estimate of the volume of all TCW discharges in 2019-2021 was 0.01% of the volume of produced water discharges during the same period.

- **How toxic are TCW discharges towards marine biota?** Acute 48-h WET testing was conducted with Inland silverside minnow and Mysid. The acute toxicity of TCW effluents was highly variable, with acute LC50s ranging from 0.2 to >50% effluent for the Inland silverside minnow and from 0.05 to 35% effluent for the Mysid. This variability appears to be influenced by end-of-pipe treatment, well operation type, stage of the discharge, brine type, and the chemical additives used for each well operation. A subset of TCW Category III effluents that formed gels and a TCW Category I effluent with multiple chemical additives were the most toxic effluents collected. Although TCW Category I and III effluent are equally toxic, the Mysid was generally more sensitive to TCW effluents than was the Inland silverside minnow.

  The lowest NOEC observed in 48-h WET tests was greater than the critical dilution (CD) for a majority of both TCW Category I (7 of 13 samples) and TCW Category III (9 of 15 samples). Recognizing that the duration of the median TCW discharge was 1-h, a series of toxicity tests using 2-h exposure was performed. These tests showed that toxicity for 2-h exposures was generally less than toxicity in 48-h exposure tests. This suggests that, since TCW discharges are of short duration, the comparison of 48-h NOEC with critical dilutions as an indicator of potential for acute toxicity has a high degree of conservatism.

  Based on a comparison of JIP study and literature data, there were no significant differences in the acute toxicities of TCW and PW effluents to the Mysid. Thus, as TCW effluents are similar in potency and variability to but have demonstrably smaller and shorter duration discharges than PW effluents, TCW effluents are unlikely to present a greater risk to the receiving environment than PW effluents.

- **What is the typical chemical composition of discharged TCW effluents? How variable is the chemical composition of a discharge?** Of the four categories of fluids identified during planning for this study, only TCW Category I (brine-based completion fluids) and Category III (workover and treatment fluids) were sampled during the study period. TCW Category I and TCW Category III fluids are composed of chloride and bromide brines and may contain chemical products comprised of organic substances. TCW Category III fluids contained more added chemical products than did TCW Category I fluids. Substantial variability in effluent salinity and in effluent concentrations of bromide and calcium was observed among samples collected at different times during a discharge.

- **What can be said about the cause of toxicity? Can general toxicity-composition connections be made?** Multiple lines of evidence were used to identify individual substances and classes of substances potentially contributing to toxicity, and potential sources of these substances. Toxicity-composition evaluations of TCW effluents can be summarized as follows:
  - Ionic composition, specifically Ca^{2+} concentration, appeared to be associated with the toxicity of TCW Category 1 effluents. Toxicity to Inland silverside minnow toxicity did not appear to be influenced by Ca^{2+} to the same extent as toxicity to the Mysid.
  - Organics (based on the DOC and TOC concentrations used as surrogate for organic chemical products or organics picked up downhole) and TSS appeared to contribute to Mysid and Inland silverside minnow toxicity in most TCW Category III effluents.
  - Chemical products potentially present in TCW effluents contain primarily organic substances that could potentially contribute to aquatic toxicity in the TCW effluent samples.
- **What are the estimated concentrations of substances in GOM surface waters at the critical effluent dilution (CD), i.e., the concentration predicted to exist in the effluent plume at the edge of the 100-m mixing zone?** The composition of effluents diluted to the critical dilution applicable to discharges sampled for this study (0.03 – 1.25% effluent) mainly reflected the composition of the laboratory control seawater (LCSW) used as a diluent. Components displaying highly variable concentrations likely reflected contributions from the effluent, including substances used in formulating the fluids and substances picked up downhole. For TCW Category I effluents, these components included bromide, DOC, TOC zinc, thallium, and barium. For TCW Category III effluents, these components included bromide, DOC, TOC, thallium, arsenic, and cadmium.
- **What substances are currently used in TCW fluids? What are their general aquatic hazard characteristics?** Substances used in TCW fluids include $CaCl_2$ and $CaBr_2$ brines and chemical products. Participants reported 87 chemical products that were used in formulating TCW fluids discharged to GOM surface water. Substances and aquatic hazard characteristics can be summarized as follows:
  - Brine components can contribute to aquatic hazard by causing ionic imbalances.
  - Of the 87 chemical products reported, approximately 85% were identified as "Not Assessed." For chemical products where GHS classification information was not provided in SDS Section 2, no aquatic hazard assessment could be made, and no conclusion about potential for aquatic toxicity is implied.

  - Among the minority of chemical products whose SDS presented GHS classifications, there were products in each of the three GHS acute aquatic toxicity categories: GHC Category 1 – Very toxic; GHS Category 2 – Toxic; and GHS Category 3 – Harmful. For most of the chemical products, no GHS data were presented in SDS, and no assessment of hazard was conducted.
  - The most frequently used chemical products in TCW Category I effluents were corrosion inhibitors, defoamers, oxygen scavengers, and non-emulsifiers. The most frequently used products in TCW Category III effluents are acids, biocides, fluid additives, breakers, pH control, and non-emulsifiers.
  - TCW Category III effluents contained more added chemical products than did TCW Category I effluents, including those with a GHS acute aquatic toxicity classification. The chemical functionalities of these products are electrophilic and lytic biocides, cationic and non-ionic surfactants, breakers, corrosion inhibitors, non-emulsifiers, and defoamers.
  - Safety Data Sheets did not indicate that any product used to formulate fluids contained priority pollutant metals. No priority pollutant organics were detected in any effluent sample diluted to the CD.
- **What substances could potentially be associated with acute aquatic toxicity at the CD?** A 2-tier screening of measured concentrations of substances against available acute water quality criteria was conducted. The screening did not identify any substance with a concentration greater than (or equal to) the water quality criteria at the CD.

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Appendix Tables

Table A1. TCW Effluent Sample Area, Block, and API Well No.

Sample ID	Area	Block	API Well No.
HV63	Mississippi Canyon	502AC	608174097300
JK70	Viosca Knoll	999	608164046000
RD67	Walker Ridge	425	608124008102
RU61	Green Canyon	640	608114072600
XP62	South Timbalier	37	177154128600
NY50	Green Canyon	825	608114069601
LC54	Mississippi Canyon	809	608174112602
AU71	Mississippi Canyon	807	608174047905
YO64	Mississippi Canyon	807	608174047905
FP89	Mississippi Canyon	519	608174141100
ZG57	Walker Ridge	718	608124012701
GQ67	Mississippi Canyon	392	608174133401
YU91	Mississippi Canyon	520	608174139900
LX98	Mississippi Canyon	807	608174048702
IS88	Mississippi Canyon	807	608174048702
RU72	Ewing Bank	873	608105004901
IH80[1]	Mississippi Canyon	809	608174109102
BT52	Green Canyon	338	608114035403
SH87	Mississippi Canyon	807	608174048702
EP57[2]	Walker Ridge	758	608124012500
TR84[2]	Walker Ridge	758	608124012500
RC74[2]	Walker Ridge	508	608124012900
OD76[2]	Walker Ridge	508	608124012900
TF74[2]	Walker Ridge	508	608124012900
QK91	Walker Ridge	718	608124013202
DO57	Viosca Knoll	999	608124005600
PO80	East Breaks	157	608044015100
JH68	Ship Shoal	349	177124155200
UP92	Walker Ridge	508	608124010400

Notes:

[1] Sample IH80 was not discharged to surface water; [2] Samples were collected at a single structure and at different times during a single discharge: structure 18 (samples EP57 and TR84) and structure 19 (samples RC74, OD76, and TF74).

Table A2. TCW Effluent Discharge Characteristics

TCW Sample	HV63	JK70	RD67	RU61	XP62	NY50
Sample Collection Date	12/19/2019	11/8/2019	11/24/2019	1/2/2020	1/21/2020	2/8/2020
Job/Operation Type	Completion / Zonal isolation	Completion	Workover	Completion	Completion	Completion
TCW Fluid Category	I	III	I	I	I	III
TCW Fluid Description	CaCl2 Brine (10.5 ppg)	CaBr2 Brine (12.1 ppg)	CaCl2 Brine (11.6 ppg)	CaBr2 completion brine (12.1 ppg); KCl brine; HCl/Acetic acid treatment	CaCl2 Brine (10.5 ppg)	CaCl2 Brine (8.4 - 11.5 ppg); CaCl2-CaBr2 Brine 11-15 PPG
Time Discharge Commenced	1500	0650	2030	0015	0750	0540
Duration of Discharge (hours)	1.25	0.45	1.50	0.08	0.03	2.33
Pipe Diameter (inches)	18	18	12	4	6	8
Total Discharge Volume (bbl)	965	272	1,476	100	10	891
Discharge Rate (bbl/day)	18,528	14,400	23,616	28,800	7,200	12,830
Water Column Depth (ft.)	2,300[4]	4,119	8,832	4,250	62	4,976
Depth of Discharge (ft.) Relative to Water Surface	Not Reported	-15	-35	+50	+90	-12
Depth Difference (End-of-Pipe and Seafloor) (meters)	710[4]	1,251	2,681	1,311	46	1,513
CD (% Effluent)[5]	0.44	0.39	0.48	0.55	0.19	0.39
Is there Wastewater Treatment Before Discharge?	No	No	No	No	No	No.

Table A2. TCW Effluent Discharge Characteristics

TCW Sample	LC54	AU71	YO64[1]	FP89	ZG57	GQ67
Sample Collection Date	2/15/2020	3/14/2020	3/14/2020	3/18/2020	2/27/2020	4/24/2020
Job/Operation Type	Completion	Completion	Completion was open-hole with no fracturing	Treatment / Frac. job	Completion; Flow-back	Workover for plug/abandon. Cleaning Spacer/Soap Pill
TCW Fluid Category	I	I	III,gel	III	I	III
TCW Fluid Description	NaCl Brine (8.6 ppg)	NaCl brine; (9.5 ppg)	Gelled spacer between brines of differing weights.	Completion; Fracturing Fluid (Linear Gel)	CaBr2 completion fluid w/cross-linker	Workover Spacer. 12.4ppg NaBr2 to 12.6 ppg completion CaBr2 brine.
Time Discharge Commenced	0600	1300	1300	0528	Ongoing discharge; sample collected at 0730	1940; 2030
Duration of Discharge (hours)	0.08	0.40	0.40	1.00	72 based on the COC; The total length of the flowback was 31 days. The Study participant believed that most TCW effluents discharged within the first 24h.	1.67
Pipe Diameter (inches)	16	6.765	6.765	18	18	16
Total Discharge Volume (bbl)	320	189	189	473	2,534 bbls over the 31-day period; most of this volume was discharged in the first 2 days.	118
Discharge Rate (bbl/day)	92,160	11,340	11,340	11,352	A diffuser "duck bill" system is used. CORMIX modeling was conducted specifically for the platform. Discharge characteristics were not reported. The platform-specific critical effluent dilution of 0.291% was used.	1,699
Water Column Depth (ft.)	3,650	2,945	2,945	6,595		7,210
Depth of Discharge (ft.) Relative to Water Surface	-27	-12	-12	-36		-36
Depth Difference (End-of-Pipe and Seafloor) (meters)	1,104	894	894	1,999		2,208
CD (% Effluent)[5]	1.25	0.39	0.39	0.39	0.291	0.1
Is there Wastewater Treatment Before Discharge?	No	No	No	No	Yes. TCW fluids are sent through a treatment package of surge tanks; a weir box; solids filters; absorption media; and carbon vessels.	No.

Table A2. TCW Effluent Discharge Characteristics

TCW Sample	**YU91[1]**	**LX98**	**IS88**	**RU72[2]**	**IH80[3]**	**BT52**
Sample Collection Date	4/27/2020	4/20/2020	4/19/2020	4/30/2020	4/23/2020	5/1/2020
Job/Operation Type	Treatment; Frac. Job	Workover; Coiled tubing clean out-related fluid	Workover	Treatment	Treatment / Wellbore Cleaning spacer	Treatment
TCW Fluid Category	III, gel	III	III	III	III (not discharged to surface water)	III
TCW Fluid Description	A Completion/Cat III with 78% CaBr2 brine; lnear gel w/cross-linkers.Sample had a "Jell-O" like consistency.	Category III Workover - Packer Fluid – 8.5 ppg 2% KCl. According to Operator, the fluid has been present in the well for 19 years and was stored in a pit before discharge to surface water.	Packer fluid	Category III KCl brine frac-pack w/proppant. Linear gel. Proppant beads were identified in the sample container at a thickness of approx. 1-2 inches on bottom of container.	12 ppg CaBr2 (78% Sol.) Spacer chemicals in the sample include well cleaner. A separate phase was observed in the laboratory after settling for 24-h.	Category III frac. fluid brine / seawater; linear gel w/ breakers / cross-linkers.
Time Discharge Commenced	1105 (sample collected)	2204	0111	1315	Sample Not discharged to surface water. Discharge information not applicable.	2125
Duration of Discharge (hours)	1.50	0.40	0.18	0.42		1.08
Pipe Diameter (inches)	The discharge is through a 16" pipe that is flush with the underside of the ship's hull.	14	14	16		3
Total Discharge Volume (bbl)	498	543	543	118		256
Discharge Rate (bbl/day)	7,968	32,544	47,520	6,797		5,673
Water Column Depth (ft.)	6,700	2,955	2,955	773		3,325
Depth of Discharge (ft.) Relative to Water Surface	The current draft of the ship is the depth below the waterline at which the fluids are discharged (-36').	-15	-15	-15		+20
Depth Difference (End-of-Pipe and Seafloor) (meters)	2,031	896	896	231		1,020
CD (% Effluent)[5]	0.41	0.56	0.65	0.36		0.23
Is there Wastewater Treatment Before Discharge?	No.	No.	No	No.		No.

Table A2. TCW Effluent Discharge Characteristics

TCW Sample	SH87	EP57 - Begin	TR84 - Middle	RC74 - Begin	OD76 - Middle[1]	TF74 - End
Sample Collection Date	5/12/2020	5/10/2020	5/12/2020	5.24.20	5.25.20	5.25.20
Job/Operation Type	Treatment / Frac. job reversal	New well; Completion; Flow-back	New well; Completion; Flow-back	Treatment / Single Frac. Job; frac fluid reverse out	Treatment / Frac. Job; frac fluid reverse out	Treatment / Frac. Job; frac fluid reverse out
TCW Fluid Category	III	I	I	III	III, gel	III
TCW Fluid Description	Frac-fluid without radioactive tracers w/proppant	Operator indicated that TCW fluid use would be similar to ZG57: CaBr2 and CaBr2 completion fluid w/cross-linker	Operator indicated that TCW fluid use would be similar to ZG57: CaBr2 and CaBr2 completion fluid w/cross-linker	Frac. Gel with some Category III CaCl2 brine. No radioactive tracer.	Gel/Category III CaCl2 brine; Operator indicated that the sample may contain some proppant. No radioactive tracer.	The sample consists of a "cleaned-up" Category III CaCl2 brine with a small amount of proppant. No radioactive tracer.
Time Discharge Commenced	0957	1530	1530	2317 (sample collected at 2320); discharge ended at 0206	2317 (sample collected at 0124); discharge ended at 0206	2317 (sample collected at 0201); discharge ended at 0206
Duration of Discharge (hours)	3.38	1.42	38.6	0.05	2.10	0.61
Pipe Diameter (inches)	14	18	18	16	16	16
Total Discharge Volume (bbl)	568	132	2,087	30	1,211	1,577
Discharge Rate (bbl/day)	4,029	2,236	3,130	520	14,063	27,360
Water Column Depth (ft.)	2,940	A diffuser "duck bill" system is used. CORMIX modeling was conducted specifically for the platform. Discharge characteristics were not reported.	A diffuser "duck bill" system is used. CORMIX modeling was conducted specifically for the platform. Discharge characteristics were not reported.	9,558	9,558	9,558
Depth of Discharge (ft.) Relative to Water Surface	-12			-40	-40	-40
Depth Difference (End-of-Pipe and Seafloor) (meters)	892			2,901	2,901	2,901
CD (% Effluent)[5]	0.33	0.16	0.21	0.05	0.39	0.56
Is there Wastewater Treatment Before Discharge?	No.	Yes. A treatment package of surge tanks; a weir box; solids filters; absorption media; and granular activated carbon (GAC) vessels.	A treatment package of surge tanks; weir box; solids filters; absorption media; and GAC vessels. The GAC filters were "spent" when sample TCW-18B was collected.	No	No	No

Table A2. TCW Effluent Discharge Characteristics

TCW Sample	QK91	DO57	PO80	JH68	UP92
Sample Collection Date	2/18/2021	4/10/2021		4/13/2021	4/13/2021
Job/Operation Type	Platform JSN PN005 is a new well completion; long-term Flow-back	New well completion;long term Flow-back	Completion	Treatment w/acid; acids are not discharged to surface water.	Workover / Abandonment (open-water tubing pull); this is a deep-water discharge
TCW Fluid Category	I	I	I	III	I
TCW Fluid Description	CaBr2 brine; chemical products are used: corrosion inhibitor (dosage 0.18 gallons per hour [gph]), H2S scavenger (0.03 gph), defoamer (2.1 gph), and emulsion breaker (6.5 gph).	CaBr2 brine; chemical products are used: emulsion breaker; antifoamer; corrosion inhibitor; and scavenger.	CaBr2 brine; no chemical products added. The brine originated from behind the production annulus. The returned brine was a mixture of brine from the original completion and what was used by the drilling rig for the well kill.	A brine was used as a base fluid; chemical products used (<5% of total volume going downhole). Acetic and hydrofluoric acids; pH control; corrosion inhibitor: deemulsifier: surfactants: defoamers: biocides.	An 11.8 ppg brine (CaCl/CaBr). Chemical products potentially present (soap pills and possibly hydrate inhibition while bull heading; corrosion inhibitor; H2S scavenger)
Time Discharge Commenced	0550	1105	1330	2120	0705
Duration of Discharge (hours)	96; measured from the start time to the time the sample was collected. The discharge is ongoing.	48; measured from the start time to the time the sample was collected. The discharge is ongoing.	0.5	0.67	1.0
Pipe Diameter (inches)	18	18	16	2	5.375
Total Discharge Volume (bbl)	1,096	600	250	184	71
Discharge Rate (bbl/day)	274	300	11,995	6,624	1,704
Water Column Depth (ft.)	A diffuser "duck bill" system is used. CORMIX modeling was conducted specifically for the platform. Discharge characteristics were not reported.	A diffuser "duck bill" system is used. CORMIX modeling was conducted specifically for the platform. Discharge characteristics were not reported.	Not provided by Operator	372	9,558
Depth of Discharge (ft.) Relative to Water Surface			Not provided by Operator	-20	9,558 (Operator indicated a seafloor discharge)
Depth Difference (End-of-Pipe and Seafloor) (meters)			313 (provided by Operator)	107	2,941
CD (% Effluent)[5]	0.291	0.291	0.39	0.24	0.35
Is there Wastewater Treatment Before Discharge?	Yes. A treatment package of surge tanks; a weir box; solids filters; absorption media; and granular activated carbon (GAC) vessels.	Yes. A treatment package of surge tanks; a weir box; solids filters; absorption media; and granular activated carbon (GAC) vessels.	No	Yes. All effluents were sent through filter/carbon treatment systems. GAC filtration (for naphthalene removal) and sock filters for TSS.	Yes. Tank storage; filtration (shakers/filter pod - to keep larger debris out of CT unit)

Notes:
%; percent
CaBr; calcium bromide
NaCl; sodium chloride
ppg; pounds per gallon
TCW; treatment, completion, and workover
[1]. TCW Category III gel samples that require pre-mixing before conducting the standard acute WET test.
[2]. TCW Category III samples that require pre-preparation before WET testing including the removal of proppant beads.
[3]. TCW Category III samples that require an alternative toxicity test method to address the presence of a separate phase (Water Accommodated Fraction
[4] Identified as 2,330' (implied feet) on the WET test sample chain of custody.
[5] CD; critical effluent dilution identified using the produced water tables identified in the USEPA Region 6 GP.

Table A3. Substances Potentially in Brines and Chemical Additives by TCW Effluent Sample

TCW Sample	TCW Cat. Type	Substances Potentially Present[1]
HV63	I	$CaCl_2$ brine 10.5 ppg. Operator indicated that no chemical additives were used.
JK70	III	$CaBr_2$ brine; Misc. Amines/Quaternary Ammonium Salts; tributyl phosphate; isopropyl alcohol; glutaraldehyde; ethoxylated alcohol; ethylene glycol monobutyl ether; (2-(2-Methoxy methyl ethoxy)Methylethoxy) Propanol; Hydroxy ethyl cellulose; Xanthan Gum; Benzenesulfonic acid, C10-16-alkyl derivatives, compounds with 2-Propanamine; Dodecylbenzenesulfonic acid; 2-Ethylhexanol
RD67	I	$CaCl_2$ brine; $CaBr_2$ brine; tributyl phosphate; isopropanol; ammonium salt; quaternary ammonium compounds; ethylene glycol monobutyl ether; xylene; methanol
RU61	I	$CaBr_2$ brine 12.1 ppg; KCl brine; acetic acid; hydrochloric acid; isopropanol; ammonium salt; quaternary ammonium compounds; xylene; methanol; dipropylene glycol monomethyl ether
XP62	I	$CaCl_2$ brine 8.4 - 11.6 ppg
NY50	III	$CaCl_2$ brine, $CaBr_2$ brine; isopropanol; ethylene glycol monobutyl ether; ammonium salt; quaternary ammonium compounds; xylene; methanol
LC54	I	Glutaraldehyde; Methanol; isopropanol; ethylene glycol monobutyl ether; ammonium salt; quaternary ammonium compounds; xylene; methanol; NaCl
AU71	I	NaCl; ethylene glycol monobutyl ether; hydrotreated light petroleum distillate; D-Glucopyranose, oligomeric, decyl octyl glycosides; orange, sweet, extract; sodium hydroxide; isopropanol; ammonium salt; quaternary ammonium compounds; xylene; methanol; dipropylene glycol monomethyl ether; didecyldimethylammonium chloride (DDAC); ethyl alcohol; methyl alcohol
YO64	III,gel	Ethylene glycol monobutyl ether; hydrotreated light petroleum distillate; D-Glucopyranose, oligomeric, decyl octyl glycosides; orange, sweet, extract; sodium hydroxide; isopropanol; ammonium salt; quaternary ammonium compounds; xylene; methanol; dipropylene glycol monomethyl ether; DDAC; ethyl alcohol; methyl alcohol; NaCl
FP89	III	SeaQuest Linear Gel; tetrakis(hydroxymethyl)phosphonium sulphate(2:1); Hemicellulase enzyme; Cocamidopropyl betaine; Glycol ether; Guar gum; cationic polymer in solution; Ethoxylated alcohol; potassium carbonate; Hydrochloric acid; Acetic anhydride; Hydrofluoric acid; Xylene; Acetic acid; 2-Butoxyethanol
ZG57	I	$CaBr_2$ brine; kerosene; naphthalene; ethylbenzene; methanol; quaternary ammonium compound; fatty acid-amine condensate; ethylene glycol; 2-mercaptoethanol; oxyalkylate; diethanolamine; heavy aromatic naphtha; naphthalene; substituted alkylamine; 2-Butoxyethanol; sodium molybdate; inorganic salt; proprietary polyol compound; proprietary amine compound; proprietary diol compound 1&2; proprietary lactam compound;
GQ67	III	2.4 ppg $NaBr_2$ brine and 12.6ppg completion $CaBr_2$ brine; Tetraclean 107 (alcohols C9-11 ethoxylated, proprietary organic alcohol)
YU91	III, gel	Sodium carbonate; hydrochloric acid; acetic anhydride; hydrofluoric acid; acetic acid; NaCl brine 8.4-10 ppg; SeaQuest Linear Gel - Crosslinked ulexite; Water Frac H
LX98	III	Ammonium bisulfite; KCl brine
IS88	III	Ammonium bisulfite; sodium hydroxide; DDAC; ethyl alcohol; methyl alcohol
RU72	III	KCl brine, proppant beads present in sample (no SDS provided), Operator indicated a linear gel was present (no SDS provided).
BT52	III	No SDSs provided.
SH87	III	NaCl; Chlorous acid, sodium salt; sodium chloride; borate salts; dipropylene glycol monomethyl ether; cobalt acetate; ethylene glycol; Silicon Dioxide, (amorphous as glass); Mullite; Silica Crystalline-Cristobalite; chlorous acid, sodium salt; sodium chloride
EP57	I	See TCW-10; Operator indicated that the job type and chemical use is similar.
TR84	I	See TCW-10; Operator indicated that the job type and chemical use is similar.
RC74	III	$CaCl_2$ brine; Borate salts; dipropylene glycol monomethyl ether; diesel; ethylene glycol; methanol; ceramic materials and wares, chemicals (proppant); sodium hydroxide; T-803; soy methyl ester; oil tracer; chlorous acid; sodium salt; NaCl
OD76	III,gel	
TF74	III	

Table A3. Substances Potentially in Brines and Chemical Additives by TCW Effluent Sample

TCW Sample	TCW Cat. Type	Substances Potentially Present
QK91	I	$CaBr_2$ brine; kerosene; naphthalene; ethylbenzene; methanol; QAC; Fatty acid-amine condensate; Ethylene Glycol; 2-Mercaptoethanol;Oxyalkylate; Diethanolamine; Heavy Aromatic Naphtha; Naphthalene; proprietary substituted alkylamine; 2-butoxyethanol
DO57	I	$CaBr_2$ brine; kerosene; naphthalene; ethylbenzene; methanol; QAC; Fatty acid-amine condensate; Ethylene Glycol; 2-Mercaptoethanol;Oxyalkylate; Diethanolamine; Heavy Aromatic Naphtha; Naphthalene; proprietary substituted alkylamine; 2-butoxyethanol
PO80	I	$CaBr_2$ base brine; no chemical products added
JH68	III	Base brine (type not identified); Ammonium chloride; hydrochloric acid; 2,2 Dibromo-3-nitrilopropionamide; 2-Monobromo-3-nitrilopropionamide;2-Bromo-2-nitro-1,3-propanediol; Acetic anhydride; Acetic acid; Citric acid; potassium iodide; sodium carbonate; hydroxyacetic acid; and Hydrofluoric acid
UP92	I	11.8 ppg CaCl/CaBr brine; Ethanolamine; Xanthum gum;Dipropylene glycol monomethyl ether; 2-Methoxy-1-propanol; Triethylene glycol, monobutyl ether; Alcohol ethoxylates; Benzenesulfonic acid, C10-16-alkyl derivs, compds. with 2-propanamine; Benzenesulfonic acid, C10-16-alkyl derivatives; 2-Ethylhexanol; Substituted Alkylamine; Ethanolamine; Methyl alcohol; Diethanolamine; Hexadecene; and Octadecene

Notes:

[1] Safety Data Sheets did not indicate that any product used to formulate fluids contained priority pollutant metals. No priority pollutant organic (16 polycyclic aromatic hydrocarbons [PAHs]) was detected in any effluent sample diluted to the critical effluent dilution (CD).

Table A4. Laboratory Analytical Parameters

Water Quality Parameters	Sample Type	Directly Measured or Estimated?
Total Dissolved Solids (Residue, Filterable)	Critical effluent dilution	Direct measurement
pH	Undiluted (100%) effluent	Direct measurement
Dissolved Organic Carbon (DOC)	Critical effluent dilution	Direct measurement
Alkalinity, Total (As CaCO3)	Critical effluent dilution / Undiluted (100%) Effluent	Direct measurement for both sample types
HCO_3^- (Estimated as 1.22 * Total Alk.)	Critical effluent dilution / Undiluted (100%) Effluent	Estimated
Nitrogen, Ammonia (As N)	Critical effluent dilution	Direct measurement
Hardness, Total (as CaCO3)	Critical effluent dilution	Direct measurement
Total Suspended Solids (Residue, Non-Filterable)	Critical effluent dilution / Undiluted (100%) Effluent	Direct measurement / Estimated
Chemical Oxygen Demand (COD)	Critical effluent dilution	Direct measurement
Sulfide	Critical effluent dilution	Direct measurement
Specific Gravity	Undiluted (100%) effluent	Direct measurement
Total Organic Carbon (TOC)	Critical effluent dilution / Undiluted (100%) Effluent	Direct measurement / Estimated
Metals (Total/Dissolved)		
As	Critical effluent dilution	Direct measurement
Ba	Critical effluent dilution	Direct measurement
Cd	Critical effluent dilution	Direct measurement
Cr	Critical effluent dilution	Direct measurement
Cu	Critical effluent dilution	Direct measurement
Pb	Critical effluent dilution	Direct measurement
Hg	Critical effluent dilution	Direct measurement
Ni	Critical effluent dilution	Direct measurement
Se	Critical effluent dilution	Direct measurement
Tl	Critical effluent dilution	Direct measurement
Zn	Critical effluent dilution	Direct measurement
Cations/Anions		
Br, Total	Critical effluent dilution / Undiluted (100%) Effluent	Direct measurement / Estimated
Ca, Total/dissolved	Critical effluent dilution / Undiluted (100%) Effluent	Direct measurement / Estimated
Cl, Total	Critical effluent dilution / Undiluted (100%) Effluent	Direct measurement / Estimated
Mg, Total/dissolved	Critical effluent dilution / Undiluted (100%) Effluent	Direct measurement / Estimated
K, Total/dissolved	Critical effluent dilution	Direct measurement
Na, Total/dissolved	Critical effluent dilution / Undiluted (100%) Effluent	Direct measurement / Estimated
SO_4^{2-}, Total	Critical effluent dilution	Direct measurement
Polycyclic Aromatic Hydrocarbons (PAHs)		
Acenaphthene	Critical effluent dilution	Direct measurement
Acenaphthylene	Critical effluent dilution	Direct measurement
Anthracene	Critical effluent dilution	Direct measurement
Benzo(a)anthracene	Critical effluent dilution	Direct measurement
Benzo(a)pyrene	Critical effluent dilution	Direct measurement
Benzo(b)fluoranthene	Critical effluent dilution	Direct measurement
Benzo(g,h,i)perylene	Critical effluent dilution	Direct measurement
Benzo(k)fluoranthene	Critical effluent dilution	Direct measurement
Chrysene	Critical effluent dilution	Direct measurement
Dibenzo(a,h)anthracene	Critical effluent dilution	Direct measurement
Fluoranthene	Critical effluent dilution	Direct measurement
Fluorene	Critical effluent dilution	Direct measurement
Indeno(1,2,3-cd)pyrene	Critical effluent dilution	Direct measurement
Naphthalene	Critical effluent dilution	Direct measurement
Phenanthrene	Critical effluent dilution	Direct measurement
Pyrene	Critical effluent dilution	Direct measurement

Table A5. Laboratory Analytical Results for Laboratory Control Seawater and TCW Effluent Samples

Constituent	Units	WET Lab Diluent-1	WET Lab Diluent-2	WET-Lab Diluent 3
Critical Effluent Dilution	%	--	--	--
Date	--	11/11/2019	3/2/2020	
Water Quality Parameters (Total)				
Hardness (as CaCO3)	mg/L	4,430	4,150	4260
Alkalinity, Total (As CaCO3)	mg/L	55	92.5	75
HCO_3^- (Estimated as 1.22 * Total Alk.)	mg/L	67.1	112.9	91.5
Total Suspended Solids (Residue, Non-Filterable)	mg/L	ND<5.2	ND<5	26.8
Nitrogen, Ammonia (As N)[1]	mg/L	ND<0.5	ND<0.5	<0.5
Chemical Oxygen Demand	mg/L	ND<300	ND<300	ND<300
Organic Carbon, Total	mg/L	ND<2	ND<4	1.58
Sulfide	mg/L	ND<0.02	0.03	0.029
Specific Gravity	@4 ˚C	LCSW not analyzed.	LCSW not analyzed.	1.02
Water Quality Parameters (Dissolved)				
Total Dissolved Solids (Residue, Filterable)	mg/L	20,300	24,400	23,200
Dissolved Organic Carbon	mg/L	ND<2	ND<2	ND<2
Metals (Total)				
As	mg/L	ND<0.01	ND<0.1	ND<0.1
Ba	mg/L	0.022	ND<0.1	ND<0.1
Cd	mg/L	0.002	0.013	ND<0.01
Ca	mg/L	273	261	277
Cr	mg/L	ND<0.01	ND<0.1	ND<0.1
Cu	mg/L	0.017	ND<0.03	0.03
Pb	mg/L	ND<0.005	ND<0.05	ND<0.05
Mg	mg/L	910	848	866
Hg	mg/L	0.0000009	0.0000039	0.0000011
Ni	mg/L	ND<0.005	ND<0.05	0.019
K	mg/L	280	283	279
Se	mg/L	0.132	0.307	0.054
Na	mg/L	6,560	6,630	7,130
Tl	mg/L	ND<0.006	ND<0.06	ND<0.06
Zn	mg/L	0.012	ND<0.1	0.024
Metals (Dissolved)				
As	mg/L	ND<0.01	ND<0.1	ND<0.1
Ba	mg/L	0.0235	ND<0.1	ND<0.1
Cd	mg/L	0.0022	ND<0.01	0.0069
Ca	mg/L	256	259	290
Cr	mg/L	ND<0.01	ND<0.1	ND<0.1
Cu	mg/L	0.0131	ND<0.05	0.024
Pb	mg/L	ND<0.005	ND<0.05	ND<0.05
Mg	mg/L	837	848	920
Hg	mg/L	ND<0.0000005	0.0000011	0.0000011
Ni	mg/L	ND<0.005	ND<0.05	ND<0.05
K	mg/L	243	278	293
Se	mg/L	0.147	ND<0.2	ND<0.2
Na	mg/L	6,790	6,700	7430
Tl	mg/L	0.0072	0.123	ND<0.06
Zn	mg/L	ND<0.01	ND<0.1	0.016
Inorganic Anions (Total)				
Br	mg/L	37.5	37.6	31.6
Cl	mg/L	13,000	13,700	15,500
SO_4^{2-}	mg/L	1,830	2,070	2,430
Polycyclic Aromatic Hydrocarbons (PAHs)				
Acenaphthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Acenaphthylene	mg/L	ND<0.004	ND<0.004	ND<0.004
Anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(a)anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(a)pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(b)fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(g,h,i)perylene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(k)fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Chrysene	mg/L	ND<0.004	ND<0.004	ND<0.004
Dibenzo(a,h)anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Fluorene	mg/L	ND<0.004	ND<0.004	ND<0.004
Indeno(1,2,3-cd)pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Naphthalene	mg/L	ND<0.004	ND<0.004	ND<0.004
Phenanthrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004

Table A5. Laboratory Analytical Results for Laboratory Control Seawater and TCW Effluent Samples

Constituent	Units	HV63	JK70	RD67
Critical Effluent Dilution	%	0.44	0.39	0.48
Date	--	12/20/2019	11/8/2019	11/25/2019
Water Quality Parameters (Total)				
Hardness (as CaCO3)	mg/L	5,810	4,560	5,220
Alkalinity, Total (As CaCO3)	mg/L	75	52.5	77.5
HCO_3^- (Estimated as 1.22 * Total Alk.)	mg/L	91.5	64.1	94.6
Total Suspended Solids (Residue, Non-Filterable)	mg/L	10.2	19	6.6
Nitrogen, Ammonia (As N)[1]	mg/L	ND<0.5	ND<0.5	ND<0.5
Chemical Oxygen Demand	mg/L	ND<300	ND<300	ND<300
Organic Carbon, Total	mg/L	ND<8	15	5.2
Sulfide	mg/L	ND<0.02	0.02	0.02
Specific Gravity	@4 ˚C	1.26	1.03	1.24
Water Quality Parameters (Dissolved)				
Total Dissolved Solids (Residue, Filterable)	mg/L	23,900	20,300	27,300
Dissolved Organic Carbon	mg/L	ND<2	16.1	4.34
Metals (Total)				
As	mg/L	ND<0.01	ND<0.01	ND<0.01
Ba	mg/L	0.027	0.026	0.043
Cd	mg/L	0.002	0.003	0.002
Ca	mg/L	834	282	707
Cr	mg/L	ND<0.01	ND<0.01	ND<0.01
Cu	mg/L	0.006	0.017	0.008
Pb	mg/L	ND<0.005	ND<0.005	ND<0.005
Mg	mg/L	905	937	839
Hg	mg/L	0.0000022	0.0000011	0.0000011
Ni	mg/L	ND<0.005	ND<0.005	ND<0.005
K	mg/L	277	401	279
Se	mg/L	0.143	0.148	0.165
Na	mg/L	6,930	6,740	6,880
Tl	mg/L	ND<0.006	0.01	0.008
Zn	mg/L	0.02	0.014	0.143
Metals (Dissolved)				
As	mg/L	ND<0.01	0.0139	ND<0.01
Ba	mg/L	0.0309	0.0259	0.133
Cd	mg/L	0.0016	0.0021	0.0015
Ca	mg/L	771	284	701
Cr	mg/L	ND<0.01	ND<0.01	ND<0.01
Cu	mg/L	0.0058	0.0132	0.0117
Pb	mg/L	ND<0.005	ND<0.005	ND<0.005
Mg	mg/L	831	929	833
Hg	mg/L	0.0000016	ND<0.0000005	ND<0.0000005
Ni	mg/L	ND<0.005	ND<0.005	ND<0.005
K	mg/L	278	273	290
Se	mg/L	0.155	0.165	0.147
Na	mg/L	6,980	7,440	6,900
Tl	mg/L	ND<0.006	0.0065	ND<0.006
Zn	mg/L	0.0307	ND<0.01	0.166
Inorganic Anions (Total)				
Br	mg/L	38.1	37.8	116
Cl	mg/L	14,400	13,300	14300
SO_4^{2-}	mg/L	1,900	1,750	2020
Polycyclic Aromatic Hydrocarbons (PAHs)				
Acenaphthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Acenaphthylene	mg/L	ND<0.004	ND<0.004	ND<0.004
Anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(a)anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(a)pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(b)fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(g,h,i)perylene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(k)fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Chrysene	mg/L	ND<0.004	ND<0.004	ND<0.004
Dibenzo(a,h)anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Fluorene	mg/L	ND<0.004	ND<0.004	ND<0.004
Indeno(1,2,3-cd)pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Naphthalene	mg/L	ND<0.004	ND<0.004	ND<0.004
Phenanthrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004

Table A5. Laboratory Analytical Results for Laboratory Control Seawater and TCW Effluent Samples

Constituent	Units	RU61	XP62	NY50
Critical Effluent Dilution	%	0.55	0.19	0.39
Date	--	1/6/2020	1/23/2020	2/11/2020
Water Quality Parameters (Total)				
Hardness (as CaCO3)	mg/L	5,730	4,740	4,620
Alkalinity, Total (As CaCO3)	mg/L	77.5	87.5	95
HCO_3^- (Estimated as 1.22 * Total Alk.)	mg/L	94.6	106.8	115.9
Total Suspended Solids (Residue, Non-Filterable)	mg/L	10.6	7	16.4
Nitrogen, Ammonia (As N)[1]	mg/L	ND<0.5	ND<0.5	0.52
Chemical Oxygen Demand	mg/L	1,420	ND<150	ND<300
Organic Carbon, Total	mg/L	406	ND<2	ND<2
Sulfide	mg/L	0.021	0.027	0.026
Specific Gravity	@4 ˚C	1.45	1.3	1.12
Water Quality Parameters (Dissolved)				
Total Dissolved Solids (Residue, Filterable)	mg/L	29,700	24,900	23,400
Dissolved Organic Carbon	mg/L	385	ND<2	ND<2
Metals (Total)				
As	mg/L	ND<0.01	ND<0.15	ND<0.1
Ba	mg/L	0.077	ND<0.1	ND<0.1
Cd	mg/L	0.002	ND<0.02	0.01
Ca	mg/L	828	513	412
Cr	mg/L	ND<0.01	ND<0.1	ND<0.1
Cu	mg/L	0.009	ND<0.05	ND<0.03
Pb	mg/L	ND<0.005	ND<0.05	ND<0.05
Mg	mg/L	890	839	873
Hg	mg/L	0.0000012	0.0000009	0.0000010
Ni	mg/L	ND<0.005	ND<0.05	ND<0.05
K	mg/L	286	288	274
Se	mg/L	0.159	ND<0.3	ND<0.2
Na	mg/L	6,970	7,070	7,030
Tl	mg/L	0.008	ND<0.06	ND<0.06
Zn	mg/L	0.092	ND<0.1	ND<0.1
Metals (Dissolved)				
As	mg/L	ND<0.01	ND<0.15	ND<0.1
Ba	mg/L	0.0402	ND<0.1	ND<0.1
Cd	mg/L	0.0016	ND<0.02	ND<0.01
Ca	mg/L	808	505	400
Cr	mg/L	ND<0.01	ND<0.1	ND<0.1
Cu	mg/L	0.0077	ND<0.05	ND<0.05
Pb	mg/L	ND<0.005	ND<0.05	ND<0.05
Mg	mg/L	866	826	863
Hg	mg/L	0.000001	ND<0.0000005	0.0000008
Ni	mg/L	ND<0.005	ND<0.05	ND<0.05
K	mg/L	287	285	312
Se	mg/L	0.161	ND<0.3	ND<0.2
Na	mg/L	6,900	6,960	6,990
Tl	mg/L	0.0065	ND<0.06	ND<0.06
Zn	mg/L	0.0767	ND<0.1	ND<0.1
Inorganic Anions (Total)				
Br	mg/L	2,630	41.7	90.0
Cl	mg/L	13,200	14,100	14,100
SO_4^{2-}	mg/L	2,120	1,810	2,230
Polycyclic Aromatic Hydrocarbons (PAHs)				
Acenaphthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Acenaphthylene	mg/L	ND<0.004	ND<0.004	ND<0.004
Anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(a)anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(a)pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(b)fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(g,h,i)perylene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(k)fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Chrysene	mg/L	ND<0.004	ND<0.004	ND<0.004
Dibenzo(a,h)anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Fluorene	mg/L	ND<0.004	ND<0.004	ND<0.004
Indeno(1,2,3-cd)pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Naphthalene	mg/L	ND<0.004	ND<0.004	ND<0.004
Phenanthrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004

Constituent	Units	LC54	AU71	YO64
Critical Effluent Dilution	%	1.25	0.39	0.39
Date	--	2/18/2020	3/18/2020	5/12/2020
Water Quality Parameters (Total)				
Hardness (as CaCO3)	mg/L	4,920	4,340	3,040
Alkalinity, Total (As CaCO3)	mg/L	97.5	70	90
HCO_3^- (Estimated as 1.22 * Total Alk.)	mg/L	119.0	85.4	109.8
Total Suspended Solids (Residue, Non-Filterable)	mg/L	ND<5	18.6	76.6
Nitrogen, Ammonia (As N)[1]	mg/L	ND<0.5	ND<0.5	ND<0.5
Chemical Oxygen Demand	mg/L	ND<150	ND<300	580
Organic Carbon, Total	mg/L	12.1	7.7	70.3
Sulfide	mg/L	0.031	0.023	ND<0.02
Specific Gravity	@4 ˚C	1.07	1.15	[See Note 1]
Water Quality Parameters (Dissolved)				
Total Dissolved Solids (Residue, Filterable)	mg/L	26,000	23,500	26,900
Dissolved Organic Carbon	mg/L	7.8	7.48	126
Metals (Total)				
As	mg/L	0.111	ND<0.1	ND<0.1
Ba	mg/L	ND<0.1	ND<0.1	ND<0.1
Cd	mg/L	ND<0.01	ND<0.01	ND<0.01
Ca	mg/L	429	276	220
Cr	mg/L	ND<0.1	ND<0.1	ND<0.1
Cu	mg/L	0.035	ND<0.03	0.034
Pb	mg/L	ND<0.05	ND<0.05	ND<0.05
Mg	mg/L	935	887	604
Hg	mg/L	0.0000009	0.0000015	0.0000017
Ni	mg/L	ND<0.05	ND<0.05	ND<0.05
K	mg/L	381	381	201
Se	mg/L	0.344	ND<0.2	ND<0.2
Na	mg/L	7690	7450	4830
Tl	mg/L	ND<0.06	ND<0.06	ND<0.06
Zn	mg/L	0.105	ND<0.1	0.226
Metals (Dissolved)				
As	mg/L	ND<0.1	ND<0.1	ND<0.1
Ba	mg/L	ND<0.1	ND<0.1	ND<0.1
Cd	mg/L	ND<0.01	ND<0.01	ND<0.01
Ca	mg/L	388	267	307
Cr	mg/L	ND<0.1	ND<0.1	ND<0.1
Cu	mg/L	ND<0.05	ND<0.05	ND<0.05
Pb	mg/L	ND<0.05	ND<0.05	ND<0.05
Mg	mg/L	857	857	844
Hg	mg/L	0.000001	0.0000015	0.0000016
Ni	mg/L	ND<0.05	ND<0.05	ND<0.05
K	mg/L	312	373	298
Se	mg/L	0.208	ND<0.4	0.341
Na	mg/L	7020	7260	6660
Tl	mg/L	ND<0.06	0.085	ND<0.06
Zn	mg/L	ND<0.1	ND<0.1	0.356
Inorganic Anions (Total)				
Br	mg/L	59.7	44.1	263
Cl	mg/L	15,700	15,400	13,000
SO_4^{2-}	mg/L	2,140	2,100	1,860
Polycyclic Aromatic Hydrocarbons (PAHs)				
Acenaphthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Acenaphthylene	mg/L	ND<0.004	ND<0.004	ND<0.004
Anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(a)anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(a)pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(b)fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(g,h,i)perylene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(k)fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Chrysene	mg/L	ND<0.004	ND<0.004	ND<0.004
Dibenzo(a,h)anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Fluorene	mg/L	ND<0.004	ND<0.004	ND<0.004
Indeno(1,2,3-cd)pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Naphthalene	mg/L	ND<0.004	ND<0.004	ND<0.004
Phenanthrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004

Constituent	Units	FP89	ZG57	GQ67
Critical Effluent Dilution	%	0.39	0.291	0.1
Date	--	3/18/2020	3/2/2020	5/14/2020
Water Quality Parameters (Total)				
Hardness (as CaCO3)	mg/L	4,190	3,980	4,630
Alkalinity, Total (As CaCO3)	mg/L	77.5	77.5	77.5
HCO_3^- (Estimated as 1.22 * Total Alk.)	mg/L	94.6	94.6	94.6
Total Suspended Solids (Residue, Non-Filterable)	mg/L	17.8	ND<5	ND<5
Nitrogen, Ammonia (As N)[1]	mg/L	ND<0.5	ND<0.5	ND<0.5
Chemical Oxygen Demand	mg/L	ND<300	ND<300	ND<300
Organic Carbon, Total	mg/L	9	ND<4	2.7
Sulfide	mg/L	0.02	0.028	ND<0.02
Specific Gravity	@4 ˚C	1.04	1.02	1.49
Water Quality Parameters (Dissolved)				
Total Dissolved Solids (Residue, Filterable)	mg/L	24,400	23,700	24,800
Dissolved Organic Carbon	mg/L	9.14	ND<2	ND<2
Metals (Total)				
As	mg/L	ND<0.1	ND<0.1	ND<0.1
Ba	mg/L	ND<0.1	ND<0.1	ND<0.1
Cd	mg/L	ND<0.01	ND<0.01	ND<0.01
Ca	mg/L	261	251	387
Cr	mg/L	ND<0.1	ND<0.1	ND<0.1
Cu	mg/L	ND<0.03	ND<0.03	ND<0.03
Pb	mg/L	ND<0.05	ND<0.05	ND<0.05
Mg	mg/L	858	814	889
Hg	mg/L	0.0000012	0.0000014	0.0000010
Ni	mg/L	ND<0.05	ND<0.05	ND<0.05
K	mg/L	367	272	417
Se	mg/L	ND<0.2	0.461	0
Na	mg/L	6970	6410	6,920
Tl	mg/L	ND<0.06	ND<0.06	ND<0.1
Zn	mg/L	ND<0.1	ND<0.1	ND<0.1
Metals (Dissolved)				
As	mg/L	ND<0.1	ND<0.1	ND<0.1
Ba	mg/L	ND<0.1	ND<0.1	ND<0.1
Cd	mg/L	ND<0.01	ND<0.01	ND<0.01
Ca	mg/L	260	253	372
Cr	mg/L	ND<0.1	ND<0.1	ND<0.1
Cu	mg/L	ND<0.05	ND<0.03	ND<0.05
Pb	mg/L	ND<0.05	ND<0.05	ND<0.05
Mg	mg/L	853	828	852
Hg	mg/L	0.0000010	0.0000012	0.0000011
Ni	mg/L	ND<0.05	ND<0.05	ND<0.05
K	mg/L	368	276	300
Se	mg/L	ND<0.4	0.359	0.283
Na	mg/L	6990	6540	6,920
Tl	mg/L	ND<0.06	ND<0.1	ND<0.06
Zn	mg/L	ND<0.1	ND<0.1	ND<0.1
Inorganic Anions (Total)				
Br	mg/L	37.8	37.5	490
Cl	mg/L	14,500	13,800	14,000
SO_4^{2-}	mg/L	2,140	1,990	1,940
Polycyclic Aromatic Hydrocarbons (PAHs)				
Acenaphthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Acenaphthylene	mg/L	ND<0.004	ND<0.004	ND<0.004
Anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(a)anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(a)pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(b)fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(g,h,i)perylene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(k)fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Chrysene	mg/L	ND<0.004	ND<0.004	ND<0.004
Dibenzo(a,h)anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Fluorene	mg/L	ND<0.004	ND<0.004	ND<0.004
Indeno(1,2,3-cd)pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Naphthalene	mg/L	ND<0.004	ND<0.004	ND<0.004
Phenanthrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004

Constituent	Units	YU91	LX98	IS88
Critical Effluent Dilution	%	0.41	0.56	0.65
Date	--	5/28/2020	5/8/2020	5/28/2020
Water Quality Parameters (Total)				
Hardness (as CaCO3)	mg/L	3,670	3,870	4,140
Alkalinity, Total (As CaCO3)	mg/L	72.5	75	72.5
HCO_3^- (Estimated as 1.22 * Total Alk.)	mg/L	88.5	73.8	88.5
Total Suspended Solids (Residue, Non-Filterable)	mg/L	22.8	15.4	14
Nitrogen, Ammonia (As N)[1]	mg/L	ND<0.50	ND<0.5	ND<0.5
Chemical Oxygen Demand	mg/L	ND<300	ND<300	ND<300
Organic Carbon, Total	mg/L	6	ND<2	ND<2
Sulfide	mg/L	0.02	ND<0.02	0.026
Specific Gravity	@4 ˚C	[See Note 1]	1.01	1.03
Water Quality Parameters (Dissolved)				
Total Dissolved Solids (Residue, Filterable)	mg/L	24,000	24,600	25,400
Dissolved Organic Carbon	mg/L	6.12	ND<2	ND<2
Metals (Total)				
As	mg/L	ND<0.1	ND<0.1	ND<0.1
Ba	mg/L	ND<0.1	BD<0.1	ND<0.1
Cd	mg/L	ND<0.05	ND<0.01	ND<0.01
Ca	mg/L	234	237	254
Cr	mg/L	ND<0.1	ND<0.1	ND<0.1
Cu	mg/L	0.044	ND<0.03	0.037
Pb	mg/L	ND<0.050	ND<0.05	ND<0.05
Mg	mg/L	749	796	851
Hg	mg/L	0.0000013	0.0000013	0.0000027
Ni	mg/L	ND<0.50	ND<0.05	ND<0.05
K	mg/L	247	499	417
Se	mg/L	0.473	0.314	ND<0.2
Na	mg/L	5,810	6,280	6,730
Tl	mg/L	ND<0.06	ND<0.06	0.092
Zn	mg/L	ND<0.1	ND<0.1	0.152
Metals (Dissolved)				
As	mg/L	ND<0.1	ND<0.1	ND<0.1
Ba	mg/L	ND<0.1	ND<0.1	ND<0.1
Cd	mg/L	<0.05	ND<0.01	ND<0.01
Ca	mg/L	282	221	216
Cr	mg/L	ND<0.100	ND<0.1	ND<0.1
Cu	mg/L	ND<0.05	ND<0.05	ND<0.05
Pb	mg/L	ND<0.05	ND<0.05	ND<0.05
Mg	mg/L	906	746	735
Hg	mg/L	0.0000010	0.0000014	0.0000023
Ni	mg/L	ND<0.05	ND<0.05	ND<0.05
K	mg/L	301	504	445
Se	mg/L	0.445	0.272	0.381
Na	mg/L	7,020	5,890	5,840
Tl	mg/L	ND<0.06	ND<0.06	0.119
Zn	mg/L	ND<0.1	ND<0.1	ND<0.1
Inorganic Anions (Total)				
Br	mg/L	54.7	39.5	38.7
Cl	mg/L	14,100	13,800	13,800
SO_4^{2-}	mg/L	1,980	1,880	1,980
Polycyclic Aromatic Hydrocarbons (PAHs)				
Acenaphthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Acenaphthylene	mg/L	ND<0.004	ND<0.004	ND<0.004
Anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(a)anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(a)pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(b)fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(g,h,i)perylene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(k)fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Chrysene	mg/L	ND<0.004	ND<0.004	ND<0.004
Dibenzo(a,h)anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Fluorene	mg/L	ND<0.004	ND<0.004	ND<0.004
Indeno(1,2,3-cd)pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Naphthalene	mg/L	ND<0.004	ND<0.004	ND<0.004
Phenanthrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004

Table A5. Laboratory Analytical Results for Laboratory Control Seawater and TCW Effluent Samples

Constituent	Units	RU72	IH80[2]	BT52[3]
Critical Effluent Dilution	%	0.36	Sample not analyzed.	Sample not analyzed.
Date	--	5/22/2020		
Water Quality Parameters (Total)				
Hardness (as CaCO3)	mg/L	4,240	Sample not analyzed.	Sample not analyzed.
Alkalinity, Total (As CaCO3)	mg/L	105		
HCO_3^- (Estimated as 1.22 * Total Alk.)	mg/L	128.1		
Total Suspended Solids (Residue, Non-Filterable)	mg/L	19		
Nitrogen, Ammonia (As N)[1]	mg/L	ND<0.5		
Chemical Oxygen Demand	mg/L	ND<300		
Organic Carbon, Total	mg/L	16.2		
Sulfide	mg/L	ND<0.02		
Specific Gravity	@4 ˚C	1.04		
Water Quality Parameters (Dissolved)				
Total Dissolved Solids (Residue, Filterable)	mg/L	32,900	Sample not analyzed.	Sample not analyzed.
Dissolved Organic Carbon	mg/L	16.5		
Metals (Total)				
As	mg/L	ND<0.1	Sample not analyzed	Sample not analyzed.
Ba	mg/L	ND<0.1		
Cd	mg/L	ND<0.01		
Ca	mg/L	263		
Cr	mg/L	ND<0.1		
Cu	mg/L	0.034		
Pb	mg/L	ND<0.05		
Mg	mg/L	870		
Hg	mg/L	0.0000011		
Ni	mg/L	ND<0.05		
K	mg/L	391		
Se	mg/L	0.234		
Na	mg/L	6,840		
Tl	mg/L	ND<0.06		
Zn	mg/L	ND<0.1		
Metals (Dissolved)				
As	mg/L	0.288	Sample not analyzed.	Sample not analyzed.
Ba	mg/L	ND<0.1		
Cd	mg/L	0.013		
Ca	mg/L	284		
Cr	mg/L	ND<0.1		
Cu	mg/L	ND<0.05		
Pb	mg/L	ND<0.05		
Mg	mg/L	927		
Hg	mg/L	0.0000012		
Ni	mg/L	ND<0.05		
K	mg/L	430		
Se	mg/L	0.465		
Na	mg/L	8,310		
Tl	mg/L	ND<0.06		
Zn	mg/L	ND<0.1		
Inorganic Anions (Total)				
Br	mg/L	49	Sample not analyzed.	Sample not analyzed.
Cl	mg/L	13,900		
SO_4^{2-}	mg/L	1,790		
Polycyclic Aromatic Hydrocarbons (PAHs)				
Acenaphthene	mg/L	ND<0.004	Sample not analyzed.	Sample not analyzed.
Acenaphthylene	mg/L	ND<0.004		
Anthracene	mg/L	ND<0.004		
Benzo(a)anthracene	mg/L	ND<0.004		
Benzo(a)pyrene	mg/L	ND<0.004		
Benzo(b)fluoranthene	mg/L	ND<0.004		
Benzo(g,h,i)perylene	mg/L	ND<0.004		
Benzo(k)fluoranthene	mg/L	ND<0.004		
Chrysene	mg/L	ND<0.004		
Dibenzo(a,h)anthracene	mg/L	ND<0.004		
Fluoranthene	mg/L	ND<0.004		
Fluorene	mg/L	ND<0.004		
Indeno(1,2,3-cd)pyrene	mg/L	ND<0.004		
Naphthalene	mg/L	ND<0.004		
Phenanthrene	mg/L	ND<0.004		
Pyrene	mg/L	ND<0.004		

Table A5. Laboratory Analytical Results for Laboratory Control Seawater and TCW Effluent Samples

Constituent	Units	SH87	EP57-Begin	TR84-Middle
Critical Effluent Dilution	%	0.33	0.16	0.21
Date	--	5/12/2020	5/10/2020	5/12/2020
Water Quality Parameters (Total)				
Hardness (as CaCO3)	mg/L	4310	4490	922
Alkalinity, Total (As CaCO3)	mg/L	80	82.5	80
HCO_3^- (Estimated as 1.22 * Total Alk.)	mg/L	97.6	100.7	97.6
Total Suspended Solids (Residue, Non-Filterable)	mg/L	9	12.2	17
Nitrogen, Ammonia (As N)[1]	mg/L	ND<0.5	ND<0.5	ND<0.5
Chemical Oxygen Demand	mg/L	ND<300	ND<300	ND<300
Organic Carbon, Total	mg/L	ND<2	ND<2	ND<2
Sulfide	mg/L	ND<0.02	ND<0.02	ND<0.02
Specific Gravity	@4 ˚C	1.05	1.05	1.06
Water Quality Parameters (Dissolved)				
Total Dissolved Solids (Residue, Filterable)	mg/L	23,700	20,300	21,800
Dissolved Organic Carbon	mg/L	ND<2	ND<2	ND<2
Metals (Total)				
As	mg/L	0.181	ND<0.1	ND<0.1
Ba	mg/L	ND<0.1	ND<0.1	ND<0.1
Cd	mg/L	0.01	ND<0.01	0.01
Ca	mg/L	265	280	285
Cr	mg/L	ND<0.1	ND<0.1	ND<0.1
Cu	mg/L	0.038	0.046	0.046
Pb	mg/L	ND<0.05	ND<0.05	ND<0.05
Mg	mg/L	886	922	922
Hg	mg/L	0.0000013	0.0000022	0.0000014
Ni	mg/L	ND<0.05	ND<0.05	ND<0.05
K	mg/L	310	306	305
Se	mg/L	0.352	0.369	0.327
Na	mg/L	6990	7080	7,070
Tl	mg/L	ND<0.06	ND<0.06	ND<0.06
Zn	mg/L	ND<0.1	ND<0.1	ND<0.1
Metals (Dissolved)				
As	mg/L	ND<0.1	ND<0.1	ND<0.1
Ba	mg/L	ND<0.1	ND<0.1	ND<0.1
Cd	mg/L	ND<0.01	ND<0.01	ND<0.01
Ca	mg/L	267	273	271
Cr	mg/L	ND<0.1	ND<0.1	ND<0.1
Cu	mg/L	ND<0.05	0.046	ND<0.05
Pb	mg/L	ND<0.05	ND<0.05	ND<0.05
Mg	mg/L	895	901	878
Hg	mg/L	0.0000008	0.0000005	0.0000005
Ni	mg/L	ND<0.05	ND<0.05	ND<0.05
K	mg/L	310	309	299
Se	mg/L	0.352	0.282	0.369
Na	mg/L	6990	6970	6790
Tl	mg/L	ND<0.06	ND<0.06	ND<0.06
Zn	mg/L	ND<0.1	ND<0.1	ND<0.1
Inorganic Anions (Total)				
Br	mg/L	44.1	54.9	77
Cl	mg/L	13600	13300	13,300
SO_4^{2-}	mg/L	1830	1850	1,620
Polycyclic Aromatic Hydrocarbons (PAHs)				
Acenaphthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Acenaphthylene	mg/L	ND<0.004	ND<0.004	ND<0.004
Anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(a)anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(a)pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(b)fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(g,h,i)perylene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(k)fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Chrysene	mg/L	ND<0.004	ND<0.004	ND<0.004
Dibenzo(a,h)anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Fluorene	mg/L	ND<0.004	ND<0.004	ND<0.004
Indeno(1,2,3-cd)pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Naphthalene	mg/L	ND<0.004	ND<0.004	ND<0.004
Phenanthrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004

Table A5. Laboratory Analytical Results for Laboratory Control Seawater and TCW Effluent Samples

Constituent	Units	RC74-Begin	OD76-Middle	TF74-End
Critical Effluent Dilution	%	0.05	0.39	0.56
Date	--	5/24/2020	5/25/2020	5/25/2020
Water Quality Parameters (Total)				
Hardness (as CaCO3)	mg/L	4830	4180	9720
Alkalinity, Total (As CaCO3)	mg/L	72.5	75	77.5
HCO_3^- (Estimated as 1.22 * Total Alk.)	mg/L	88.5	91.5	94.6
Total Suspended Solids (Residue, Non-Filterable)	mg/L	18.6	16	27
Nitrogen, Ammonia (As N)[1]	mg/L	ND<0.5	ND<0.5	ND<0.5
Chemical Oxygen Demand	mg/L	ND<300	ND<300	960
Organic Carbon, Total	mg/L	ND<40	ND<40	41.3
Sulfide	mg/L	ND<0.02	ND<0.02	ND<0.02
Specific Gravity	@4 ˚C	1.03	[See Note 1]	1.66
Water Quality Parameters (Dissolved)				
Total Dissolved Solids (Residue, Filterable)	mg/L	25,200	25,800	39,400
Dissolved Organic Carbon	mg/L	ND<40	ND<40	43.9
Metals (Total)				
As	mg/L	ND<0.1	ND<0.1	ND<0.1
Ba	mg/L	ND<0.1	ND<0.1	0.135
Cd	mg/L	ND<0.01	ND<0.01	ND<0.01
Ca	mg/L	296	267	2370
Cr	mg/L	ND<0.1	ND<0.1	ND<0.1
Cu	mg/L	ND<0.03	ND<0.03	0.055
Pb	mg/L	ND<0.05	ND<0.05	ND<0.05
Mg	mg/L	993	853	926
Hg	mg/L	0.0000011	0.0000068	0.0000017
Ni	mg/L	ND<0.05	ND<0.05	ND<0.05
K	mg/L	302	296	291
Se	mg/L	ND<0.2	0.337	0.218
Na	mg/L	7,640	6,960	7,260
Tl	mg/L	ND<0.06	ND<0.06	ND<0.06
Zn	mg/L	ND<0.1	ND<0.1	ND<0.1
Metals (Dissolved)				
As	mg/L	ND<0.1	ND<0.1	ND<0.1
Ba	mg/L	ND<0.1	ND<0.1	0.138
Cd	mg/L	ND<0.01	ND<0.01	ND<0.01
Ca	mg/L	274	313	2140
Cr	mg/L	ND<0.1	ND<0.1	ND<0.1
Cu	mg/L	ND<0.05	ND<0.05	ND<0.05
Pb	mg/L	ND<0.05	ND<0.05	ND<0.05
Mg	mg/L	922	1030	839
Hg	mg/L	0.0000005	0.0000021	0.0000008
Ni	mg/L	ND<0.05	ND<0.05	ND<0.05
K	mg/L	285	290	271
Se	mg/L	ND<0.2	0.389	0.317
Na	mg/L	7110	7890	6550
Tl	mg/L	ND<0.1	ND<0.06	ND<0.1
Zn	mg/L	ND<0.1	ND<0.1	ND<0.1
Inorganic Anions (Total)				
Br	mg/L	38.8	36.7	8,850
Cl	mg/L	13,900	13,800	13,700
SO_4^{2-}	mg/L	1,890	2,000	1,880
Polycyclic Aromatic Hydrocarbons (PAHs)				
Acenaphthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Acenaphthylene	mg/L	ND<0.004	ND<0.004	ND<0.004
Anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(a)anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(a)pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(b)fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(g,h,i)perylene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(k)fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Chrysene	mg/L	ND<0.004	ND<0.004	ND<0.004
Dibenzo(a,h)anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Fluorene	mg/L	ND<0.004	ND<0.004	ND<0.004
Indeno(1,2,3-cd)pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Naphthalene	mg/L	ND<0.004	ND<0.004	ND<0.004
Phenanthrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004

Table A5. Laboratory Analytical Results for Laboratory Control Seawater and TCW Effluent Samples

Constituent	Units	QK91	DO57	PO80
Critical Effluent Dilution	%	0.291	0.291	0.39
Date	--	2/18/2021	4/10/2021	5/7/2021
Water Quality Parameters (Total)				
Hardness (as CaCO3)	mg/L	4,220	4,040	5,230
Alkalinity, Total (As CaCO3)	mg/L	77.5	92.5	90
HCO_3^- (Estimated as 1.22 * Total Alk.)	mg/L	94.6	112.9	109.8
Total Suspended Solids (Residue, Non-Filterable)	mg/L	7.2	9	7.2
Nitrogen, Ammonia (As N)[1]	mg/L	ND<0.5	ND<0.5	ND<0.5
Chemical Oxygen Demand	mg/L	ND<300	720	320
Organic Carbon, Total	mg/L	ND<4	176	7.6
Sulfide	mg/L	0.037	0.042	0.035
Specific Gravity	@4 ˚C	1.05	1.02	1.35
Water Quality Parameters (Dissolved)				
Total Dissolved Solids (Residue, Filterable)	mg/L	21,200	25,400	27,900
Dissolved Organic Carbon	mg/L	ND<2	158	7.33
Metals (Total)				
As	mg/L	ND<0.1	ND<0.1	ND<0.1
Ba	mg/L	ND<0.1	0.37	ND<0.1
Cd	mg/L	ND<0.01	ND<0.01	ND<0.01
Ca	mg/L	278	284	631
Cr	mg/L	ND<0.1	ND<0.1	ND<0.1
Cu	mg/L	0.04	ND<0.03	ND<0.03
Pb	mg/L	ND<0.05	ND<0.05	ND<0.05
Mg	mg/L	855	808	887
Hg	mg/L	0.00	0.0000010	0.0000014
Ni	mg/L	ND<0.05	ND<0.05	ND<0.05
K	mg/L	273	267	290
Se	mg/L	ND<0.2	ND<0.2	ND<0.2
Na	mg/L	6,990	6,690	7,430
Tl	mg/L	ND<0.06	0.06	ND<0.06
Zn	mg/L	ND<0.1	ND<0.1	0.608
Metals (Dissolved)				
As	mg/L	ND<0.1	ND<0.1	ND<0.1
Ba	mg/L	ND<0.1	0.427	ND<0.1
Cd	mg/L	ND<0.01	ND<0.01	ND<0.01
Ca	mg/L	301	320	652
Cr	mg/L	ND<0.1	ND<0.1	ND<0.1
Cu	mg/L	0.042	ND<0.05	ND<0.05
Pb	mg/L	0.034	ND<0.05	ND<0.05
Mg	mg/L	931	890	918
Hg	mg/L	0.0000006	ND<0.0000005	0.0000013
Ni	mg/L	ND<0.05	ND<0.05	ND<0.05
K	mg/L	290	299	311
Se	mg/L	ND<0.2	ND<0.2	ND<0.2
Na	mg/L	7480	7690	7,650
Tl	mg/L	ND<0.06	ND<0.06	ND<0.06
Zn	mg/L	ND<0.1	ND<0.1	0.51
Inorganic Anions (Total)				
Br	mg/L	104	182	1,150
Cl	mg/L	14,300	13,400	14,100
SO_4^{2-}	mg/L	2,230	2,090	2,100
Polycyclic Aromatic Hydrocarbons (PAHs)				
Acenaphthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Acenaphthylene	mg/L	ND<0.004	ND<0.004	ND<0.004
Anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(a)anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(a)pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(b)fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(g,h,i)perylene	mg/L	ND<0.004	ND<0.004	ND<0.004
Benzo(k)fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Chrysene	mg/L	ND<0.004	ND<0.004	ND<0.004
Dibenzo(a,h)anthracene	mg/L	ND<0.004	ND<0.004	ND<0.004
Fluoranthene	mg/L	ND<0.004	ND<0.004	ND<0.004
Fluorene	mg/L	ND<0.004	ND<0.004	ND<0.004
Indeno(1,2,3-cd)pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Naphthalene	mg/L	ND<0.004	ND<0.004	ND<0.004
Phenanthrene	mg/L	ND<0.004	ND<0.004	ND<0.004
Pyrene	mg/L	ND<0.004	ND<0.004	ND<0.004

Constituent	Units	JH68	UP92
Critical Effluent Dilution	%	0.24	0.15
Date	--	4/13/2021	4/23/2021
Water Quality Parameters (Total)			
Hardness (as CaCO3)	mg/L	4,550	4,470
Alkalinity, Total (As CaCO3)	mg/L	90	87.5
HCO_3^- (Estimated as 1.22 * Total Alk.)	mg/L	109.8	106.8
Total Suspended Solids (Residue, Non-Filterable)	mg/L	5.6	5.4
Nitrogen, Ammonia (As N)[1]	mg/L	ND<2.5	ND<0.5
Chemical Oxygen Demand	mg/L	ND<300	340
Organic Carbon, Total	mg/L	ND<2	6.3
Sulfide	mg/L	0.045	0.035
Specific Gravity	@4 ˚C	1.04	1.42
Water Quality Parameters (Dissolved)			
Total Dissolved Solids (Residue, Filterable)	mg/L	19,600	26,200
Dissolved Organic Carbon	mg/L	ND<4	6.33
Metals (Total)			
As	mg/L	ND<0.1	ND<0.1
Ba	mg/L	ND<0.1	ND<0.1
Cd	mg/L	ND<0.01	ND<0.01
Ca	mg/L	299	409
Cr	mg/L	ND<0.1	ND<0.1
Cu	mg/L	ND<0.03	ND<0.03
Pb	mg/L	ND<0.05	ND<0.05
Mg	mg/L	924	838
Hg	mg/L	0.0000017	0.00
Ni	mg/L	ND<0.05	ND<0.05
K	mg/L	295	267
Se	mg/L	ND<0.2	ND<0.2
Na	mg/L	7,650	6,880
Tl	mg/L	ND<0.06	ND<0.06
Zn	mg/L	ND<0.1	ND<0.1
Metals (Dissolved)			
As	mg/L	ND<0.1	ND<0.1
Ba	mg/L	ND<0.1	ND<0.1
Cd	mg/L	ND<0.01	ND<0.01
Ca	mg/L	300	420
Cr	mg/L	ND<0.1	ND<0.1
Cu	mg/L	0.0532	ND<0.05
Pb	mg/L	ND<0.05	ND<0.05
Mg	mg/L	902	874
Hg	mg/L	ND<0.0000005	ND<0.0000005
Ni	mg/L	ND<0.05	ND<0.05
K	mg/L	308	278
Se	mg/L	ND<0.2	ND<0.2
Na	mg/L	7880	7180
Tl	mg/L	ND<0.06	ND<0.06
Zn	mg/L	ND<0.1	ND<0.1
Inorganic Anions (Total)			
Br	mg/L	25	512
Cl	mg/L	13,700	12,000
SO_4^{2-}	mg/L	2,090	1,890
Polycyclic Aromatic Hydrocarbons (PAHs)			
Acenaphthene	mg/L	ND<0.004	ND<0.004
Acenaphthylene	mg/L	ND<0.004	ND<0.004
Anthracene	mg/L	ND<0.004	ND<0.004
Benzo(a)anthracene	mg/L	ND<0.004	ND<0.004
Benzo(a)pyrene	mg/L	ND<0.004	ND<0.004
Benzo(b)fluoranthene	mg/L	ND<0.004	ND<0.004
Benzo(g,h,i)perylene	mg/L	ND<0.004	ND<0.004
Benzo(k)fluoranthene	mg/L	ND<0.004	ND<0.004
Chrysene	mg/L	ND<0.004	ND<0.004
Dibenzo(a,h)anthracene	mg/L	ND<0.004	ND<0.004
Fluoranthene	mg/L	ND<0.004	ND<0.004
Fluorene	mg/L	ND<0.004	ND<0.004
Indeno(1,2,3-cd)pyrene	mg/L	ND<0.004	ND<0.004
Naphthalene	mg/L	ND<0.004	ND<0.004
Phenanthrene	mg/L	ND<0.004	ND<0.004
Pyrene	mg/L	ND<0.004	ND<0.004

Notes:
mg/L; milligrams per liter
%; percent
˚C; degrees Celcius
ND; not detected above the laboratory reporting limit

[1] Due to their viscosity, the analysis of specific gravity was not conducted on Category III gel samples. Also, TCW Category III sample RU72 had insufficient sample volume due to the presence of proppant.
[2] IH80; sample contained a separate phase. Sample was not discharged.
[3] BT52; insufficient sample volume was collected in the field.

Table A6. GHS Acute Aquatic Toxicity
Classification of Chemical Products in TCW Category I Effluents

TCW Sample	Product Code	GHS Acute Aquatic Toxicity Category Classification	Notes
HV63	No chemical additives	--	--
RD67	Defoamer 1	Acute 2	Identified in SDS Section 2.
	Viscosifier 1	Not Assessed	Identified as Not Classified in SDS Section 2. Contains no hazardous substances in concentrations above cut-off values according to the competent authority. No ecological data.
	Non-emulsifier 1	Acute 2	Identified in SDS Section 2.
RU61	Acid 1	Not Assessed	No GHS classification provided in Section 2. Contains 30-60% acetic acid. 48-h EC50 = 65 mg/L (Daphnia magna). Effect concentrations in the aquatic environment are attributable to a change in pH.
	Acid 2	Not Assessed	No GHS classification provided in Section 2. Contains 30-60% hydrochloric acid. LC50s for fish range from 20.5 - 282 mg/L; LC50 for pH (3.25-3.5). 48-h EC50 for Daphnia magna is 4.92 mg/L.
	Non-emulsifier 1	Acute 2	Identified in SDS Section 2.
XP62	No chemical additives	--	--
LC54	Biocide 1	Acute 1	Identified in SDS Section 2.
	Non-emulsifier 1	Acute 2	Identified in SDS Section 2.
AU71	Well cleaner 1	Not Assessed	No GHS classification provided in Section 2. Manufacturer product toxicity data provided in SDS Section 12 reports product data of: Algae Toxicity EC50 (72h) >10 mg/L (Pseudokirchneriella subcapitata). Acute Crustaceans Toxicity: EC50 (48h) >10 mg/L (Daphnia magna).
	pH Control 3	Not Assessed	No GHS classification for aquatic toxicity identified in Section 2 or for individual substances in Section 3. Product contains sodium hydroxide (10-30%); no other substances identified. 24/48/96-h LC50s for fish range from 125-189 mg/L; 48-h EC50 for Ceriodaphnia sp. Is 40.4 mg/L.
	Non-emulsifier 1	Acute 2	Identified in SDS Section 2.
	Viscosifier 2	Not Assessed	No GHS classification provided in Section 2. No GHS classification for individual substances (dipropylene glycol monomethyl ether; 30-60%) provided in Section 3. SDS indicates in Section 12 that the product is not classified as hazardous to the environment. A NOEC of 0.5 mg/L (*Daphnia magna*) was identified in the SDS for dipropylene glycol monomethyl ether.
	Biocide 4	Acute 3	Identified in SDS Section 2.

Table A6. GHS Acute Aquatic Toxicity
Classification of Chemical Products in TCW Category I Effluents

TCW Sample	Product Code	GHS Acute Aquatic Toxicity Category Classification	Notes
ZG57	Defoamer 2	Not Assessed	No GHS classification provided in Section 2. Product consists of kerosene (60-100%); naphthalene (1-5%); and ethylbenzene (0.1-1%). Product toxicity to daphnia and other aquatic invertebrates: LC50 Ceriodaphnia dubia: 4,063 mg/l Exposure time: 48 hrs Test substance: Product. NOEC Ceriodaphnia dubia: 2,500 mg/l Exposure time: 48 hrs Test substance.
	Corrosion inhibitor 1	Not Assessed	No GHS classification provided in Section 2. Product consists of methanol (30-60%); QAC (10-30%); Fatty acid-amine condensate (5-10%); Ethylene Glycol (5-10%); 2-Mercaptoethanol (5-10%);Oxyalkylate (1-5%); Diethanolamine (1-5%); Heavy Aromatic Naphtha (1-5%); and Naphthalene (0.1-1%). Fish and invertebrate L(E)C50s for methanol are >100 mg/L. No fish or invertebrate toxicity data are reported for QAC.
	Oxygen Scavenger 2	Not Assessed	No GHS classification provided in section 2. Substances identified are a proprietary substituted alkylamine (10-30%); ethylene glycol (5-10%); and 2-butoxyethanol (1-5%). Toxicity data identify a 96-h LC50 of >1.908 mg/L for fish exposed to the substituted alkylamine and a 48-h LC50 of 20.352 mg/L for the Daphnid.
	Scale inhibitor 2	Not Assessed	No GHS classification is provided in Section 2. Substances identified are ethylene glycol (10-30%); sodium molybdate (1-5%); and Inorganic salt (0.1-1%). SDS indicates that this product has no known ecotoxicological effects. Fish and invertebrate L(E)C50s for ethylene glycol are >100 mg/L.
	Completion Fluid Additive 1	Not Assessed	No GHS classification is provided in Section 2. Substances identified are calcium bromide (50-60%) and several proprietary compounds (<25%). No toxicity data are provided in Section 12. The section also indicates that the product is not considered harmful to aquatic organisms or to cause long-term adverse effects in the environment.

Table A6. GHS Acute Aquatic Toxicity
Classification of Chemical Products in TCW Category I Effluents

TCW Sample	Product Code	GHS Acute Aquatic Toxicity Category Classification	Notes
EP57	Defoamer 2	Not Assessed	No GHS classification provided in Section 2. Product consists of kerosene (60-100%); naphthalene (1-5%); and ethylbenzene (0.1-1%). Product toxicity to daphnia and other aquatic invertebrates: LC50 Ceriodaphnia dubia: 4,063 mg/l Exposure time: 48 hrs Test substance: Product. NOEC Ceriodaphnia dubia: 2,500 mg/l Exposure time: 48 hrs Test substance.
	Corrosion inhibitor 1	Not Assessed	No GHS classification provided in Section 2. Product consists of methanol (30-60%); QAC (10-30%); Fatty acid-amine condensate (5-10%); Ethylene Glycol (5-10%); 2-Mercaptoethanol (5-10%);Oxyalkylate (1-5%); Diethanolamine (1-5%); Heavy Aromatic Naphtha (1-5%); and Naphthalene (0.1-1%). Fish and invertebrate L(E)C50s for methanol are >100 mg/L. No fish or invertebrate toxicity data are reported for QAC.
	Oxygen Scavenger 2	Not Assessed	No GHS classification provided in section 2. Substances identified are a proprietary substituted alkylamine (10-30%); ethylene glycol (5-10%); and 2-butoxyethanol (1-5%). Toxicity data identify a 96-h LC50 of >1.908 mg/L for fish exposed to the substituted alkylamine and a 48-h LC50 of 20.352 mg/L for the Daphnid.
	Scale inhibitor 2	Not Assessed	No GHS classification is provided in Section 2. Substances identified are ethylene glycol (10-30%); sodium molybdate (1-5%); and Inorganic salt (0.1-1%). SDS indicates that this product has no known ecotoxicological effects. Fish and invertebrate L(E)C50s for ethylene glycol are >100 mg/L.
	Completion Fluid Additive 1	Not Assessed	No GHS classification is provided in Section 2. Substances identified are calcium bromide (50-60%) and several proprietary compounds (<25%). No toxicity data are provided in Section 12. The section also indicates that the product is not considered harmful to aquatic organisms or to cause long-term adverse effects in the environment.

Table A6. GHS Acute Aquatic Toxicity
Classification of Chemical Products in TCW Category I Effluents

TCW Sample	Product Code	GHS Acute Aquatic Toxicity Category Classification	Notes
TR84	Defoamer 2	Not Assessed	No GHS classification provided in Section 2. Product consists of kerosene (60-100%); naphthalene (1-5%); and ethylbenzene (0.1-1%). Product toxicity to daphnia and other aquatic invertebrates: LC50 Ceriodaphnia dubia: 4,063 mg/l Exposure time: 48 hrs Test substance: Product. NOEC Ceriodaphnia dubia: 2,500 mg/l Exposure time: 48 hrs Test substance.
	Corrosion inhibitor 1	Not Assessed	No GHS classification provided in Section 2. Product consists of methanol (30-60%); QAC (10-30%); Fatty acid-amine condensate (5-10%); Ethylene Glycol (5-10%); 2-Mercaptoethanol (5-10%);Oxyalkylate (1-5%); Diethanolamine (1-5%); Heavy Aromatic Naphtha (1-5%); and Naphthalene (0.1-1%). Fish and invertebrate L(E)C50s for methanol are >100 mg/L. No fish or invertebrate toxicity data are reported for QAC.
	Oxygen Scavenger 2	Not Assessed	No GHS classification provided in section 2. Substances identified are a proprietary substituted alkylamine (10-30%); ethylene glycol (5-10%); and 2-butoxyethanol (1-5%). Toxicity data identify a 96-h LC50 of >1.908 mg/L for fish exposed to the substituted alkylamine and a 48-h LC50 of 20.352 mg/L for the Daphnid.
	Scale inhibitor 2	Not Assessed	No GHS classification is provided in Section 2. Substances identified are ethylene glycol (10-30%); sodium molybdate (1-5%); and Inorganic salt (0.1-1%). SDS indicates that this product has no known ecotoxicological effects. Fish and invertebrate L(E)C50s for ethylene glycol are >100 mg/L.
	Completion Fluid Additive 1	Not Assessed	No GHS classification is provided in Section 2. Substances identified are calcium bromide (50-60%) and several proprietary compounds (<25%). No toxicity data are provided in Section 12. The section also indicates that the product is not considered harmful to aquatic organisms or to cause long-term adverse effects in the environment.

Table A6. GHS Acute Aquatic Toxicity
Classification of Chemical Products in TCW Category I Effluents

TCW Sample	Product Code	GHS Acute Aquatic Toxicity Category Classification	Notes
QK91	Defoamer 2	Not Assessed	No GHS classification is provided in Section 2. Substances identified are kerosene (60-100%), naphthalene (1-5%), ethylbenzene (0.1-1%). Toxicity data for the product provided in SDS Section 12 identify a 48-h LC50 of 4,063 mg/L and a 48-h NOEC of 2,500 mg/L for *Ceriodaphnia dubia* . The section also indicates that the product is considered harmful to aquatic life with long lasting effects.
	Corrosion inhibitor 1	Not Assessed	No GHS classification provided in Section 2. Product consists of methanol (30-60%); QAC (10-30%); Fatty acid-amine condensate (5-10%); Ethylene Glycol (5-10%); 2-Mercaptoethanol (5-10%);Oxyalkylate (1-5%); Diethanolamine (1-5%); Heavy Aromatic Naphtha (1-5%); and Naphthalene (0.1-1%). Fish and invertebrate L(E)C50s for methanol are >100 mg/L. No fish or invertebrate toxicity data are reported for QAC.
	Breaker 3	Not Assessed	No GHS classification is provided in Section 2. Substances identified are Heavy Aromatic Naphtha (30 - 60%), Organic sulfonic acid (10 - 30%), Isopropanol (5 - 10%), Naphthalene (1 - 5%), Oxyalkylated Polymer (1 - 5%),1,2,4-Trimethylbenzene (1 - 5%), and Sulfuric Acid (0.1 - 1%). No product toxicity data are provided in SDS Section 12. A 96-h LC50 of 3.5 mg/L for *Oncorhynchus mykiss* (rainbow trout) is reported for Heavy Aromatic Naphtha. The section also indicates that the product is considered toxic to aquatic life with long lasting effects.
	Oxygen Scavenger 2	Not Assessed	No GHS classification provided in section 2. Substances identified are a proprietary substituted alkylamine (10-30%); ethylene glycol (5-10%); and 2-butoxyethanol (1-5%). Toxicity data identify a 96-h LC50 of >1.908 mg/L for fish exposed to the substituted alkylamine and a 48-h LC50 of 20.352 mg/L for the Daphnid.
DO57	Defoamer 2	Not Assessed	No GHS classification is provided in Section 2. Substances identified are kerosene (60-100%), naphthalene (1-5%), ethylbenzene (0.1-1%). Toxicity data for the product provided in SDS Section 12 identify a 48-h LC50 of 4,063 mg/L and a 48-h NOEC of 2,500 mg/L for *Ceriodaphnia dubia* . The section also indicates that the product is considered harmful to aquatic life with long lasting effects.
	Corrosion inhibitor 1	Not Assessed	No GHS classification provided in Section 2. Product consists of methanol (30-60%); QAC (10-30%); Fatty acid-amine condensate (5-10%); Ethylene Glycol (5-10%); 2-Mercaptoethanol (5-10%);Oxyalkylate (1-5%); Diethanolamine (1-5%); Heavy Aromatic Naphtha (1-5%); and Naphthalene (0.1-1%). Fish and invertebrate L(E)C50s for methanol are >100 mg/L. No fish or invertebrate toxicity data are reported for QAC.
	Breaker 3	Not Assessed	No GHS classification is provided in Section 2. Substances identified are Heavy Aromatic Naphtha (30 - 60%), Organic sulfonic acid (10 - 30%), Isopropanol (5 - 10%), Naphthalene (1 - 5%), Oxyalkylated Polymer (1 - 5%),1,2,4-Trimethylbenzene (1 - 5%), and Sulfuric Acid (0.1 - 1%). No product toxicity data are provided in SDS Section 12. A 96-h LC50 of 3.5 mg/L for *Oncorhynchus mykiss* (rainbow trout) is reported for Heavy Aromatic Naphtha. The section also indicates that the product is considered toxic to aquatic life with long lasting effects.

Table A6. GHS Acute Aquatic Toxicity
Classification of Chemical Products in TCW Category I Effluents

TCW Sample	Product Code	GHS Acute Aquatic Toxicity Category Classification	Notes
DO57	Oxygen Scavenger 2	Not Assessed	No GHS classification provided in section 2. Substances identified are a proprietary substituted alkylamine (10-30%); ethylene glycol (5-10%); and 2-butoxyethanol (1-5%). Toxicity data identify a 96-h LC50 of >1.908 mg/L for fish exposed to the substituted alkylamine and a 48-h LC50 of 20.352 mg/L for the Daphnid.
PO80	No chemical additives	--	--
UP92	Fluid stabilizer 1	Not Assessed	No GHS classification provided in SDS Section 2. Substances identified are Ethanolamine (60 - 100%). No product toxicity data provided in SDS Section 12. Fish Toxicity data for components are: 227 mg/L: 96 h Pimephales promelas mg/L LC50 flow-through; 3684 mg/L: 96 h Brachydanio rerio mg/L LC50 static; 300 - 1000 mg/L: 96 h Lepomis macrochirus mg/L LC50 static; 114 - 196 mg/L: 96 h Oncorhynchus mykiss mg/L LC50 static; 200 mg/L: 96 h Oncorhynchus mykiss mg/L LC50 flow-through. Invertebrate data for components are 65 mg/L: 48 h Daphnia magna mg/L EC50.
	Viscosifier 5	Not Assessed	No GHS classification provided in SDS Section 2. Substances identified are Xanthum gum (100%). No toxicity data were provided; SDS Section 12 does indicate, however, that the environmental impact of this product has not been fully investigated.
	Fluid stabilizer 1	Not Assessed	No GHS classification provided in SDS Section 2. Substances identified are Ethanolamine (60-100%). SDS Section 12 indicates that 0% of the mixture consists of components(s) of unknown hazards to the aquatic environment. Toxicity data provided for Ethanolamine in SDS Section 12 are: 227 mg/L: 96 h *Pimephales promelas* mg/L LC50 flow-through; 3684 mg/L: 96 h *Brachydanio rerio* mg/L LC50 static; 300 - 1000 mg/L: 96 h *Lepomis macrochirus* mg/L LC50 static; 114 - 196 mg/L: 96 h *Oncorhynchus mykiss* mg/L LC50 static; 200 mg/L: 96 h *Oncorhynchus mykiss* mg/L LC50 flow-through; and 65 mg/L: 48 h *Daphnia magna* mg/L EC50.
	Defoamer 6	Not Assessed	No GHS classification provided in SDS Section 2; the section does indicate, however, that the product is harmful to aquatic life with long lasting effects. Harmful to aquatic life. No information on composition was provided in SDS Section 3. No toxicity data were provided; SDS Section 12 does indicate, however, that the environmental impact of this product has not been fully investigated.
	Viscosifier 6	Not Assessed	No GHS classification provided in SDS Section 2. SDS Section 3 identified Dipropylene glycol monomethyl ether (60-70%) and 2-Methoxy-1-propanol (1%). Toxicity data provided in SDS Section 12 for Dipropylene glycol monomethyl ether indicate LC50s >1,000 mg/L: 10,000 mg/L: 96 h *Pimephales promelas* mg/L LC50 static; 1,919: 48 h *Daphnia magna* mg/L LC50. For this reason, toxicity is unlikely.

Table A6. GHS Acute Aquatic Toxicity
Classification of Chemical Products in TCW Category I Effluents

TCW Sample	Product Code	GHS Acute Aquatic Toxicity Category Classification	Notes
UP92	Surfactant 3	Not Assessed	No GHS classification provided in SDS Section 2. Composition information was provided in SDS Section 3: Triethylene glycol, monobutyl ether (30-60%); Alcohol ethoxylates (30-60%); Benzenesulfonic acid, C10-16-alkyl derivs, compds. with 2-propanamine (5-15%); Benzenesulfonic acid, C10-16-alkyl derivatives (<5%); and 2-Ethylhexanol (<5%). Toxicity data provided in SDS Section 12 are as follows: Triethylene glycol, monobutyl ether 2,200 - 4,600 mg/L: 96h *Leuciscus idus* mg/L LC50 static; 2,400 mg/L: 96 h *Pimephales promelas* mg/L LC50; 2,400 mg/L: 96h *Pimephales promelas* mg/L LC50 static; 500 mg/L: 48 h *Daphnia magna* mg/L EC50; Benzenesulfonic acid, C10-16-alkyl derivatives: 3 mg/L: 96 h *Oncorhynchus mykiss* mg/L LC50 static; 2.9 mg/L: 48 h *Daphnia magna* mg/L EC50; **2-**Ethylhexanol**;** 10.0 - 33.0 mg/L: 96 h *Lepomis macrochirus* mg/L LC50 static; 27 - 29.5 mg/L: 96 h *Pimephales promelas* mg/L LC50 flow-through; 32 - 37 mg/L: 96 h *Oncorhynchus mykiss* mg/L LC50 static; 29.7 mg/L: 96 h *Pimephales promelas* mg/L LC50 static; 7.5 mg/L: 96 h *Oncorhynchus mykiss* mg/L LC50.
	Hydrogen sulfide scavenger 1	Not Assessed	No GHS classification provided in SDS Section 2; the section does indicate, however, that the product is harmful to aquatic life and that 90% of the mixture consists of ingredient(s) of unknown toxicity. Composition information provided in SDS Section 3: Substituted Alkylamine (30-60%); Ethanolamine (1-5%); Methyl alcohol (0.1-1%); and Diethanolamine (0.1-1%). Toxicity data provided in SDS Section 12: Ethanolamine: 114 - 196 mg/L: 96 h *Oncorhynchus mykiss* mg/L LC50 static 300 - 1000: 96 h *Lepomis macrochirus* mg/L LC50 static 227: 96 h *Pimephales promelas* mg/L LC50 flow-through 3684: 96 h *Brachydanio rerio* mg/L LC50 static 200: 96 h *Oncorhynchus mykiss* mg/L LC50 flow-through; 65 mg/L: 48 h *Daphnia magna* mg/L EC50; Methyl alcohol: 13,500 - 17,600 mg/L: 96 h *Lepomis macrochirus* mg/L LC50 flow-through; 18 - 20 mL/L: 96 h Oncorhynchus mykiss mL/L LC50 static; 19,500 - 20,700 mg/L: 96 h *Oncorhynchus mykiss* mg/L LC50 flow-through; 28,200 mg/L: 96 h *Pimephales promelas* mg/L LC50 flow-through; 100 mg/L: 96 h *Pimephales promelas* mg/L LC50 static; Diethanolamine: 1,200 - 1,580 mg/L: 96 h *Pimephales promelas* mg/L LC50 static; 4,460 - 4,980 mg/L: 96 h *Pimephales promelas* mg/L LC50 flow-through; 600 - 1,000 mg/L: 96 h *Lepomis macrochirus* mg/L LC50 static; 55 mg/L: 48 h *Daphnia magna* mg/L EC50.
	Base fluid 1	Not Assessed	No GHS classification provided in SDS Section 2. Composition information was provided in SDS Section 3: Hexadecene (60-70%); and Octadecene (30-40%). SDS Section 12 did not provide toxicity data but inidcated that the environmental impact of the product has not been fully investigated.

Table A7. GHS Acute Aquatic Toxicity
Classification of Chemical Products in Category III Effluents

TCW Sample	Product Code	GHS Acute/Chronic Aquatic Toxicity Category Classification	Notes
JK70	Non-emulsifier 3	Not Assessed	No GHS classification identified in Section 2. Insufficient information provided on composition for proprietary substances (QACs). No ecological data
	Clay Stabilizer 2	Not Assessed	No GHS classification identified in Section 2. Insufficient information provided on composition for proprietary substances (QACs). No ecological data.
	Corrosion inhibitor 2	Not Assessed	No GHS classification identified in Section 2. Insufficient information provided on composition for proprietary substances (QACs).
	Defoamer 3	Not Assessed	No GHS classification identified in Section 2. Insufficient information provided on composition for proprietary substances (TBP 40-60% w/w). No ecological data.
	Oxygen Scavenger 3	Not Assessed	No GHS classification identified in Section 2. Insufficient information provided on composition for proprietary substances ("proprietary poly-functional organic"). No ecological data.
	Synthetic Mud Casing Scrubber 1	Not Assessed	No GHS classification identified in Section 2. Insufficient information provided on composition for proprietary substances ("surfactant blend"). 96h LC-50 (fish) identified in SDS: >100 mg/L
	Defoamer 4	Not Assessed	No GHS classification identified in Section 2. No information provided on composition for substances. No ecological data.
	Viscosifier 3	Not Assessed	No GHS classification identified in Section 2. No information provided on composition for substances. No ecological data.
	Viscosifier 4	Not Assessed	No GHS classification identified in Section 2. Insufficient information provided on composition. No ecological data.

Table A7. GHS Acute Aquatic Toxicity
Classification of Chemical Products in Category III Effluents

TCW Sample	Product Code	GHS Acute/Chronic Aquatic Toxicity Category Classification	Notes
JK70	Fluid additive 1	Not Assessed	Identified as Not Classified for environmental hazards in SDS Section 2. Benzenesulfonic acid, C10-16-alkyl derivatives, compounds with 2-Propanamine (10-30% w/w). Environmental hazards identified as "Not classified" in SDS Section 2
	Biocide 5	Not Assessed	No GHS classification identified in Section 2. Substance identified is glutaraldehyde (25% w/w). No ecological data provided in SDS.
NY50	Viscosifier 1	Not Assessed	Identified as Not Classified in SDS Section 2. Contains no hazardous substances in concentrations above cut-off values according to the competent authority. No ecological data.
	Non-emulsifier 1	Acute 2	Identified in SDS Section 2.
YO64	Well cleaner 1	Not Assessed	No GHS classification provided in Section 2. Manufacturer product toxicity data provided in SDS Section 12 reports product data of: Algae Toxicity EC50 (72h) >10 mg/L (Pseudokirchneriella subcapitata). Acute Crustaceans Toxicity: EC50 (48h) >10 mg/L (Daphnia magna).
	pH Control 3	Not Assessed	No GHS classification for aquatic toxicity identified in Section 2 or for individual substances in Section 3. Product contains sodium hydroxide (10-30%); no other substances identified. 24/48/96-h LC50s for fish range from 125-189 mg/L; 48-h EC50 for Ceriodaphnia sp. Is 40.4 mg/L.
	Non-emulsifier 1	Acute 2	Identified in SDS Section 2.
	Viscosifier 2	Not Assessed	No GHS classification provided in Section 2. No GHS classification for individual substances (dipropylene glycol monomethyl ether; 30-60%) provided in Section 3.
	Biocide 4	Acute 3	Identified in SDS Section 2.

Table A7. GHS Acute Aquatic Toxicity
Classification of Chemical Products in Category III Effluents

TCW Sample	Product Code	GHS Acute/Chronic Aquatic Toxicity Category Classification	Notes
FP89	Surfactant 1	Not Assessed	No GHS classification provided in Section 2. Amphoteric surfactant. Only 1 substance identifed (cocamidopropyl betaine 10 - 20%). No ecological data provided.
	Biocide 3	Acute 1	Identified in SDS Section 2.
	Linear gel 1	Not Assessed	No GHS classification provided in Section 2. SDS indicates that the product contains no hazardous substances. No information on composition. No ecological information
	Breaker 2	Not Assessed	No GHS classification provided in Section 2. Limited composition information (hemicellulase enzyme; 0.1 - 1%). No ecological data provided.
	Gellant 1	Not Assessed	No GHS classification provided in Section 2. Product consists of glycol ether (60 - 65%) and guar gum (30 - 35%). No ecological data provided.
	Non-emulsifier 2	Not Assessed	No GHS classification provided in Section 2. Substances identified include a cationic polymer in solution (1-5%); and ethoxylated alcohol (1-5%). No CAS Nos. provided.
	pH Control 2	Not Assessed	No GHS classification provided in Section 2. Percentage of the mixture consisting of ingredient(s) of unknown hazards to the aquatic environment: 2%. Product contains Potassium carbonate (40 - 50%); this is the only substance identified.
	Biocide 2	Acute 1	Identified in SDS Section 2.
	Clay Stabilizer 1	Not Assessed	No GHS classification provided in Section 2. Ammonium chloride (1-5%) is the only substance identified. No ecotoxicological information provided.

Table A7. GHS Acute Aquatic Toxicity
Classification of Chemical Products in Category III Effluents

TCW Sample	Product Code	GHS Acute/Chronic Aquatic Toxicity Category Classification	Notes
FP89	Acid 3	Not Assessed	No GHS classification identified in Section 2. Substances identified are ammonium bifluoride (1-5%); acetic anhydride (1-5%); acetic acid (1-5%); hydrochloric acid (5-10%); hydrofluoric acid (1-5%). No ecological information provided.
	Solvent 1	Not Assessed	No GHS classification identified in Section 2. Substances identified are xylene (70-80%); acetic acid (10-20%); 2-Butoxyethanol (10-20%). LC50 data identified in Section 12 for xylene identify a 96h LC50 of 2.6 mg/L for fish and a 48-h LC50 of >3.4 mg/L for Daphnia.
GQ67	Surfactant 2	Not Assessed	No GHS classification provided in Section 2. Substances identified are alcohols (C9-11 ethoxylated) (10%) and proprietary organic alcohol (10-30%). No toxicity data are available.
YU91	Clay Stabilizer 1	Not Assessed	No GHS classification provided in Section 2. Ammonium chloride (1-5%) is the only substance identified. No ecotoxicological information provided.
	pH Control 1	Not Assessed	No GHS classification is provided in Section 2. Substances identified are sodium carbonate (60-100%). Toxicity data are: TLM24 385 mg/L (*Lepomis macrochirus*) LC50 310-1220 mg/L (*Pimephales promelas*) LC50 (96h) 300 mg/L (*Lepomis macrochirus*); EC50 265 mg/L (*Daphnia magna*) EC50 (48h) 200 – 227 mg/L (*Ceriodaphnia sp* .)
	Acid 3	Not Assessed	No GHS classification identified in Section 2. Substances identified are ammonium bifluoride (1-5%); acetic anhydride (1-5%); acetic acid (1-5%); hydrochloric acid (5-10%); hydrofluoric acid (1-5%). No ecological information provided.
	Linear Gel 2	Not Assessed	No GHS classification provided in Section 2. Substance identified is ulexite (0.1-1%).
	Fluid Additive 3	Not Assessed	SDS Section 2 indicates that the product is not classified. The SDS also indicates that the product contains no hazardous substances in concentrations above cut-off values according to the competent authority
LX98	Oxygen Scavenger 1	Acute 3	Identified in SDS Section 2.
IS88	Oxygen Scavenger 1	Acute 3	Identified in SDS Section 2.

Table A7. GHS Acute Aquatic Toxicity
Classification of Chemical Products in Category III Effluents

TCW Sample	Product Code	GHS Acute/Chronic Aquatic Toxicity Category Classification	Notes
IS88	pH Control 3	Not Assessed	No GHS classification for aquatic toxicity identified in Section 2 or for individual substances in Section 3. Product contains sodium hydroxide (10-30%); no other substances identified. 24/48/96-h LC50s for fish range from 125-189 mg/L; 48-h EC50 for Ceriodaphnia sp. is 40.4 mg/L.
	Biocide 4	Acute 3	Identified in SDS Section 2.
RU72	No SDSs provided	--	--
BT52	No SDSs provided	--	--
SH87	Activator 1	Acute 2; Chronic 2	Identified in SDS Section 2.
	Breaker 1	Acute 2	Identified in SDS Section 2.
	Fluid Additive 3	Not Assessed	SDS Section 2 indicates that the product is not classified. The SDS also indicates that the product contains no hazardous substances.
	Initiator 1	Not Assessed	No GHS classification for aquatic toxicity identified in Section 2. Product contains ethylene glycol (10-30%); no other substances identified. 96-h LC50s for fish are >100 mg/L; 48-h EC50 reported for invertebrates are >100 mg/L.
	Proppant 1	Not Assessed	This product is a ceramic proppant. No toxicity data presented in the SDS.
RC74	Crosslinker 1	Not Assessed	No GHS classification is provided in Section 2. Substances identified are borate salts (30-60%) and dipropylene glycol monomethyl ether (30-60%). Borate salts: Acute 96-h LC50 for fish are >100 mg/L; 48-h EC50 for invertebrates are >100 mg/L. Dipropylene glycol monomethyl ether: a NOEC of 0.5 mg/L was reported for Daphnia magna; no fish data are available.

Table A7. GHS Acute Aquatic Toxicity
Classification of Chemical Products in Category III Effluents

TCW Sample	Product Code	GHS Acute/Chronic Aquatic Toxicity Category Classification	Notes
RC74	Stabilizer 1	Not Assessed	This product is identified in Section 2 as not classified. No composition or toxicity data are available.
	Fluid Additive 2	Not Assessed	No GHS classification identified in Section 2. Substances identified are borate salts (0.1-1%) and diesel (0.1-1%).Borate salts: Acute 96-h LC50 for fish are >100 mg/L; 48-h EC50 for invertebrates are >100 mg/L. Diesel: LC50 for fish = 35 mg/L and an LL50 (96h) of 21 mg/L (*Oncorhynchus mykiss*); 48-h EL50 for Daphnia magna is 210 mg/L.
	Proppant 2	Not Assessed	This product is proppant. No applicable toxicity data.
	Scale Inhibitor 1	Not Assessed	No GHS classification is identified in Section 2. Substances identified are ethylene glycol (10-30%) and methanol (0.1-1%). Acute LC50s for fish and invertebrates exposed to ethylene glycol are >100 mg/L. Acute toxicity is not expected. Also, SDS Section 12 indicates that this product has no known ecotoxicological effects
	Oil Tracer 1	No Acute Classification	Chronic toxicity identified in SDS Section 2 only; an acute classification was not identified.
	Defoamer 5	Not Assessed	No GHS classification was identified in Section 2. There was no information on composition or aquatic toxicity. SDS Section 12 indicates that the environmental impact of this product has not been fully investigated.
	Diagnostic Additive 1	Not Assessed	No GHS classification was identified in Section 2. There was no information on composition or aquatic toxicity.
	Breaker 1	Acute 2	Identified in SDS Section 2.
	Fluid Additive 3	Not Assessed	No GHS classification was identified in Section 2. There was no information on composition or aquatic toxicity.
OD76	Crosslinker 1	Not Assessed	No GHS classification is provided in Section 2. Substances identified are borate salts (30-60%) and dipropylene glycol monomethyl ether (30-60%). Borate salts: Acute 96-h LC50 for fish are >100 mg/L; 48-h EC50 for invertebrates are >100 mg/L. Dipropylene glycol monomethyl ether: a NOEC of 0.5 mg/L was reported for Daphnia magna; no fish data are available.
	Stabilizer 1	Not Assessed	This product is identified in Section 2 as not classified. No composition or toxicity data are available.
	Fluid Additive 2	Not Assessed	No GHS classification identified in Section 2. Substances identified are borate salts (0.1-1%) and diesel (0.1-1%).Borate salts: Acute 96-h LC50 for fish are >100 mg/L; 48-h EC50 for invertebrates are >100 mg/L. Diesel: LC50 for fish = 35 mg/L and an LL50 (96h) of 21 mg/L (Oncorhynchus mykiss); 48-h EL50 for Daphnia magna is 210 mg/L.
	Proppant 2	Not Assessed	This product is proppant. No applicable toxicity data.

Table A7. GHS Acute Aquatic Toxicity
Classification of Chemical Products in Category III Effluents

TCW Sample	Product Code	GHS Acute/Chronic Aquatic Toxicity Category Classification	Notes
OD76	Scale Inhibitor 1	Not Assessed	No GHS classification is identified in Section 2. Substances identified are ethylene glycol (10-30%) and methanol (0.1-1%). Acute LC50s for fish and invertebrates exposed to ethylene glycol are >100 mg/L. Acute toxicity is not expected. Also, SDS Section 12 indicates that this product has no known ecotoxicological effects
	Oil Tracer 1	No Acute Classification	Chronic toxicity Identified in SDS Section 2 only; an acute classification was not identified.
	Defoamer 5	Not Assessed	No GHS classification was identified in Section 2. There was no information on composition or aquatic toxicity. SDS Section 12 indicates that the environmental impact of this product has not been fully investigated.
	Diagnostic Additive 1	Not Assessed	No GHS classification was identified in Section 2. There was no information on composition or aquatic toxicity.
	Breaker 1	Acute 2	Identified in SDS Section 2.
	Fluid Additive 3	Not Assessed	No GHS classification was identified in Section 2. There was no information on composition or aquatic toxicity.
TF74	Crosslinker 1	Not Assessed	No GHS classification is provided in Section 2. Substances identified are borate salts (30-60%) and dipropylene glycol monomethyl ether (30-60%). Borate salts: Acute 96-h LC50 for fish are >100 mg/L; 48-h EC50 for invertebrates are >100 mg/L. Dipropylene glycol monomethyl ether: a NOEC of 0.5 mg/L was reported for Daphnia magna; no fish data are available.
	Stabilizer 1	Not Assessed	This product is identified in Section 2 as not classified. No composition or toxicity data are available.
	Fluid Additive 2	Not Assessed	No GHS classification identified in Section 2. Substances identified are borate salts (0.1-1%) and diesel (0.1-1%).Borate salts: Acute 96-h LC50 for fish are >100 mg/L; 48-h EC50 for invertebrates are >100 mg/L. Diesel: LC50 for fish = 35 mg/L and an LL50 (96h) of 21 mg/L (Oncorhynchus mykiss); 48-h EL50 for Daphnia magna is 210 mg/L.
	Proppant 2	Not Assessed	This product is proppant. No applicable toxicity data.
	Scale Inhibitor 1	Not Assessed	No GHS classification is identified in Section 2. Substances identified are ethylene glycol (10-30%) and methanol (0.1-1%). Acute LC50s for fish and invertebrates exposed to ethylene glycol are >100 mg/L. Acute toxicity is not expected. Also, SDS Section 12 indicates that this product has no known ecotoxicological effects

Table A7. GHS Acute Aquatic Toxicity
Classification of Chemical Products in Category III Effluents

TCW Sample	Product Code	GHS Acute/Chronic Aquatic Toxicity Category Classification	Notes
TF74	Oil Tracer 1	No Acute Classification	Chronic toxicity Identified in SDS Section 2; an acute classification was not identified.
	Defoamer 5	Not Assessed	No GHS classification was identified in Section 2. There was no information on composition or aquatic toxicity. SDS Section 12 indicates that the environmental impact of this product has not been fully investigated.
	Diagnostic Additive 1	Not Assessed	No GHS classification was identified in Section 2. There was no information on composition or aquatic toxicity.
	Breaker 1	Acute 2	Identified in SDS Section 2.
	Fluid Additive 3	Not Assessed	No GHS classification was identified in Section 2. There was no information on composition or aquatic toxicity.
JH68	Clay stabilizer 3	Not Assessed	No GHS classification was identified in the SDS. Information on composition: Ammonium chloride (1-5%). No toxicity data provided.
	Acid 4	Not Assessed	No GHS classification was identified in the SDS Section 2. Composition information: Hydrochloric acid (10-30%). Toxicity data for hydrochloric acid only: LC50 282 mg/L (*Gambusia affinis*) LC50 20.5 mg/L (*Lepomis macrochirus*) LC50 (96h) 3.25 – 3.5 (pH) (*Lepomis macrochirus*); EC50 (48h) 4.9 (pH) (*Daphnia magna*)
	Biocide 6	Not Assessed	No GHS classification provided in the SDS. Composition information:2,2 Dibromo-3-nitrilopropionamide (60 - 100%); 2-Monobromo-3-nitrilopropionamide (1 - 5%). Toxicity data provided in SDS Section 12: Acute Fish Toxicity: May be toxic to aquatic life. TLM96: 2.3 mg/l (*Oncorhynchus mykiss*) TLM96: 3.4 mg/l (*Cyprinodon variegatus*) TLM96: 2.3 mg/l (*Lepomis macrochirus*). Acute Crustaceans Toxicity: TLM: 0.72 ppm (*Americamysis bahia*) LC50: 0.37 ppm (*Crassostrea virginica*)
	Biocide 7	Not Assessed	No GHS classification was identified in the SDS Section 2. Composition information:2-Bromo-2-nitro-1,3-propanediol (60-100%); Toxicity information: Acute Fish Toxicity: TLM96: 41 ppm (*Oncorhynchus mykiss*) TLM96: 36 ppm (*Lepomis macrochirus*) LC50 (96): 58 ppm (*Pimephales promelas*) Acute Crustaceans Toxicity: TLM48: 1.4 ppm (*Daphnia magna)* TLM96: 5.9 ppm (*Americamysis bahia*).
	Solvent 2	Not Assessed	No GHS classification provided in SDS. Composition information: Ammonium chloride (5 - 10%); Acetic acid (10 - 30%). No toxicity data available.
	Acid 5	Not Assessed	No GHS classification provided in SDS Section 2. Composition information: Acetic anhydride (60 - 100%); Acetic acid (30-60%). Toxicity information: Acetic anhydride: LC50 (96h) >300.82 mg/L (*Danio rerio*) LC50 (24h) 55 mg/L (*Daphnia magna*).
	Iron Control 1	Not Assessed	No GHS classification provided in SDS Section 2. Composition information: Citric acid (60-100%). Toxicity information for citric acid: LC50 (96h) 1516 mg/L (*Lepomis macrochirus*) LC50 (48h) 440 mg/L (*Leuciscus idus melanotus*) LC50 (96h) >100 mg/L (*Pimephales promelas*); TLM96 100-330 ppm (*Crangon crangon*) EC50 (24h) 1535 mg/L (*Daphnia magna*) LC50 (48h) 160 mg/L (*Daphnia magna*) EC50 (48h) >50 mg/L (*Daphnia magna*).
	Iron Control 2	Not Assessed	No GHS classification provided in SDS Section 2. Not composition information provided. No toxicity information provided, although SDS Section 12 indicates that the product is not classified as hazardous to the environment.
	Corrosion inhibitor 3	Acute 1	Identified in SDS Section 2.

Table A7. GHS Acute Aquatic Toxicity
Classification of Chemical Products in Category III Effluents

TCW Sample	Product Code	GHS Acute/Chronic Aquatic Toxicity Category Classification	Notes
JH68	Intensifier 1	Not Assessed	No GHS classification provided in SDS Section 2. Composition information: Potassium iodide (60-100%). Toxicity information for potassium iodide: LC50 (96h) 896 mg/L (*Oncorhynchus mykiss*) LC50 (96h) 3780 mg/L (*Oncorhynchus mykiss*) (similar substance) LC100 (22d) 166,002.8 mg/L (*Oncorhynchus mykiss*); EC50 (48h) 7.5 mg/L (*Daphnia magna*) LC50 (48h) 575 mg/L (*Acartia tonsa*) EC50 (10d) 218.8 mg/L (*Corophium volutator*).
	pH Control 1	Not Assessed	No GHS classification is provided in Section 2. Substances identified are sodium carbonate (60-100%). Toxicity data for sodium carbonate are: TLM24 385 mg/L (*Lepomis macrochirus*) LC50 310-1220 mg/L (*Pimephales promelas*) LC50 (96h) 300 mg/L (*Lepomis macrochirus*); EC50 265 mg/L (*Daphnia magna*) EC50 (48h) 200 – 227 mg/L (*Ceriodaphnia sp* .)
	Solvent 3	Not Assessed	No GHS classification is provided in Section 2. Substances identified are Hydroxyacetic acid (10-30%) and Hydrofluoric acid (1-5%). Toxicity data for Hydroxyacetic acid: LC50 (96h) 164 mg/L (*Pimephales promelas*); EC50 (48h) 114 mg/L (*Daphnia magna*) EC50 (48h) 58.5 mg/L (*Acartia tonsa*). Toxicity data for Hydrofluoric acid: EC50 (96h) 51 mg/L (*Oncorhynchus mykiss*) NOEC (21d) 4 mg/L (*Oncorhynchus mykiss*); EC50 (48h) 26.48 mg/L (*Daphnia magna*) EC50 (120h) 20 mg/L (Perna perna) NOEC (21d) 3.7 mg/L (*Daphnia magna*).
	Solvent 4	Acute 2	Identified in SDS Section 2.

Table A8. Compilation of Acute Toxicity Data for Produced Water Effluents.

Reference	Sample ID	Sample Size	Species Scientific Name	Species Common Name	Observed Exposure Duration (hours)	Endpoint	L(E)C50	Concentration Units	Concentration	Arithmetic Mean Concentration	Maximum Concentration	Concentration Range
See note [1]	--	412	*Americamysis bahia*	Mysid	96	Mortality (%)	LC50	% PW	--	10.8	86.3	Not cited
		359	*Cyprinodon variegatus*	Sheepshead minnow	96	Mortality (%)	LC50	% PW	--	19.2	>100	Not cited
See note [2]	--	24	*Americamysis bahia*	Mysid	96; daily renewal	Not cited	EC50	% PFW	--	7.08	Not cited	Not cited
		~400	*Americamysis bahia*	Mysid	96; daily renewal	Not cited	LC50	%PFW	--	10.05	Not cited	Not cited
		24	*Americamysis bahia*	Mysid	168; daily renewal	Not cited	EC50	% PFW	--	5.77	Not cited	Not cited
		23	*Cyprinodon variegatus*	Sheepshead minnow	96; daily renewal	Not cited	EC50	% PFW	--	21.55	Not cited	Not cited
		~400	*Cyprinodon variegatus*	Sheepshead minnow	96; daily renewal	Not cited	LC50	% PFW	--	19.21	Not cited	Not cited
		23	*Cyprinodon variegatus*	Sheepshead minnow	168; daily renewal	Not cited	EC50	% PFW	--	19.72	Not cited	Not cited
See note [3]	--	241[a]	*Americamysis bahia*	Mysid	96	Mortality (%)	LC50	% PW	--	12.1	100	0.05 - 100
		239	*Cyprinodon variegatus*	Sheepshead minnow	96	Mortality (%)	LC50	% PW	--	27.4	100	1.17 - 100

Table A8. Compilation of Acute Toxicity Data for Produced Water Effluents.

Reference	Sample ID	Sample Size	Species Scientific Name	Species Common Name	Observed Exposure Duration (hours)	Endpoint	L(E)C50	Concentration Units	Concentration	Arithmetic Mean Concentration	Maximum Concentration	Concentration Range
See note [4]	PWS-LA3	1 (initial WET test)	*Americamysis bahia*	Mysid	24; static acute test	Mortality (%)	LC50	% PW	17	--	--	--
	PWS-LA6	1 (initial WET test)	*Americamysis bahia*	Mysid	24; static acute test	Mortality (%)	LC50	% PW	6	--	--	--
		1 (baseline WET test)	*Americamysis bahia*	Mysid	24; static acute test	Mortality (%)	LC50	% PW	6	--	--	--
	PWS-LA7	1 (initial WET test)	*Americamysis bahia*	Mysid	24; static acute test	Mortality (%)	LC50	% PW	5	--	--	--
		1 (baseline WET test)	*Americamysis bahia*	Mysid	24; static acute test	Mortality (%)	LC50	% PW	34	--	--	--
See note [5]	Sample 1	1	*Menidia beryllina*	Inland silverside minnow	48; acute static test	Mortality (%)	LC50	% PW	0.19	--	--	0.15 - 0.23
	Sample 1	1	*Americamysis bahia*	Mysid	48; acute static test	Mortality (%)	LC50	% PW	0.09	--	--	0.08 - 0.11
	Sample 2	1	*Americamysis bahia*	Mysid	48; acute static test	Mortality (%)	LC50	% PW	4.89	--	--	4.26 - 5.61
	Sample 3	1	*Americamysis bahia*	Mysid	48; acute static test	Mortality (%)	LC50	% PW	0.21	--	--	--
	Sample 4	1	*Menidia beryllina*	Inland silverside minnow	48; acute static test	Mortality (%)	LC50	% PW	0.21	--	--	0.19 - 0.24
	Sample 4	1	*Americamysis bahia*	Mysid	48; acute static test	Mortality (%)	LC50	% PW	0.15	--	--	0.13 - 0.17
	Sample 5	1	*Americamysis bahia*	Mysid	48; acute static test	Mortality (%)	LC50	% PW	3.54	--	--	2.5 - 5

References:

[1]. Neff, J.M. 2002. Bioaccumulation in Marine Organisms. Effects of Contaminants from Oil Well Produced Water; Elsevier Science Publishers, Amsterdam. 452 pp. Data collected from the Gulf of Mexico (near Lousiana)

[2]. Moffitt, C.M., Rhea, M.R., Dorn, P.B., Hall, J.F., Bruney, J.M. 1992.Short-term chronic toxicity of produced water and its variability as a function of sample time and discharge rate.In: Ray, J.P.,Engelhardt, F.R. (Eds.), Produced Water: Technological/Environmental Issues and Solutions. Plenum Press, New York, pp. 235–244. Western Outer Continental
Shelf, Gulf of Mexico. Presented as acute toxicity data in Holdway, A. 2002. The acute and chronic effects of wastes associated with offshore oil and gas production on temperate and tropical marine ecological processes. Marine Pollution Bulletin 44 (2002) 185–203.

[3].Meinhold, A.F., Holtzman,S., and DePhillips, M.P. 1996. Produced water discharges to the Gulf of Mexico: Background information for ecological risk assessment.Brookhaven National Laboratory; Biomedical and Environmental Assessment Group. Gulf of Mexico DMR data from Louisiana Department of Environmental Quality (LDEQ). Avanti Corporation (1992); "Louisiana DEQ Water Quality Data Includes Water Quality Analyses for Bays and Lakes, PW Toxicity Database, Summary of PW Pollutant Concentrations" In a Facsimile (FAX) from Lynn Bowler to Ken Huffman of USEPA Region 6.

[4].Sauer, T.C., Costa, H.J., Brown, J.S., and Ward, T.J. 1997. Toxicity Identification Evaluations of Produced-Water Effluents.Environmental Toxicology and Chemistry, Vol. 16, No. 10, pp. 2020–2028. Sample PWS-LA3; Gulf of Mexico - Offshore Louisiana; Salinity = 42 ppt; Oil production well; EB, REB, SI, GTC. Very low toxicity on day 1; toxicity completely lost by day 2. Cause of toxicity could not be identified.Sample PWS-LA6; Gulf of Mexico - Offshore Louisiana; Salinity = 230 ppt; Gas production well; EB, PCC, GTC. PW LC50 near salinity tolerance of test species; DO decreased in test medium; extremely high salinity; ionic imbalance (calcium); ammonia 162 mg/L. Ammonia and salinity were determined to be cause of toxicity. Sample PWS-LA7; Gulf of Mexico - Coastal Louisiana; Salinity = 59 ppt; Gas production well; CI. Toxicity was lost by Day 2 and the cause of toxicity could not be identified.

[5] Environmental Enterprises USA, Inc. 2020. 48-h acute WET test data for samples 1 through 5.

Notes:
EB; emulsion breaker
REB; reverse emulsion breaker
SI; scale inhibitor
GTC; gas-treating chemical
PCC; paraffin control chemical
CI; corrosion inhibitor (oil soluble)
EC50; median effects concentration
LC50; median lethal concentration
ppt; parts per thousand
PFW: produced formation water
PW; produced water
WET; whole effluent toxicity

Table A8. Compilation of Acute Toxicity Data for Produced Water Effluents.

[a] Avanti Corporation (1993); 96-h LC50 for the Mysid. "Louisiana DEQ Water Quality Data Includes Water Quality Analyses for Bays and Lakes, PW Toxicity Database, Summary of PW Pollutant Concentrations" In a Fax from Lynn Bowler to Ken Huffman of EPA Region 6. Raw data for the Mysid are:

LC50	< / >	Page	Entry
17.68		1	44
14.8		1	45
3.65		1	46
6.8		1	47
11.92		1	48
9.97		1	49
5.11		1	50
4.93	<	1	51
86.2	>	1	52
24.2		1	53
81.6	>	1	54
81.6	>	1	55
12.4		1	56
20.5		1	57
7.9		1	58
1.61		1	59
14.49		1	60
14.56		1	61
6.77		1	62
13.28		1	63
4.09		1	64
8.72		1	65
2.35		1	66
0.26		1	67
0.68		1	68
6.4		1	69
10.36		1	70
8.43		1	71
15.37		1	72
11.42		1	73
11.77		1	74
10.96		1	75
12.84		1	76
10.96		1	77
11.1		1	78
7.8		1	79
8.1		1	80
6.6		1	81
2.03		1	82
9.35		1	83
3.68		1	84

Table A8. Compilation of Acute Toxicity Data for Produced Water Effluents.

LC50	< / >	Page	Entry
10.91		2	85
5.26		2	86
5.43		2	87
3.9		2	88
20		2	89
12.9		2	90
5.27		2	91
4.91		2	92
12.24		2	93
13.93		2	94
53.79		2	95
12.5		2	96
50		2	97
1.6		2	98
7.9		2	99
6.7		2	100
7.6		2	101
8.88		2	102
6		2	103
9.6		2	104
11.67		2	105
8.22		2	106
3.49		2	107
3.47		2	108
9.76		2	109
20.16		2	110
15.4		2	111
8.1		2	112
2.49		2	113
5.12		2	114
2.94		2	115
6.25		2	116
1.71		2	117
11.02		2	118
12.1		2	119
2.31		2	120
2.31		2	121
13.51		2	122
11.56		2	123
1	<	2	124
1	<	2	125
1.29		2	126

Table A8. Compilation of Acute Toxicity Data for Produced Water Effluents.

LC50	< / >	Page	Entry
8.1		3	127
10.6		3	128
1.31		3	129
7.88		3	130
3.86		3	131
2.93		3	132
4.1		3	133
8		3	134
8		3	135
7.9		3	136
7.4		3	137
9.4		3	138
6.4		3	139
7		3	140
3.15		3	141
9.4		3	142
7.75		3	143
2.42		3	144
9.01		3	145
64.6		3	146
15.9		3	147
4.2		3	148
22.5		3	149
57.9		3	150
67.4		3	151
16.5		3	152
2.2		3	153
0.79		3	154
13.35		3	155
5.48		3	156
3.7	<	3	157
36.6		3	158
12.7		3	159
3.8		3	160
6.25	<	3	161
2.8		3	162
6.25	<	3	163
9.9		3	164
6.25	<	3	165
4.9	<	3	166
4.78		3	167
3.1		3	168
8.39		3	169
2.92		3	170
7.982		3	171
8.2		4	172
6.25	<	4	173

Table A8. Compilation of Acute Toxicity Data for Produced Water Effluents.

LC50	< / >	Page	Entry
13.1		4	174
10.3		4	175
100	>	4	176
5.75		4	177
20.5		4	178
14.95		4	179
22.3		4	180
12.25		4	181
3.79		4	182
0.048		4	183
12.84		4	184
7.12		4	185
12.38		4	186
3.39		4	187
4.82		4	188
0.96		4	189
0.91		4	190
4.88		4	191
3.61		4	192
7.15		4	193
0.18		4	194
4.8		4	195
4.86		4	196
3		4	197
2.5		4	198
3.9		4	199
9.35		4	200
13.51		4	201
12.3		4	202
5.5		4	203
8.8		4	204
3.8		4	205
12.3		4	206
100	>	4	207
9.43		4	208
17.81		4	209

Table A8. Compilation of Acute Toxicity Data for Produced Water Effluents.

LC50	< / >	Page	Entry
23.41		4	210
10.9		4	211
16.26		4	212
100	>	4	213
11.3		4	214
13.67		5	1
3.54		5	2
11.1		5	3
6.25	<	5	4
11.8		5	5
8.49		5	6
10.41		5	7
15.84		5	8
10.24		5	9
7.7		5	10
4.73		5	11
6.7		5	12
7.9		5	13
3.9		5	14
8.65		5	15
5.41		5	16
83.3	>	5	17
13.6		5	18
9.53		5	19
10.91		5	20
2.9		5	21
8.24		5	22
11.93		5	23
8.04		5	24
13.9		5	25
8.54		5	26
10.17		5	27
6.18		5	28
20.28		5	29
13.02		5	30
1.95		5	31
5.3		5	32
6.97		5	33
9.32		5	34
0.9	<	5	35
9.18		5	36
3.35		5	37
3.68		5	38
5		5	39
6.25		5	40
10.53		5	41
3.87		5	42

LC50	< / >	Page	Entry
4.3		5	43
4.24		6	215
4.98		6	216
12.7		6	217
13.07		6	218
16.97		6	219
10.14		6	220
3.54		6	221
2.26		6	222
14.74		6	223
5.89		6	224
8.806		6	225
12.84		6	226
4.76		6	227
1.26		6	228
13.51		6	229
16.45		6	230
13.36		6	231
6.125		6	232
17.05		6	233
8.6		6	234
26.1		6	235
10.6		6	236
26.1		6	237
12.82		6	238
16.2		6	239
6.99		6	240
15.14		6	241
12.1	AVG		
16.37	STD		
0.048	MIN		
100	MAX		
8.2	MED		
241	COUNT		

Table A9. Acute Aquatic Life Ecological Screening Values

Constituent	Units	Priority Pollutant?	Published/Promulgated USEPA ESVs		*Americamysis bahia*-specific 48-h LC50s for Ions			*Menidia beryllina*-specific 48-h LC50s for Ions		
			Acute ESV (mg/L)	Acute ESV Source	Ion Deficiency	Ion Excess	Source	Ion Deficiency	Ion Excess	Source
Critical Effluent Dilution	%	--	--	--	--	--	--	--	--	--
Date	--	--	--	--	--	--	--	--	--	--
Water Quality Parameters (Total)										
Hardness (as CaCO3)	mg/L	No	--	--	--	--	--	--	--	--
Alkalinity, Total (As CaCO3)	mg/L	No	No published / promulgated Acute Saltwater ESV	--	--	--	--	--	--	--
HCO_3^- (Estimated as 1.22 * Total Alk.)	mg/L	No	No published / promulgated Acute Saltwater ESV	--	--	1090	Pillard et al., 2000	--	670	Pillard et al., 2000
Total Suspended Solids (Residue, Non-Filterable)	mg/L	No	--	--	--	--	--	--	--	--
Nitrogen, Ammonia (As N)[1]	mg/L	No	5	USEPA. 1989. NRALC Ammonia (Saltwater): Acute CMC: pH = 8; Temp. 25 Deg. C; and salinity = 30 ppt[1]	--	--	--	--	--	--
Chemical Oxygen Demand	mg/L	No	--		--	--	--	--	--	--
Organic Carbon, Total	mg/L	No	--	--	--	--	--	--	--	--
Sulfide	mg/L	No	No published / promulgated Acute Saltwater ESV	--	--	--	--	--	--	--
Specific Gravity										
Water Quality Parameters (Dissolved)										
Total Dissolved Solids (Residue, Filterable)	mg/L	No	--	--	--	--	--	--	--	--
Dissolved Organic Carbon	mg/L	No	--	--	--	--	--	--	--	--
Metals (Total)										
As	mg/L	Yes	0.069	USEPA NRALC: Saltwater	--	--	--	--	--	--
Ba	mg/L	No	No published / promulgated Acute Saltwater ESV	--	--	--	--	--	--	--
Cd	mg/L	Yes	0.0402	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Ca	mg/L	No	No published / promulgated Acute Saltwater ESV	--	100	1100	Pillard et al., 2000	10	4610	Pillard et al., 2000
Cr	mg/L	Yes	0.515	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Cu	mg/L	Yes	0.0056	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Pb	mg/L	Yes	0.22	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Mg	mg/L	No	No published / promulgated Acute Saltwater ESV	--	--	2650	Pillard et al., 2000	--	2800	Pillard et al., 2000
Hg	mg/L	Yes	0.0018	USEPA NRALC: Saltwater	--	--	--	--	--	--
Ni	mg/L	Yes	0.075	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--

Table A9. Acute Aquatic Life Ecological Screening Values

Constituent	Units	Priority Pollutant?	Published/Promulgated USEPA ESVs		*Americamysis bahia* -specific 48-h LC50s for Ions			*Menidia beryllina* -specific 48-h LC50s for Ions		
			Acute ESV (mg/L)	Acute ESV Source	Ion Deficiency	Ion Excess	Source	Ion Deficiency	Ion Excess	Source
K	mg/L	No	No published / promulgated Acute Saltwater ESV	--	115	790	Pillard et al., 2000	--	1100	Pillard et al., 2000
Se	mg/L	Yes	0.29	USEPA NRALC: Saltwater	--	--	--	--	--	--
Na	mg/L	No	No published / promulgated Acute Saltwater ESV	--	--	--	--	--	--	--
Tl	mg/L	Yes	0.71	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Zn	mg/L	Yes	0.092	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Metals (Dissolved)										
As	mg/L	Yes	0.069	USEPA NRALC: Saltwater	--	--	--	--	--	--
Ba	mg/L	No	No published / promulgated Acute Saltwater ESV	--	--	--	--	--	--	--
Cd	mg/L	Yes	0.033	USEPA NRALC: Saltwater	--	--	--	--	--	--
Ca	mg/L	No	No published / promulgated Acute Saltwater ESV	--	100	1100	Pillard et al., 2000	--	4610	Pillard et al., 2000
Cr	mg/L	Yes	0.515	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Cu	mg/L	Yes	0.0048	USEPA NRALC: Saltwater	--	--	--	--	--	--
Pb	mg/L	Yes	0.14	USEPA NRALC: Saltwater	--	--	--	--	--	--
Mg	mg/L	No	No published / promulgated Acute Saltwater ESV	--	--	2650	Pillard et al., 2000	--	2800	Pillard et al., 2000
Hg	mg/L	Yes	0.0018	USEPA NRALC: Saltwater	--	--	--	--	--	--
Ni	mg/L	Yes	0.074	USEPA NRALC: Saltwater	--	--	--	--	--	--
K	mg/L	No	--	--	115	790	Pillard et al., 2000	--	1100	Pillard et al., 2000
Se	mg/L	Yes	0.29	USEPA NRALC: Saltwater	--	--	--	--	--	--
Na	mg/L	No	No published / promulgated Acute Saltwater ESV	--	--	--	--	--	--	--
Tl	mg/L	Yes	0.71	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Zn	mg/L	Yes	0.09	USEPA NRALC: Saltwater	--	--	--	--	--	--
Inorganic Anions (Total)										
Br	mg/L	No	No published / promulgated Acute Saltwater ESV	--	--	7990	Pillard et al., 2000	--	18300	Pillard et al., 2000

Table A9. Acute Aquatic Life Ecological Screening Values

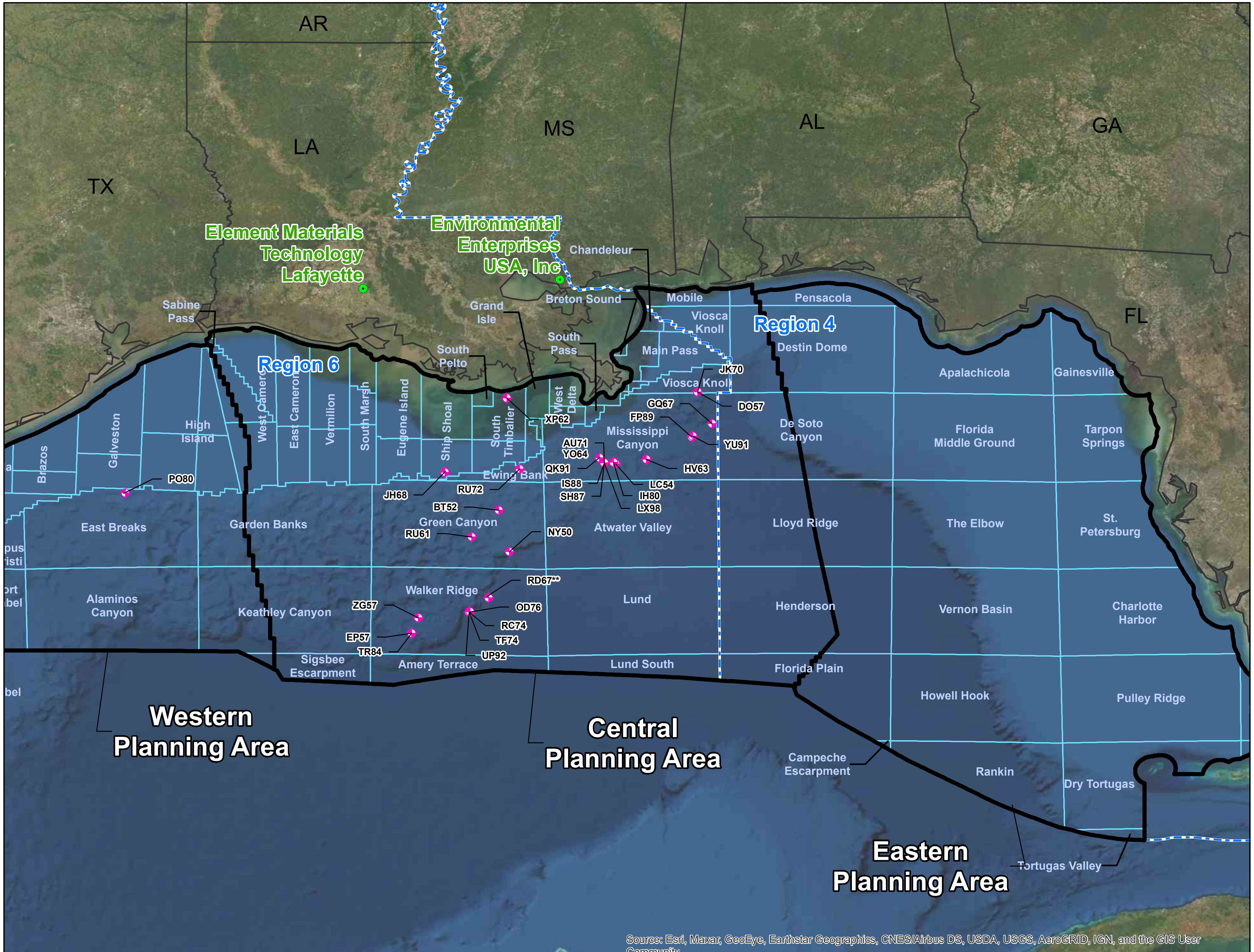
Constituent	Units	Priority Pollutant?	Published/Promulgated USEPA ESVs		*Americamysis bahia* -specific 48-h LC50s for Ions			*Menidia beryllina* -specific 48-h LC50s for Ions		
			Acute ESV (mg/L)	Acute ESV Source	Ion Deficiency	Ion Excess	Source	Ion Deficiency	Ion Excess	Source
Inorganic Anions (Total)										
Cl	mg/L	No	No published / promulgated Acute Saltwater ESV	--	--	--	--	--	--	--
SO_4^{2-}	mg/L	No	No published / promulgated Acute Saltwater ESV	--	--	16710	Pillard et al., 2000	--	26710	Pillard et al., 2000
Polycyclic Aromatic Hydrocarbons (PAHs)										
Acenaphthene	mg/L	Yes	0.32	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Acenaphthylene	mg/L	Yes	0.291	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Anthracene	mg/L	Yes	0.0018	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Benzo(a)anthracene	mg/L	Yes	0.0046	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Benzo(a)pyrene	mg/L	Yes	0.00064	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Benzo(b)fluoranthene	mg/L	Yes	0.0014	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Benzo(g,h,i)perylene	mg/L	Yes	0.00019	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Benzo(k)fluoranthene	mg/L	Yes	0.0013	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Chrysene	mg/L	Yes	0.0042	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Dibenzo(a,h)anthracene	mg/L	Yes	0.00028	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Fluoranthene	mg/L	Yes	0.0034	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Fluorene	mg/L	Yes	0.082	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Indeno(1,2,3-cd)pyrene	mg/L	Yes	0.00027	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Naphthalene	mg/L	Yes	0.78	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Phenanthrene	mg/L	Yes	0.0077	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--
Pyrene	mg/L	Yes	0.00045	USEPA Region IV ESV: Saltwater	--	--	--	--	--	--

Notes:
CMC; criteria maximum concentration
ESV; ecological screening value
h; hour
LC50; 50% lethal concentration
NRALC; National Recommended Aquatic Life Criteria
USEPA; Unites States Environmental Protection Agency
mg/L; milligrams per liter

[1].

Source	pH (S.U.)	Salinity (ppt)	Temp. (˚C)
Maximum of Laboratory Control	7.9	26	26
Closest Values in USEPA 1989	8	30	25

Appendix Figures



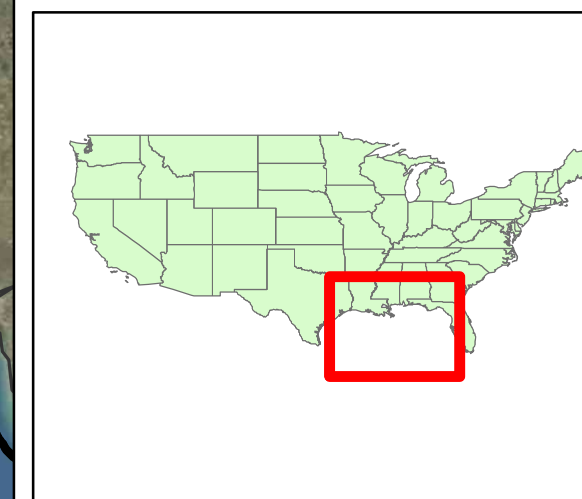
Legend

- Laboratory Locations
- Sample Locations
- Gulf of Mexico Planning Areas
- Outer Continental Shelf Official Protraction Areas
- USEPA Region Boundaries

Note:
RD67** - The location of this sample is approximate.

IH80 - After collecting sample IH80, the Operator determined that the sample was not discharged to GOM surface water. This sample was therefore not representative of TCW discharges.

References:
-USEPA Region Boundaries Exclusive Economic Zone (EPA, 2012)
-BOEM Planning Areas (BOEM, Oct 2017)
-Protraction Areas (BOEM, July 2015)



AECOM

Figure A1
TCW Effluent Sample Locations

Final Report: Joint Industry Project Study of Treatment, Completion, and Workover (TCW) Effluents

Gulf of Mexico: Western and Central Planning Regions
USEPA Region 4 NPDES General Permit No. GEG460000
USEPA Region 6 NPDES General Permit No. GMG290000

Prepared By: NAB	Checked By: JJP
Job Number: 60577789	Date: 6/24/2021

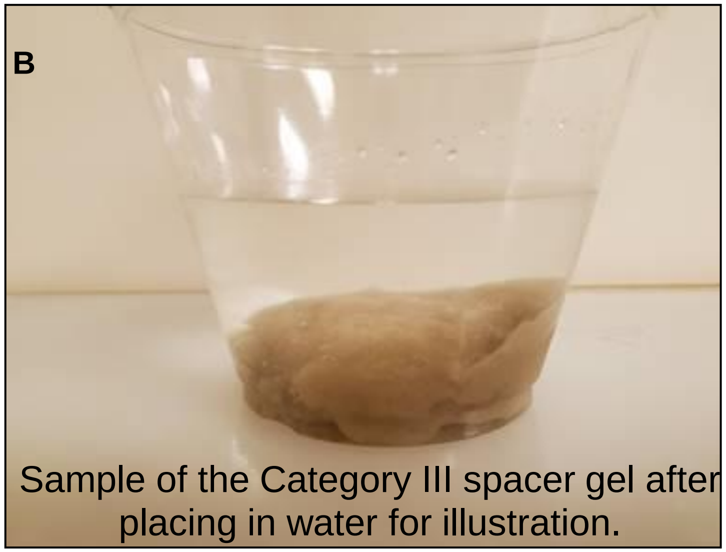
Document Path: Z:\Projects\IMS\USEPA\Gulf of Mexico\Maps\GOM_Fig_X_TCW_Effluent_Sample_Locations_02092021.mxd

Figure A2. Photographs of TCW Category III Gels

A

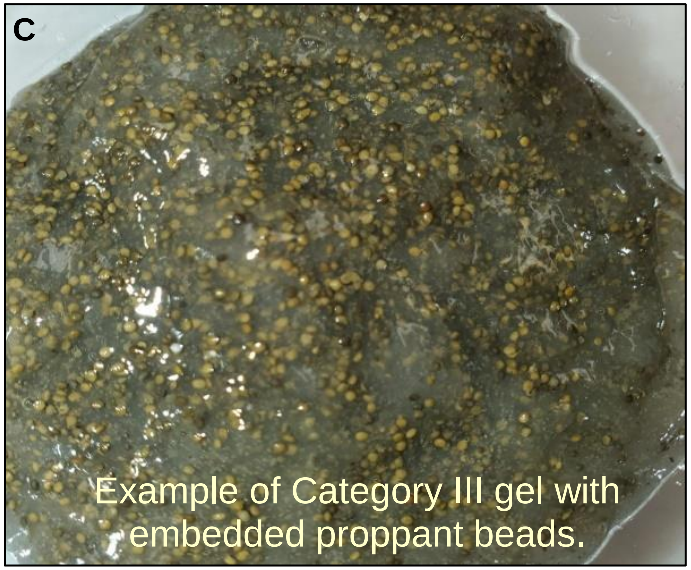
Sample of a Category III spacer gel.

B



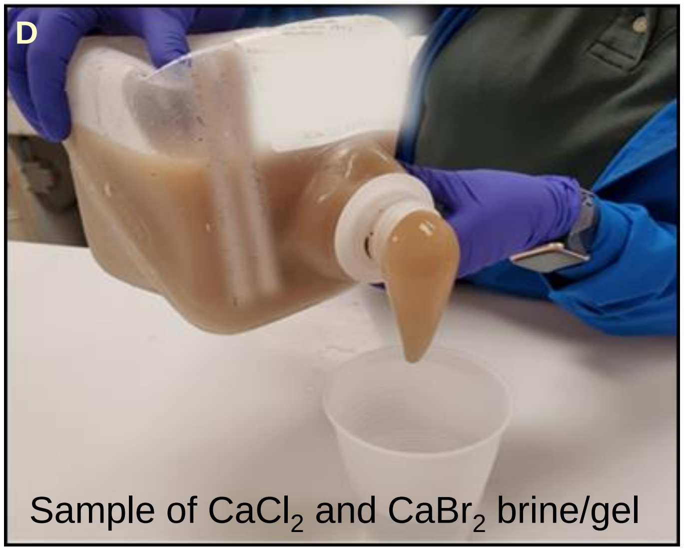
Sample of the Category III spacer gel after placing in water for illustration.

C



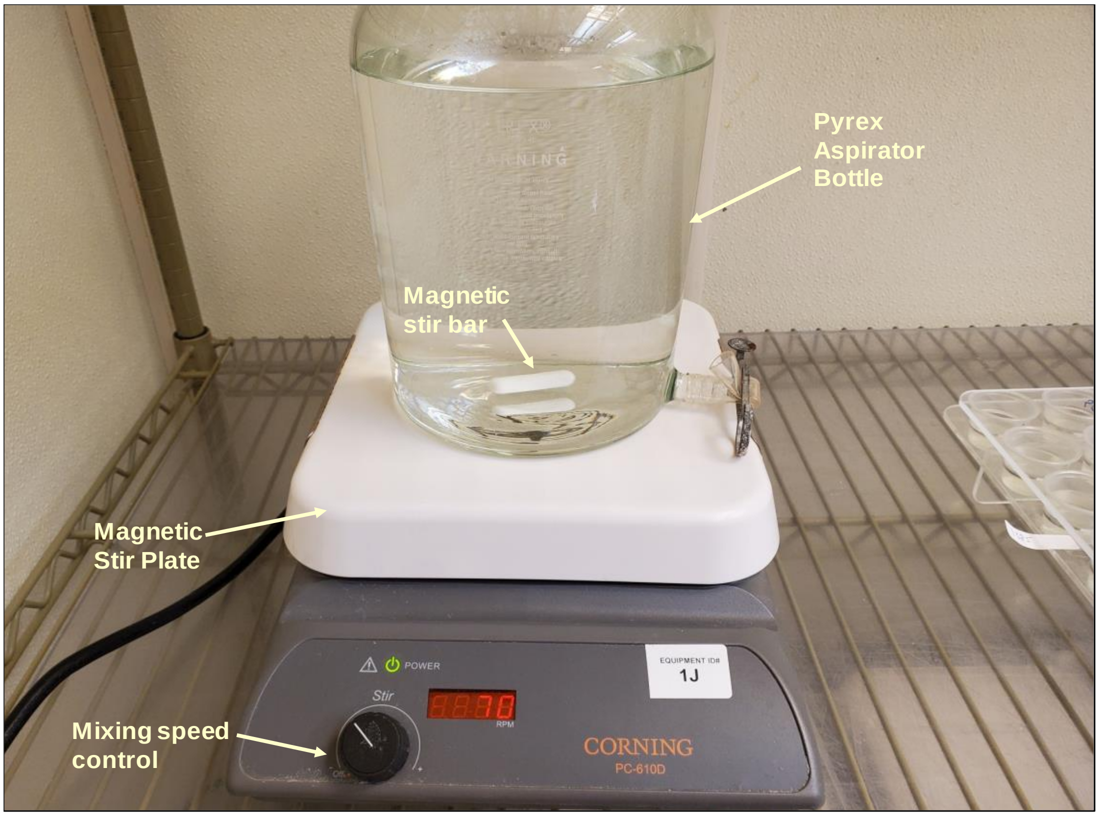
Example of Category III gel with embedded proppant beads.

D



Sample of $CaCl_2$ and $CaBr_2$ brine/gel

Figure A3. Mixing Apparatus for TCW Category III Gel Samples



Appendices

Appendix A

JIP Study Participant Survey Questionnaire Form

Job Number:
Historical, Existing or Planned?
Date or Anticipated Start Date:
SECTION 1. General Information
1. Contact Name:
2. Telephone Number:
3. Email:
4. Lease:
5. Field:
6. Operator Field:
7. Area:
8. Block:
9. API Well Number:
10. Latitude:
11. Longitude:
12. Permitted Feature Number (if available)
13. Water Column Depth:
SECTION 2. Treatment Completion and Workover (TCW) Fluids
1. What type of well treatment or workover operation is conducted? Please provide a brief description:
2. What types of TCW fluids are used?
a. Category I
b. Category II
c. Category III
d. Category IV
e. Other:
3. Are there jobs where one, or a combination of TCW fluid categories are discharged to surface waters? If yes, proceed to Section 3.
SECTION 3. Discharge of TCW Wastewaters to Surface Water
1. Are TCW wastewaters commingled and discharged as part of produced water?
2. Are TCW wastewaters discharged directly to surface water without treatment or storage in a tank?
a. If yes, is a NPDES-designated discharge point used, e.g., pipe?
b. What is the pipe diameter (inches)?
3. Are TCW wastewaters discharged to a tank on the Facility and then discharged overboard?
a. If yes, is a NPDES-designated discharge point used, e.g., pipe?
b. What is the pipe diameter (inches)?
4. Are TCW wastewaters discharged via a hose off the tank?
a. If yes, what is the hose diameter (inches)?
5. Are the TCW wastewaters discharged above the ocean surface?
a. If yes, at what height above the water column does the discharge occur?
b. If no, at what water column depth does the discharge occur?
6. Typically, how often are TCW wastewaters discharged, e.g., once a week, quarterly?
7. Typically, what is the duration of the discharge (minutes/hours)?
8. Are TCW wastewaters discharged back to the Facility and passed through a filtration system before discharging overboard?
a. Do you use a designated discharge point such as a pipe, if so, what is the diameter (in.)?
b. Do you use a hose off of the Filtration system, if so what is the diameter (in.)?
c. Are wastewaters discharged via any other structure, e.g., diffuser? If yes, please describe:
9. Is any other treatment of TCW wastewaters conducted? If yes, please describe:

SECTION 4. Discharge of Other Wastewaters (Zinc Bromide; Acid Jobs; Chemical Additives) to Surface Water
1. Are zinc bromide wastewaters sent onshore for disposal?
a. If no, how are zinc bromide wastewaters disposed?
b. Other:
2. **Applicable to TCW jobs only**: Are acid jobs conducted? If yes, how are acidic wastewaters treated?
a. Do you send onshore for disposal?
b. Do you discharge acid job wastewaters directly overboard without treatment?
c. Do you neutralize the pH and then discharge overboard?
d. Other:
3. **Applicable to TCW jobs only**: Is there the potential for corrosion inhibitors, deemulsifiers, surfactants, defoamers, or biocides to be comingled with TCW wastewaters? If yes, please identify the type:
a. Corrosion inhibitor:
b. Deemulsifier:
c. Surfactants:
d. Defoamers:
e. Biocides:
f. Other:

Appendix B

Raw Output for Latin Hypercube Sampling Evaluation

Appendix B.1. Characteristics of TCW Discharges Selected by LHS

Area		Mississippi Canyon	Green Canyon	Mississippi Canyon	Mississippi Canyon
Block		392	640	807	809
Water Column Depth (ft.)		7210	4250	2940	3650
Anticipated TCW Fluid Category[1]	I	1	1	1	1
	II	0	1	1	1
	III	0	1	1	1
	IV	0	1	0	0
Treatment Type	No Treatment/Tank Storage	0	0	0	0
	Tank Storage	1	1	1	0
	Filtration	1	0	0	0
	Other Treatment	0	0	0	0
Type of Chemical Additives	Corrosion Inhibitor	0	0	1	0
	De-emulsifier	1	1	1	0
	Surfactants	1	1	1	0
	Defoamers	1	0	1	0
	Biocides	1	1	1	0

Notes:
A "0" indicates the variable was absent; a "1" indicates the variable was present.
[1] Category II and IV effluents were not discharged to Gulf of Mexico surface waters during the Year 1 study.

Area		Mississippi Canyon	Mississippi Canyon	Ewing Bank	Mississippi Canyon
Block		437	807	873	807
Water Column Depth (ft.)		7344	2940	773	2940
Anticipated TCW Fluid Category[1]	I	1	1	1	1
	II	0	1	1	1
	III	0	1	1	1
	IV	0	0	0	0
Treatment Type	No Treatment/Tank Storage	0	0	0	0
	Tank Storage	1	1	1	1
	Filtration	0	0	0	0
	Other Treatment	1	0	0	0
Type of Chemical Additives	Corrosion Inhibitor	0	1	0	1
	De-emulsifier	1	1	0	1
	Surfactants	1	1	0	1
	Defoamers	1	1	0	1
	Biocides	1	1	0	1

Notes:

A "0" indicates the variable was absent; a "1" indicates the variable was present.

[1] Category II and IV effluents were not discharged to Gulf of Mexico surface waters during the Year 1 study.

Appendix B.1. Characteristics of TCW Discharges Selected by LHS

Area		Walker Ridge	Walker Ridge	Green Canyon	Mississippi Canyon
Block		29	508	338	392
Water Column Depth (ft.)		5190	9558	3330	7210
Anticipated TCW Fluid Category[1]	I	1	1	1	1
	II	1	1	1	0
	III	1	1	1	0
	IV	1	0	1	0
Treatment Type	No Treatment/Tank Storage	0	0	0	0
	Tank Storage	1	1	0	1
	Filtration	0	0	0	1
	Other Treatment	0	0	0	0
Type of Chemical Additives	Corrosion Inhibitor	0	1	1	0
	De-emulsifier	1	1	1	1
	Surfactants	1	1	1	1
	Defoamers	0	1	1	1
	Biocides	1	1	1	1

Notes:
A "0" indicates the variable was absent; a "1" indicates the variable was present.
[1] Category II and IV effluents were not discharged to Gulf of Mexico surface waters during the Year 1 study.

Appendix B.1. Characteristics of TCW Discharges Selected by LHS

Area		Mississippi Canyon	Green Canyon	Green Canyon	Mississippi Canyon
Block		809	824	825	807
Water Column Depth (ft.)		3600	4976	4976	3030
Anticipated TCW Fluid Category[1]	I	1	1	1	1
	II	1	0	0	1
	III	1	1	1	1
	IV	0	1	1	0
Treatment Type	No Treatment/Tank Storage	0	1	1	0
	Tank Storage	0	0	0	1
	Filtration	0	0	0	0
	Other Treatment	0	0	0	0
Type of Chemical Additives	Corrosion Inhibitor	0	1	1	1
	De-emulsifier	0	0	0	1
	Surfactants	0	1	1	1
	Defoamers	0	1	1	1
	Biocides	0	1	1	1

Notes:

A "0" indicates the variable was absent; a "1" indicates the variable was present.

[1] Category II and IV effluents were not discharged to Gulf of Mexico surface waters during the Year 1 study.

Area		Mississippi Canyon	Mississippi Canyon	Green Canyon	Mississippi Canyon
Block		809	391	743	392
Water Column Depth (ft.)		3600	7157	5470	7210
Anticipated TCW Fluid Category[1]	I	1	1	1	1
	II	0	0	0	0
	III	0	0	1	1
	IV	0	0	1	0
Treatment Type	No Treatment/Tank Storage	1	0	1	0
	Tank Storage	0	1	0	1
	Filtration	0	1	0	0
	Other Treatment	0	0	0	0
Type of Chemical Additives	Corrosion Inhibitor	0	0	1	0
	De-emulsifier	0	1	0	1
	Surfactants	0	1	1	1
	Defoamers	0	1	1	1
	Biocides	0	1	1	1

Notes:
A "0" indicates the variable was absent; a "1" indicates the variable was present.
[1] Category II and IV effluents were not discharged to Gulf of Mexico surface waters during the Year 1 study.

Appendix B.1. Characteristics of TCW Discharges Selected by LHS

Area		Mississippi Canyon	Alaminos Canyon	Green Canyon	Green Canyon
Block		393	857	782	869
Water Column Depth (ft.)		7391	9000	4427	4976
Anticipated TCW Fluid Category[1]	I	1	1	1	1
	II	0	1	0	0
	III	0	1	1	1
	IV	0	0	1	1
Treatment Type	No Treatment/Tank Storage	0	0	1	1
	Tank Storage	1	1	0	0
	Filtration	1	0	0	0
	Other Treatment	0	0	0	0
Type of Chemical Additives	Corrosion Inhibitor	0	1	1	1
	De-emulsifier	1	1	0	0
	Surfactants	1	1	1	1
	Defoamers	1	1	1	1
	Biocides	1	1	1	1

Notes:
A "0" indicates the variable was absent; a "1" indicates the variable was present.
[1] Category II and IV effluents were not discharged to Gulf of Mexico surface waters during the Year 1 study.

Appendix B.1. Characteristics of TCW Discharges Selected by LHS

Area		Mississippi Canyon	Walker Ridge	Mississippi Canyon	Green Canyon
Block		151	678	520	825
Water Column Depth (ft.)		1025	6805	6700	4976
Anticipated TCW Fluid Category[1]	I	1	1	1	1
	II	1	1	0	0
	III	1	1	1	1
	IV	0	1	1	1
Treatment Type	No Treatment/Tank Storage	0	0	1	1
	Tank Storage	1	1	0	0
	Filtration	0	0	0	0
	Other Treatment	0	0	0	0
Type of Chemical Additives	Corrosion Inhibitor	0	0	1	1
	De-emulsifier	0	1	0	0
	Surfactants	0	1	1	1
	Defoamers	0	0	1	1
	Biocides	0	1	1	1

Notes:

A "0" indicates the variable was absent; a "1" indicates the variable was present.

[1] Category II and IV effluents were not discharged to Gulf of Mexico surface waters during the Year 1 study.

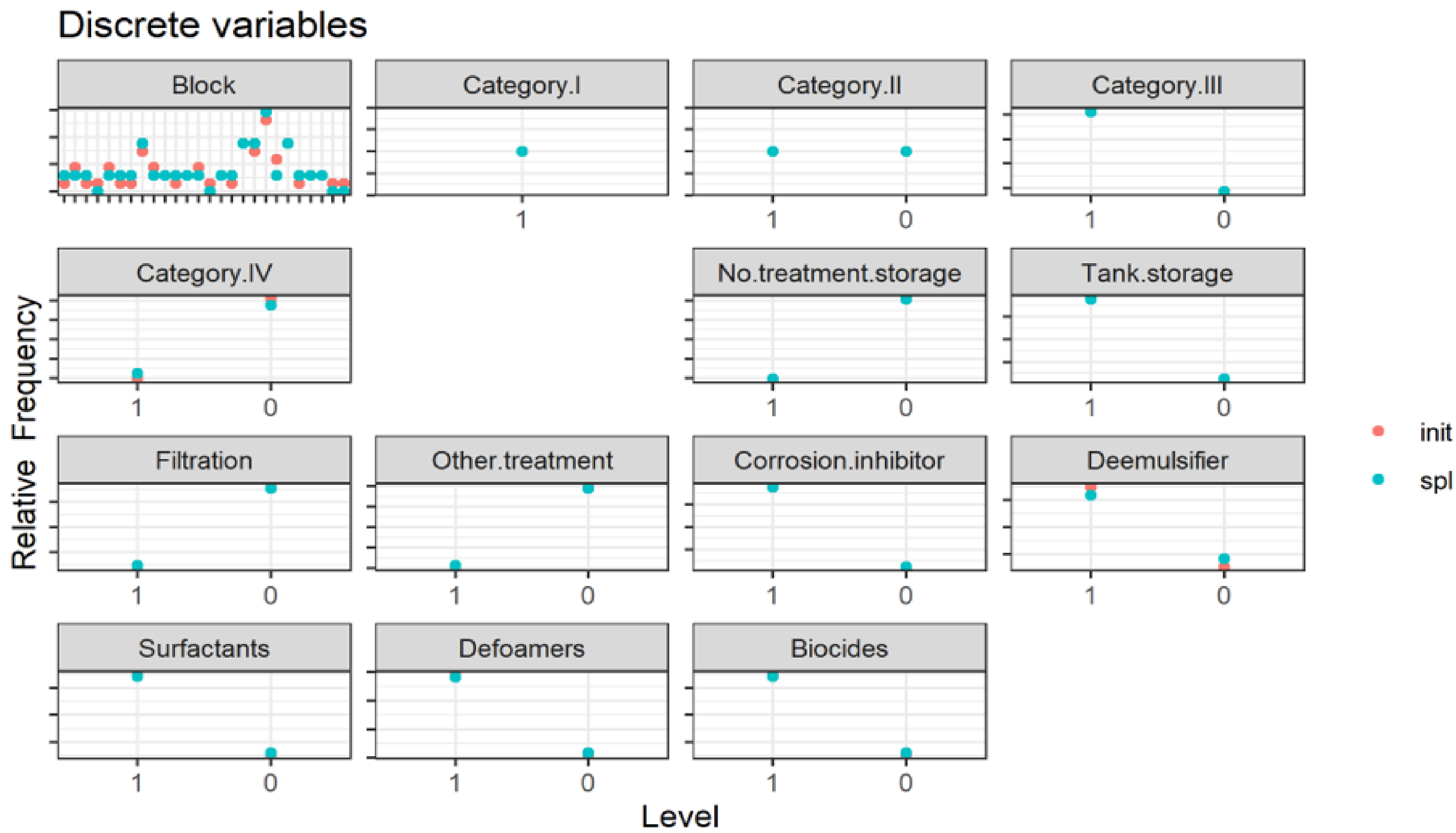
Appendix B.1. Characteristics of TCW Discharges Selected by LHS

Area		Green Canyon	Alaminos Canyon	Mississippi Canyon	Alaminos Canyon	Green Canyon
Block		826	857	807	857	825
Water Column Depth (ft.)		4976	9000	2940	7815	4976
Anticipated TCW Fluid Category[1]	I	1	1	1	1	1
	II	0	1	1	1	0
	III	1	1	1	1	1
	IV	1	0	0	0	1
Treatment Type	No Treatment/Tank Storage	1	0	0	0	1
	Tank Storage	0	1	1	1	0
	Filtration	0	0	0	0	0
	Other Treatment	0	0	0	0	0
Type of Chemical Additives	Corrosion Inhibitor	1	1	1	1	1
	De-emulsifier	0	1	1	1	0
	Surfactants	1	1	1	1	1
	Defoamers	1	1	1	1	1
	Biocides	1	1	1	1	1

Notes:
A "0" indicates the variable was absent; a "1" indicates the variable was present.
[1] Category II and IV effluents were not discharged to Gulf of Mexico surface waters during the Year 1 study.

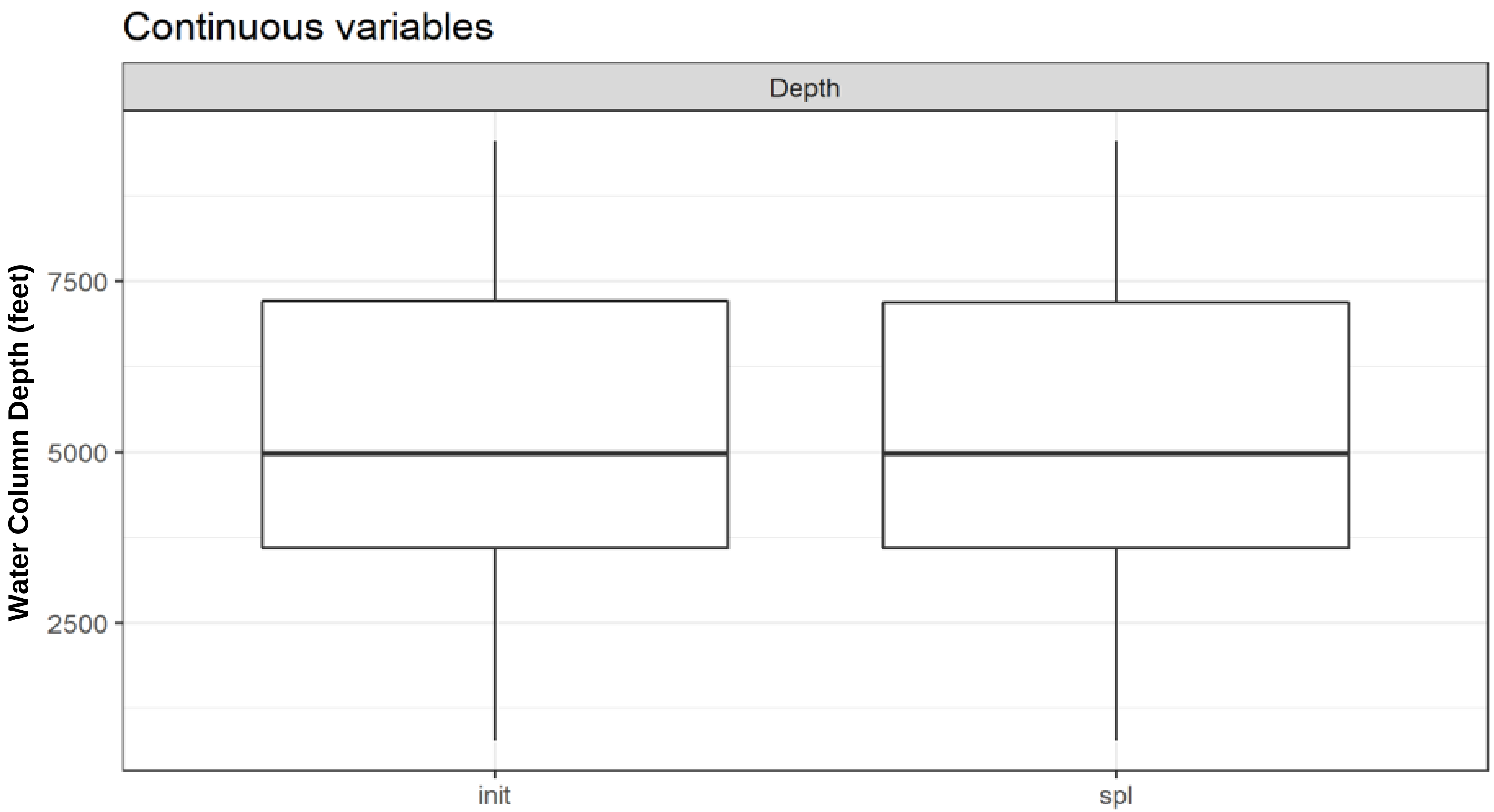
Area		Mississippi Canyon
Block		778
Water Column Depth (ft.)		5630
Anticipated TCW Fluid Category[1]	I	1
	II	0
	III	1
	IV	1
Treatment Type	No Treatment/Tank Storage	1
	Tank Storage	0
	Filtration	0
	Other Treatment	0
Type of Chemical Additives	Corrosion Inhibitor	1
	De-emulsifier	0
	Surfactants	1
	Defoamers	1
	Biocides	1

Notes:
A "0" indicates the variable was absent; a "1" indicates the variable was present.
[1] Category II and IV effluents were not discharged to Gulf of Mexico surface waters during the Year 1 study.



Notes:

"init" refers to the initial dataset of 95 discharges; "spl" refers to the selected sub-sample of 34 discharges. The overlap between "init" and "spl" indicates that the 34 discharges are representative of the the larger dataset.



Notes:
"init" refers to the initial dataset of 95 discharges; "spl" refers to the selected sub-sample of 34 discharges.

Appendix C

Supporting Documentation for Statistical Analyses

Appendix C: Supporting Documentation for Statistical Analyses

This appendix presents supporting documentation for statistical analyses. Topics that are discussed are software used, specifics on the box plots, critical values of the Spearman's Ranked Correlation Coefficient (r_s) when n<10, and details of the cluster analysis.

Software Used

Two software programs were used. SYSTAT Ver. 11 (Systat, 2004) was used to prepare boxplots, conduct the Spearman rank-order correlation and Wilcoxon rank-sum analyses, generate the regression plots and fit a quadratic (polynomial) line to the data, and generate the cluster analysis and the resulting dendrogram. ProUCL Ver. 5.1 (USEPA, 2015) was used to calculate the upper confidence limit (UCL) of the mean for the refined Tier 2 acute aquatic toxicity screening. In addition, the Latin hypercube sampling (LHS) evaluation was conducted in "R."

Box Plots

In each box plot, the center vertical line marks the median of the sample. The length of each box shows the range within which the central 50% of the values fall, with the box edges or "hinges" at the first and third quartiles. As defined by SYSTAT, the term "Hspread" is comparable to the interquartile range or midrange and is the difference between the values of the two hinges. The term "fences" is used by SYSTAT to define "outside" and "far outside values." The fences are calculated by SYSTAT as follows:

- Lower inner fence = lower hinge - (1.5 * (Hspread))
- Upper inner fence = upper hinge + (1.5 * (Hspread))
- Lower outer fence = lower hinge - (3 * (Hspread))
- Upper outer fence = upper hinge + (3 * (Hspread))

The whiskers show the range of observed values that fall within the inner fences, i.e., the range of values that fall within 1.5 Hspreads of the hinges. Outside values, i.e., values between the inner and outer fences are plotted with asterisks (*). Values beyond the outer fences, i.e., far outside values, are plotted with empty circles (^{o}).

Critical Values of Spearman Rank-order (r_s)

Statistically significant associations are reported where $p \leq 0.05$. Because *t* is not a good approximation of the sampling distribution of the Spearman r_s when n<10, the following table of non-directional critical values of r_s was used (Zar, 1984) (**Table C1**).

Table C1. Critical values of the Spearman's Ranked Correlation Coefficient (r_s) when n<10 and non-directional α = 2. Taken from Table B.19 presented in Zar (1984)

α(2):	0.50	0.20	0.10	0.05	0.02	0.01	0.005	0.002	0.001
α(1):	0.25	0.10	0.05	0.025	0.01	0.005	0.0025	0.001	0.0005
n									
4	0.600	1.000	1.000						
5	0.500	0.800	0.900	1.000	1.000				
6	0.371	0.657	0.829	0.886	0.943	1.000	1.000		
7	0.321	0.571	0.714	0.786	0.893	0.929	0.964	1.000	1.000
8	0.310	0.524	0.643	0.738	0.833	0.881	0.905	0.952	0.976
9	0.267	0.483	0.600	0.700	0.783	0.833	0.867	0.917	0.933
10	0.248	0.455	0.564	0.648	0.745	0.794	0.830	0.879	0.903

Cluster Analysis

Cluster analysis is a multivariate procedure that was used to identify natural groupings in the individual WET test endpoint data for Inland silverside minnow and Mysid. Because it is the most sensitive WET test organism, a separate ordination for the Mysid is also presented as a complement to the full ordination presented in the report. The purpose of the Mysid ordination is to illustrate that the ordination with both species is representative of the most sensitive WET test organism.

- **Details of cluster analysis**: Hierarchical and agglomerative cluster analysis was used. Hierarchical clustering produces hierarchical clusters that are displayed in a "tree" or dendrogram. Initially, each TCW effluent sample is considered by SYSTAT as a separate cluster. SYSTAT begins by joining the two "closest" TCW effluent samples as a cluster and continues in a stepwise manner joining a TCW effluent sample with another sample, a sample with a cluster, or a cluster with another cluster until all TCW effluent samples are combined into a single cluster.

  Linkage is used in an ordination to define how distances between clusters are measured. Complete linkage was selected. With the complete linkage option, SYSTAT uses the most distant pair of TCW effluent samples in two clusters to compute between-cluster distances. This method usually yields clusters that are well separated.

  Hierarchical clustering in SYSTAT also allows the user to select the type of distance metric to use between TCW effluent samples when using hierarchical clustering. Euclidean distance was selected. With Euclidean distance, the clustering is computed using normalized Euclidean distance (root mean squared distances). This metric is appropriate for use with quantitative variables. The dendrogram was qualitatively and subjectively "cut" by the user at a Euclidean distance that generated "meaningful" clusters of TCW effluent samples. Several sample-specific factors were considered by the user when identifying clusters: acute aquatic toxicity, well operation, presence and absence of chemical products, and TCW effluent chemistry.

- **Separate ordination of Mysid WET test endpoints**: Similar to the ordination for both species combined, the dendrogram indicates that TCW Category I and Category III effluents did not ordinate into two separate groups, and that patterns in acute Mysid toxicity are driven by a set of factors more complex than effluent category (**Figure C1**). Seven clusters of effluent samples were identified (Clusters 1-7) that occur along an effluent toxicity gradient. Cluster 1 includes the least toxic sample, which is a Category I effluent with end of pipe treatment (GAC and filtration). Cluster 7 contains the most toxic

TCW effluent samples, which are a mixture of Category I and Category III effluents, including gels.

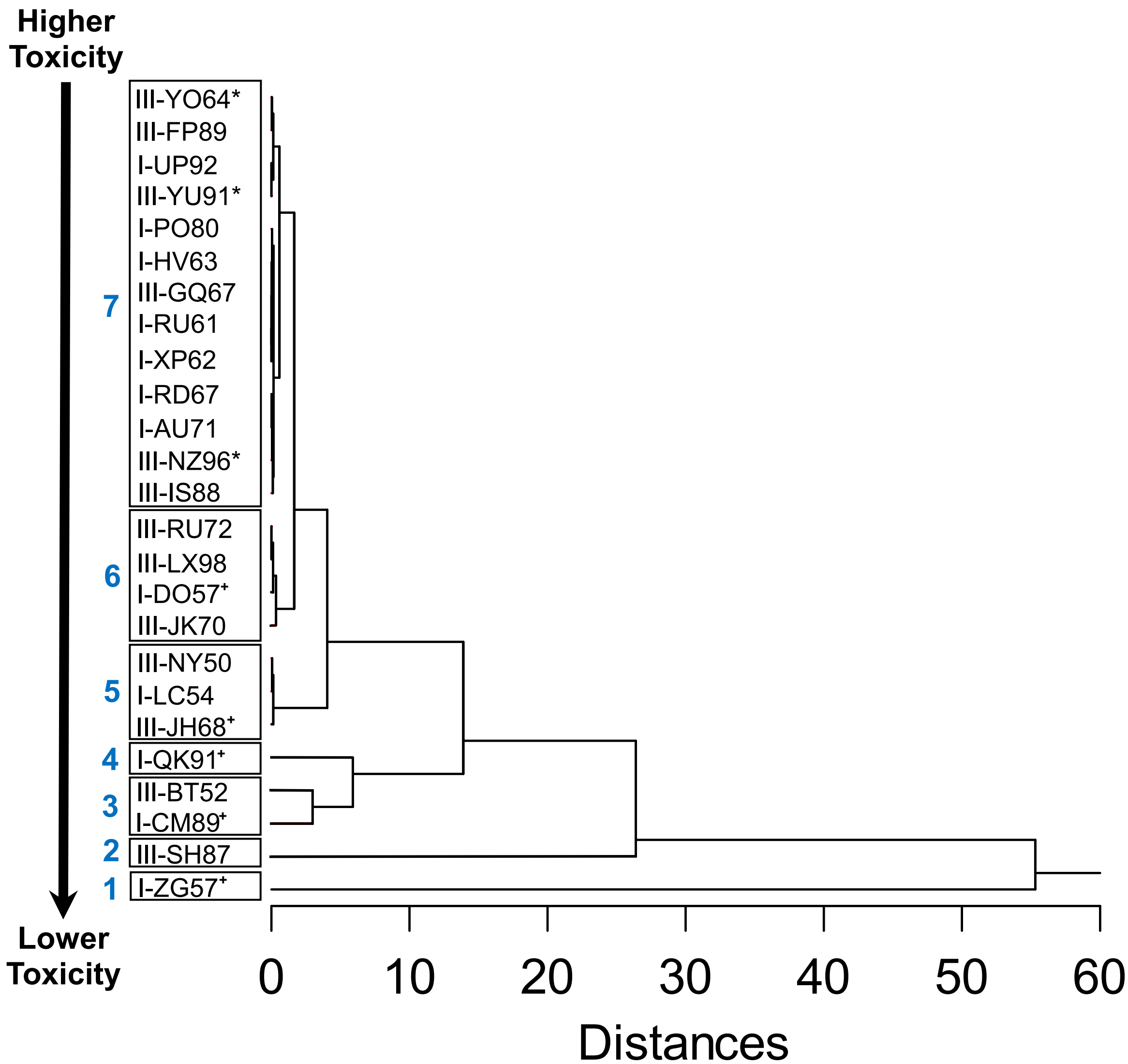


Figure C1. Cluster analysis dendrogram of the Mysid acute WET test endpoints (NOEC, LC25, LOEC, and LC50). TCW Category I effluent samples are denoted by a "I"; TCW Category III samples are denoted by a "III"; TCW Category III gel samples are denoted by a (*), and samples with end-of-pipe treatment (GAC and filtration) are denoted by a "+". The arrow illustrates a whole effluent toxicity gradient.

References

U.S. Environmental Protection Agency (Singh, A. and Maichle, R.). 2015. ProUCL Version 5.1 User Guide EPA/600/R-07/041 October 2015 accessed February 2, 2021 at https://www.epa.gov/sites/production/files/2016-05/documents/proucl_5.1_user-guide.pdf

Zar, J.H. 1984. Biostatistical Analysis. 2nd Edition, Prentice-Hall, Inc., Englewood Cliffs, 718 p.

Appendix D

Redacted Laboratory Analytical Reports

In order to keep the main study report to a practical number of pages and practical file size, the laboratory analytical reports have been assembled into a separate pdf file, which will be made available upon request to the Offshore Operators Committee.

Appendix E

Water Accommodated Fraction (WAF) Aquatic Toxicity Test Procedure and Results

Appendix E: Water Accommodated Fraction (WAF) Aquatic Toxicity Test Procedure and Results

This appendix presents the approach that was used to assess the aquatic toxicity of treatment, completion, and workover (TCW) fluid sample IH80. Category III fluid sample IH80 formed a separate phase when mixed with laboratory control seawater and thus could not be evaluated with standard acute 48-h static renewal WET testing. To characterize the aquatic toxicity of sample IH80, a water accommodated fraction (WAF) test was used. USEPA approved the adoption of the WAF procedure as a departure from the original study plan via email on November 18, 2020.

The term WAF is applied to "*an aqueous test solution containing only the fraction of a substance (or substances) that is dissolved and/or present as a stable dispersion or emulsion*" (Organization for Economic Co-operation and Development [OECD], 2019). The WAF procedure is typically used to address the aquatic toxicity of complex, multi-component substances in crude oil and refined petroleum products. A WAF can contain several dissolved substances, the concentrations of which depend on their water solubility and the mass-to-volume ratio of the preparation (OECD, 2019). Testing was conducted consistent with technical guidance (Ecotoxicology and Toxicology of Chemicals [ECETOC], 1996; OECD, 2019), and the literature (Aurand and Coelho, 2005; Jiang, Huang, Chen, Zeng, and Xu, 2012).

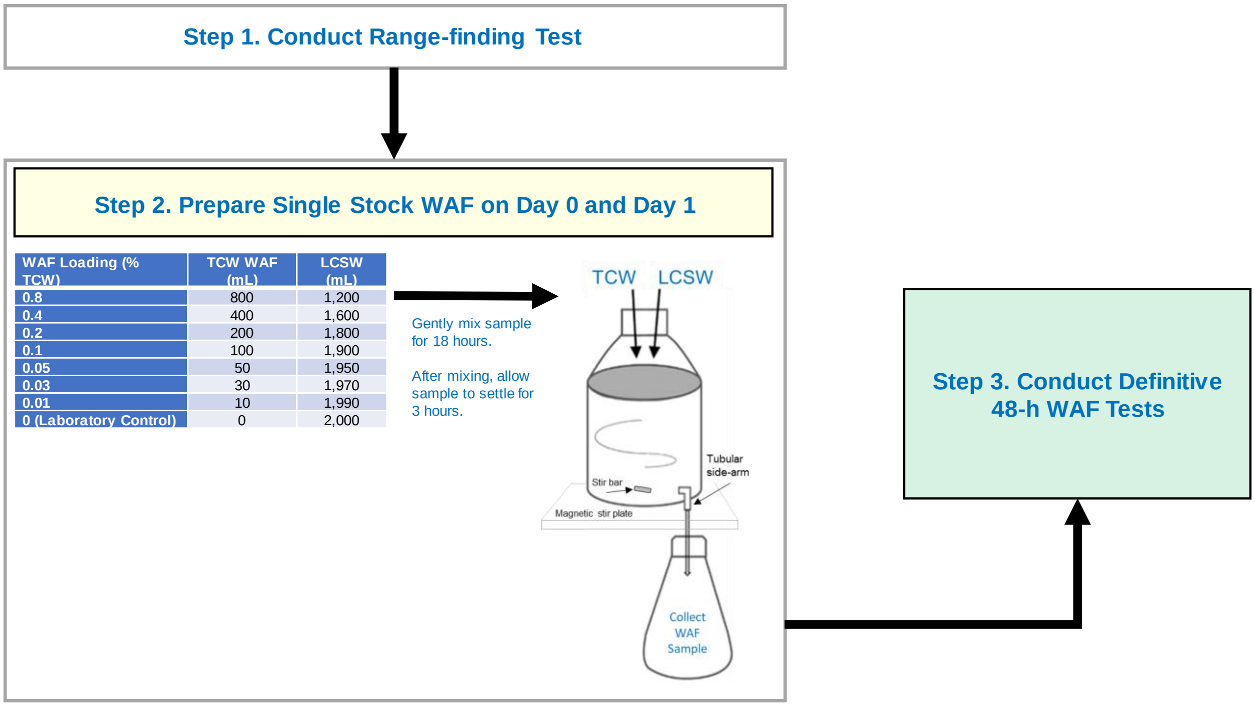
Sample Description

Based on correspondence from the JIP study participant in December 2020, sample IH80 was not discharged to surface water. The sample was inadvertently collected from a holding pit for material that was not intended to be discharged to surface water. As a result, the properties of IH80 are not representative of discharged TCW effluents.

Sample IH80 was collected on April 23, 2020, and the WAF test was conducted from November 11-12, 2020. Hence, the WAF was conducted outside of the WET sample holding time of 36 hours. Based on information provided by the JIP study participant, IH80 consisted of a 12 ppg $CaBr_2$ brine (78%), and two surfactants used as a well cleaner and spacer: "Well Cleaner 1" (17%) and "Well Cleaner 2" (4%). Sample IH80 formed a weakly soluble separate phase when mixed with LCSW and allowed to settle for 24 hours in the laboratory.

Overview of the WAF Procedure

The WAF test procedure involved a preliminary survival range-finding tests, preparation of a stock WAF, sample mixing, settling, WAF recovery, and developing WAF dilutions for use in a definitive aquatic toxicity test. The general WAF experimental design is provided below in **Figure E1**.



WAF Loading (% TCW)	TCW WAF (mL)	LCSW (mL)
0.8	800	1,200
0.4	400	1,600
0.2	200	1,800
0.1	100	1,900
0.05	50	1,950
0.03	30	1,970
0.01	10	1,990
0 (Laboratory Control)	0	2,000

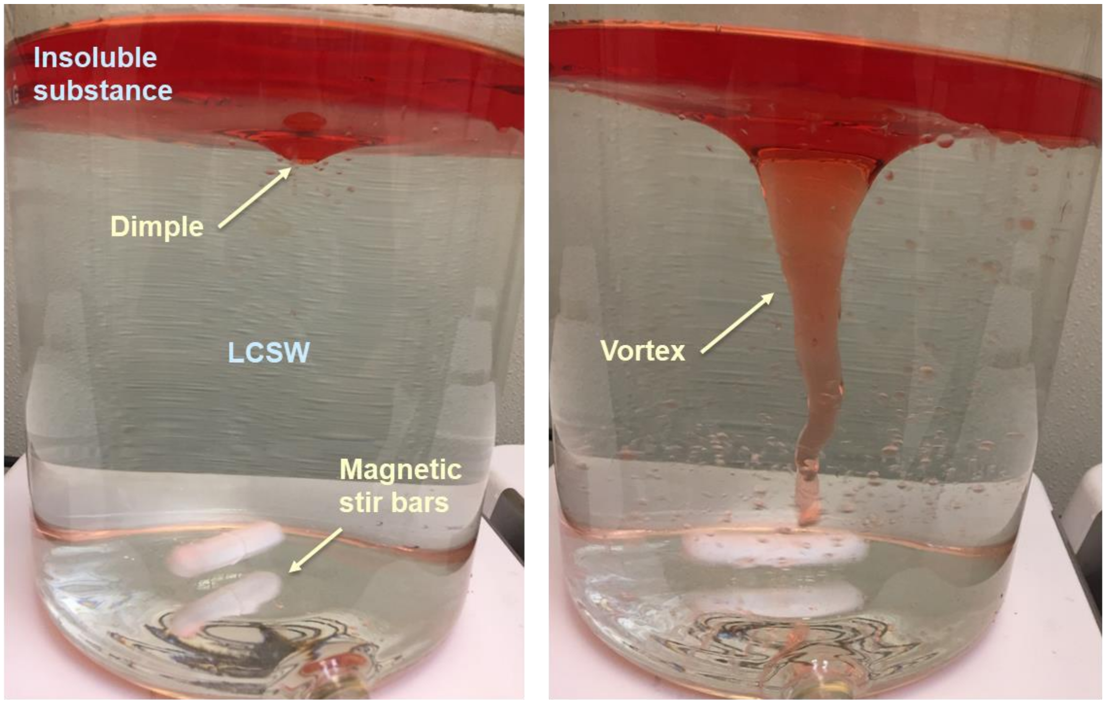
Figure E1. Water accommodated fraction (WAF) experimental design.

Stock WAF Preparation

A stock WAF was prepared with a known mass of TCW sample, mixing the sample, allowing it to settle, recovering the WAF, and developing WAF dilutions for use in a definitive aquatic toxicity test. Sample IH80 was used to prepare a single, 2% TCW by volume stock WAF on Day 0 and Day 1. Each of the 2% TCW WAFs contained 76 milliliters (ml) of sample IH80 and 3,724 mL of LCSW. The preparation of a single stock solution that is diluted for each treatment diverges from technical guidance provided by the OECD (2019) and European Center for Ecotoxicology and Toxicology of Chemicals (ECETOC) (1996). The technical guidance recommends that individual WAFs be prepared. EEUSA deemed the dilution of a single stock WAF sufficient to assess the toxicity of IH80, however, because the product fully dispersed initially. Also, the approach of preparing a single WAF stock solution has been used in other studies (Jiang, Huang, Chen, Zeng, and Xu, 2012).

Sample Mixing

The Day 0 and Day 1 WAFs were prepared in a 4.0-liter (L) glass aspirator bottle, covered, and gently mixed at 340 revolutions per minute (RPM) for 18 hours on a magnetic stir plate (Aurand and Coelho, 2005). When preparing the WAF sample, care was taken to ensure that the mixing rate did not cause the formation of a full “vortex”, an emulsion, or suspension of droplets in the aqueous phase. Hence, a slow-stir method such that a small “dimple” formed at the test solution surface was selected consistent with OECD (2019) guidance. An example of a dimple prepared by EEUSA using vegetable oil and red food dye is presented below in **Figure E2**.



Acceptable level of mixing energy - dimple forming at sample surface; no vortex.

Unacceptably high mixing energy - vortex fully formed.

Figure E2. Illustration of acceptable mixing speed for WAF test.

Settling and WAF Sample Recovery

After mixing, the WAF was allowed to settle for three hours (Aurand and Coelho, 2005). At the end of the settling period, 1,800 mL of the 2.0% TCW WAF was recovered from the tubular sidearm outlet of the aspirator bottle. The recovered TCW sample immediately dispersed when mixed with water and remained dispersed.

WAF Loading Rates and Test Dilutions

The WAF loading rate is the quantity of IH80 fluid per unit volume of LCSW used in the preparation of each WAF test medium. A single stock solution of 2.0% TCW WAF was used to prepare the individual WAF dilutions on Day 0 and Day 1. Eight treatments and seven TCW loading rates (0.01%, 0.03%, 0.05%, 0.1%,0.2%, 0.4%, and 0.8% TCW) were prepared daily, in addition to a laboratory control. Individual test chambers were labeled with the test concentration, replicate identification, and an internal laboratory reference number. WAF loadings are provided below in **Table E1.**

Table E1. Water Accommodated Fraction Loadings.		
WAF Loading (% TCW)	**TCW WAF (mL)**	**LCSW (mL)**
0.8	800	1,200
0.4	400	1,600
0.2	200	1,800
0.1	100	1,900
0.05	50	1,950
0.03	30	1,970
0.01	10	1,990
0 (Laboratory Control)	0	2,000

WAF Test Endpoints

Definitive test endpoints are a No Observable Effect Loading (NOEL); a Lowest Observed Effect Loading (LOEL), the 25% Lethal Loading (LL25), and the median Lethal Loading (LL50). The LL25 and LL50 are defined as the lethal WAF loading rate that results in 25% and 50% mortality of exposed organisms, respectively.

WAF Test Results

The 48-h LL50 for Inland silverside minnow exposed to IH80 fluid was 0.03% TCW WAF, and the 48-h LL50 for Mysid was 0.01% TCW WAF. This indicates that the well cleaner products present in IH80 contain substances which are potentially very toxic to aquatic biota. Complete WAF test results are provided below in **Table E2**.

Table E2. 48-h Water Accommodated Fraction (WAF) Aquatic Toxicity Test Results								
Sample	**WAF Test Endpoint (% TCW WAF)**							
	Inland silverside minnow				**Mysid**			
	NOEL	**LL25**	**LOEL**	**LL50**	**NOEL**	**LL25**	**LOEL**	**LL50**
IH80	0.01	0.02	0.03	0.03	<0.01	<0.01	0.01	0.014

References

Aurand, D. and Coelho, G. 2005. Cooperative aquatic toxicity testing of dispersed oil and the Chemical Response to Oil Spills: Ecological Effects Research Forum (CROSERF). Technical Report. Ecosystem Management & Associates, Lusby, MD, USA.

European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC). 1996. Monograph No. 26: Aquatic Toxicity Testing of Sparingly Soluble, Volatile and Unstable Substances. September 1996.

Jiang, Z., Huang, Y., Chen, Q., Zeng, J., Xu, X. 2012. Acute Toxicity of Crude Oil Water Accommodated Fraction on Marine Copepods: The Relative Importance of Acclimatization Temperature and Body Size. Marine Environmental Research 81 (2012) 12-17.

Organization for Economic Co-operation and Development (OECD). 2019. Guidance Document on Aqueous-phase Aquatic Toxicity Testing of Difficult Test Chemicals. Series on Testing and Assessment No. 23 (Second Edition). ENV/JM/MONO(2000)6/REV1. 8 February 2019.

Appendix F

Redacted Acute 48-h Whole Effluent Toxicity Test Laboratory Reports

In order to keep the main study report to a practical number of pages and practical file size, the toxicity reports have been assembled into a separate pdf file, which will be made available upon request to the Offshore Operators Committee.

Appendix G

CORMIX Modeling

Appendix G: CORMIX Modeling

It was recognized during JIP study planning that the critical effluent dilutions (CDs) provided in the Gulf of Mexico National Pollutant Discharge Elimination System (NPDES) Permit tables, which are based on produced water (PW) effluents, might not be appropriate for high-density TCW effluents. The U.S. Environmental Protection Agency (USEPA) expressed a preference for use of the CDs in the Permit tables unless some other factor, such as sample density, made these tables inappropriate. The Cornell Mixing Zone Expert System (CORMIX) Version 11.0GT was used to calculate TCW effluent-specific CDs using measured effluent densities. This appendix presents the CORMIX modeling approach, CORMIX inputs, and results for TCW effluents. The median ratio of effluent-specific CD to permit-table CD was 0.7, suggesting that the NPDES Permit-table CDs are not inappropriate for use for with TCW effluents.

CORMIX Modeling Approach

Nineteen CORMIX runs were conducted. TCW effluent-density-specific CORMIX runs were made for all TCW effluent samples except those that were gel effluents or were discharged through a diffuser. Also, samples with a density of 1,010 kilograms per cubic meter (kg/m^3) could not be evaluated because the CORMIX model was unable to reach convergence. Seventeen CORMIX runs were completed.

CORMIX Model Inputs

Table G.1 provides the discharge specifications for the TCW discharges. CORMIX input parameters derived from the discharges are provided in **Table G.2**. The input parameters use the actual total depth or 999 meters, whichever is less, rather than the USEPA assumed total depth of 21.2 meter (m). Most modeled discharges will not penetrate 21 m below the discharge pipe so an assumption of the actual depth will not alter modeling results.

CORMIX Model Output

All 17 completed CORMIX runs predicted the plume centerline dilutions (as percent [%] of original discharge) at 100 m from the discharge point, as shown in **Table G.3**. Effluent density appears to have a significant effect on mixing. Many of the effluents with a density of less than 1,070 kg/m^3 have a CD greater than 1%, whereas the higher density effluents ($\geq$1,100 kg/m^3) have a CD of <0.5%.

Table G.1. Discharge specifications for TCW effluent discharges. Notes: bbl: barrel; hrs; hours; ft.; feet; in.: inch; ppt; parts per thousand; %: percent; Deg.: degrees; and C; Celsius. [1] Water column depth was not reported; the operator only identified the depth difference between the end of pipe and the seafloor (1,027 feet).

Sample ID	Discharge Characteristics			Depth (ft.)		Specific Gravity (@ 4. Deg. C)	Salinity Raw Effluent (ppt)	Critical Effluent Dilution (%)	Notes
	Volume (bbl)	Duration (hrs)	Pipe Diameter (in.)	End-of-Pipe (ft. relative to water surface)	Water Column Depth (ft.)				
HV63	965	1.25	18	Not Reported	5,600	1.26	358	0.44	--
JK70	272	0.45	18	-15	4,119	1.03	57.8	0.39	--
RD67	1,476	1.5	12	-35	8,832	1.24	354	0.48	--
RU61	100	0.08	4	50	4,250	1.45	295	0.55	--
XP62	10	0.03	6	90	62	1.3	447	0.19	--
NY50	891	1.67	8	-12	4,976	1.12	175	0.39	--
LC54	320	0.08	16	-27	3,650	1.06	103	1.25	--
AU71	189	0.4	14	-12	7,210	1.15	262	0.39	--
YO64	189	0.4	6.765	-12	7,210	--	58.5	0.39	Gel sample
FP89	473	1	18	-36	6,595	1.04	64.5	0.39	--
ZG57	2,534	24	18	--	--	1.02	24.5	0.291	Discharge equipped with a diffuser
GQ67	118	1.67	16	36	7,210	1.49	390	0.1	--
YU91	498	1.5	16	-36	6,700	--	44.1	0.41	Gel sample
LX98	543	0.4	14	-15	2,955	1.01	23.7	0.56	--
IS88	543	0.18	14	-15	2,955	1.02	34.6	0.65	--
RU72	118	0.42	16	-15	773	1.04	58.5	0.36	--
BT52	256	1.08	3	20	3,325	--	58.5	0.23	Insufficient sample volume for specific gravity analysis
SH87	568	3.38	14	-12	2,940	1.05	80	0.33	--
EP57	132	1.42	18	--	--	1.05	64.1	0.291	Discharge equipped with a diffuser
TR84	2,087	16	18	--	--	1.06	91	0.291	Discharge equipped with a diffuser
RC74	30	0.05	16	-40	9,558	1.01	72	0.05	--
OD76	1,211	2.07	16	-40	9,558	--	24.9	0.39	Gel sample
TF74	1,577	0.6	16	-40	9,558	1.66	451	0.56	--
QK91	1,096	96	18	--	--	1.05	58.8	0.291	Discharge equipped with a diffuser
DO57	600	48	18	--	--	1.02	53.3	0.291	Discharge equipped with a diffuser
PO80	250	0.5	16	See note[1]	See note[1]	1.35	335	0.39	--
JH68	184	0.67	2	-20	372	1.04	63	0.24	--
UP92	71	1	5.375	9,558	9,558	1.42	355	0.15	--

Table G.2. CORMIX Input Parameters. Notes: m: meters; m^3/s: cubic meters per second; and kg/m^3: kilograms per cubic meter. [1] The depth difference between the end of pipe and the seafloor was provided by the Operator. For the purposes of modeling, the water column depth was assumed equal to the depth difference.							
Sample	**Total Depth (HD, HA) (m)**	**Port Height Above Bottom (H0) (m)**	**Pipe Diameter (D0) (m)**	**Flow Rate (Q0) (m^3/s)**	**Effluent Density (RHO0) (kg/m^3)**	**Surface Density (RHOAS) (kg/m^3)**	**Bottom density (RHOAB) (kg/m^3)**
HV63	999.0	998.8	0.457	0.0341	1260.0	1017.0	1198.8
JK70	999.0	998.8	0.457	0.0267	1030.0	1017.0	1198.8
RD67	999.0	998.8	0.305	0.0435	1240.0	1017.0	1198.8
RU61	999.0	998.8	0.102	0.0552	1450.0	1017.0	1198.8
XP62	18.9	18.7	0.152	0.0147	1300.0	1017.0	1020.4
NY50	999.0	998.8	0.203	0.0236	1120.0	1017.0	1198.8
LC54	999.0	998.8	0.406	0.1767	1060.0	1017.0	1198.8
AU71	999.0	998.8	0.356	0.0209	1150.0	1017.0	1198.8
YO64	Not modeled, gel sample						
FP89	999.0	998.8	0.457	0.0209	1040.0	1017.0	1198.8
ZG57	Not modeled; discharge equipped with a diffuser						
GQ67	999.0	998.8	0.406	0.013	1490.0	1017.0	1198.8
YU91	Not modeled, gel sample						
LX98	900.9	900.7	0.356	0.06	1010.0	1017.0	1181.0
IS88	900.9	900.7	0.356	0.1332	1020.0	1017.0	1181.0
RU72	235.7	235.5	0.406	0.0124	1040.0	1017.0	1059.9
BT52	Not modeled, insufficient sample volume to determine specific gravity						
SH87	896.3	896.1	0.356	0.0074	1050.0	1017.0	1180.1
EP57	Not modeled; discharge equipped with a diffuser						
TR84	Not modeled; discharge equipped with a diffuser						
RC74	999.7	999.5	0.406	0.0265	1010.0	1017.0	1198.9
OD76	Not modeled, gel sample						
TF74	999.7	999.5	0.406	0.1161	1660.0	1017.0	1198.9
QK91	Not modeled; discharge equipped with a diffuser						
DO57	Not modeled; discharge equipped with a diffuser						
PO80	313.1[1]	312.9[1]	0.406	0.0221	1350.0	1017.0	1074.0
JH68	113.4	113.2	0.051	0.0121	1040.0	1017.0	1037.6
UP92	999.7	999.5	0.137	0.0031	1420.0	1017.0	1198.9

Table G.3. Critical Effluent Dilutions for PW and TCW Effluents. Notes: "CD"; critical effluent dilution.

Sample ID	Effluent Density (kg/m3)	PW CD (% Effluent)	TCW CD (% Effluent)	Ratio TCW:PW CDs
HV63	1,260	0.44	0.16	0.4
JK70	1,030	0.39	8.37	21.5
RD67	1,240	0.48	0.19	0.4
RU61	1,450	0.55	0.15	0.3
XP62	1,300	0.19	0.17	0.9
NY50	1,120	0.39	0.23	0.6
LC54	1,060	1.25	0.88	0.7
AU71	1,150	0.39	0.19	0.5
FP89	1,040	0.39	6.56	16.8
GQ67	1,490	0.1	0.07	0.7
IS88	1,020	0.65	3.47	5.3
RU72	1,040	0.36	4.53	12.6
SH87	1,050	0.33	3.2	9.7
TF74	1,660	0.56	0.16	0.3
PO80	1,350	0.39	0.12	0.3
JH68	1,040	0.24	0.49	2.0
UP92	1,420	0.15	0.04	0.3

Appendix H

Supplemental WET Test laboratory Protocol

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aecom.com

Project name:
Joint Industry Project (JIP) for Treatment, Completion, and Workover Discharges

Project ref:
60577789

From: Jeffrey Park (AECOM); Ken Fucik (MVI); Joseph Smith (MVI)

Date:
March 10, 2020

To: David Daniels (Environmental Enterprises USA, Inc.)

CC: Greg Southworth (OOC); Ray Arnold (Chevron); Ashley Haynes (Chevron); Sarah Hughes (Shell); Tom Parkerton (ExxonMobil); Danelle Belhateche (AECOM); Dianne Naeger (AECOM); Ken Fucik (MVI); Joe Smith (MVI)

Memo

Subject: Supplemental Whole Effluent Toxicity (WET) Testing

This technical memorandum describes proposed supplemental acute static-renewal 48-hour (48-h) whole effluent toxicity (WET) testing for *Americamysis bahia* (Mysid) and/or *Menidia beryllina* (Atlantic silverside minnow) exposed to Treatment, Completion, and Workover (TCW) effluents. The supplemental WET testing was proposed by the JIP Steering Group and will support subsequent risk evaluations including (1) toxicity stability, and (2) exposure under more realistic conditions. This memorandum is intended for use by the selected WET testing laboratory Environmental Enterprises USA, Inc. (EEUSA).

SUPPLEMENTAL WET TESTING

Supplemental WET testing will only be applied to historical and future TCW discharge samples where the minimum NOEC of the single most sensitive WET test organism(s) is less than the critical dilution (%).[1] If *A. bahia* and *M. beryllina* both exhibit a NOEC that is less than the critical dilution, then both species will be tested. Otherwise, the supplemental testing will be limited to a single species only. Two supplemental WET tests will be conducted concurrently: **Test 1**: a standard 48-h static-renewal acute test to assess toxicity stability, and **Test 2**: a 2-h pulsed exposure with subsequent transfer to laboratory control seawater for 46-h (**Figure 1)**.

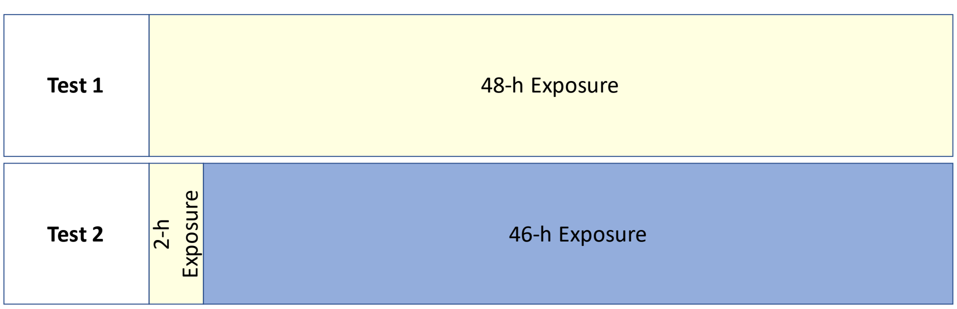

Figure 1. Study design for supplemental WET testing.
(yellow coloration indicates exposure to TCW fluid effluents; blue coloration indicates transfer to laboratory control seawater).

[1] Samples will be outside of the WET sample holding time of 36-h.

For both tests, three concentrations plus a laboratory control will be run. The exposure concentrations will be prepared such that the test series will bracket the critical effluent dilution.

The supplemental WET testing will be conducted consistent with (USEPA) 2002 guidance document *Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms Fifth Edition* (EPA-821-R-02-012), except where noted in this memorandum. Supplemental WET test details are provided below:

- **Test 1. Evaluate Stability of Sample Toxicity**: With this treatment type, the 48-h exposures will be repeated consistent with EPA-821-R-02-012:
  - Three concentrations plus a laboratory control will be run. The exposure concentrations will be prepared such that the test series will bracket the critical effluent dilution.
  - Five replicates per treatment (each consisting of eight individuals) will be prepared. After 48-h, the test will be terminated.
  - Survival data at 24-h and 48-h will be reported. WET test endpoints will be calculated by EEUSA including the IC25/LC50 and NOEC/LOEC.
- **Test 2. Pulsed Exposure Testing:** Pulsed exposure testing will include simple modifications to EPA-821-R-02-012:
  - Three concentrations plus a laboratory control will be run. The exposure concentrations will be prepared such that the test series will bracket the critical effluent dilution.
  - Five replicates per treatment (each consisting of eight individuals) will be prepared.
  - WET test organisms will be exposed to TCW effluents for 2-h. Survival data will be recorded at 0.5-h intervals over the 2-h exposure, followed by the careful transfer of all surviving test organisms to laboratory control seawater for the remaining 46-h exposure. The transfer of WET test organisms will also be conducted for the laboratory control:
    - *A. bahia* and *M. beryllina* will be gradually transferred to the new clean exposure chambers using a double renewal with clean seawater. Care will be taken to minimize the amount of TCW treatment water that is transferred. An example is provided below for a 0.8 percent (%) effluent dilution:
      - Remove detritus with a pipette.
      - Pour down replicate to approximately 10 milliliters (mL).
      - Renewal 1: Pour organisms into 200 mL seawater by dipping the container corner into the solution and slowly releasing the organisms (0.04% TCW treatment water maximum).
      - Pour down the replicate to approximately 10 mL.
      - Renewal 2: Pour organisms into 200 mL seawater by dipping the container corner into the solution and slowly releasing the organisms (0.002% TCW treatment water maximum).
  - After transfer to clean laboratory control seawater, the standard observations of WET test organism survival will be recorded. WET test endpoints will be calculated by EEUSA including the IC25/LC50 and NOEC/LOEC. The data may identify potential latent effects from the pulsed exposure.[2]
- **Success Criteria:** Data will meet individual WET test data quality objectives for all toxicity tests performed consistent with EPA-821-R-02-012. All water quality parameters (dissolved oxygen, pH, salinity, and temperature) will be maintained within recommended ranges identified in EPA-821-R-02-012 for the duration of all toxicity tests performed. Slight deviations in water quality parameters will be corrected and flagged by EEUSA as necessary/warranted.

[2] Current research suggests that post-exposure effects are important to consider when evaluating effects associated with effluent pulses (Gordon et al. 2012.

LITERATURE CITED

Gordon, A.K., Mantel, S.K., Muller, N.W.J. 2012. Review of Toxicological Effects Caused by Episodic Stressor Exposure. Environmental Toxicology and Chemistry. 31:1169–1174.

U.S. Department of Defense (DoD). 2018. Final Demonstration Plan Derivation and Demonstration of an Environmentally Relevant Approach for Stormwater Toxicity Testing Compliance Monitoring ESTCP Project #ER-201727 Environmental Restoration Project Version 2 September 2018.

U.S. Environmental Protection Agency (USEPA). 2002. Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms; Fifth Edition. Office of Water (4303T); EPA-821-R-02-012. October 2002.

Appendix I

Redacted Supplemental Whole Effluent Toxicity Test Laboratory Reports

In order to keep the main study report to a practical number of pages and practical file size, the toxicity reports have been assembled into a separate pdf file, which will be made available upon request to the Offshore Operators Committee.

Appendix J

Rationale for the 2-Hour Exposure used in Supplemental WET Testing

Appendix J: Rationale for the 2-hour Exposure used in Supplemental WET Testing

Supplemental whole effluent toxicity (WET) testing was performed on treatment, completion, and workover (TCW) effluents to understand how exposures representative of actual operational practices and shorter than the prescribed 48-hr exposure used in acute WET tests would influence toxicity end points. This appendix presents descriptive discharge duration statistics for the duration of TCW effluent discharges sampled in 2019, 2020, and 2021. The data show that 75% of discharge durations were 2 hours or less. Two hours was selected as a reasonable exposure duration for the supplemental WET tests.

SYSTAT Ver. 11 (Systat, 2004) was used to generate descriptive statistics, a Shapiro-Wilk *W* goodness-of-fit test, a quantile plot, and a histogram. ProUCL Ver. 5.1 (USEPA, 2015) was used to generate percentiles. Statistically significant results are noted where $p \leq 0.05$.

Data used in the Evaluation

Raw discharge duration data are presented in **Table J.1**. Samples CM89 and NZ96 represent the summed duration for individual samples collected over the discharge.

Table J.1. Raw discharge data used in the evaluation.

Sample	Discharge Duration (Hours)
HV63	1.25
JK70	0.45
RD67	1.5
RU61	0.08
XP62	0.03
NY50	1.67
LC54	0.08
AU71	0.4
YO64	0.4
FP89	1.0
ZG57	72.0
GQ67	1.67
YU91	1.5
LX98	0.4
IS88	0.18
RU72	0.42
BT52	1.08
SH87	3.38
CM89	40.0
NZ96	2.76
QK91	96.0
DO57	48.0
PO80	0.5
JH68	0.67
UP92	1.0

Data Distribution

The goodness-of-fit test results indicate that the discharge data are not normally distributed (**Table J.2**). The discharge duration is highly positively skewed (“right-tailed”) because of four data points associated with long-term flowback discharges (discharge duration 40 - 96 hours) (**Figure J.1)**; this is also reflected in kurtosis >3.0.

Table J.2. Goodness-of-fit, skewness, and kurtosis. The statistically significant (boldfaced) *p*-value indicates that the data are not normally distributed.

Descriptive Statistic	Units	Value
Sample Size	--	25
Skewness	--	2.5
Kurtosis	--	5.6
Shapiro-Wilk W Statistic	--	0.5
Shapiro-Wilk W *p*-value	--	**<0.0001**

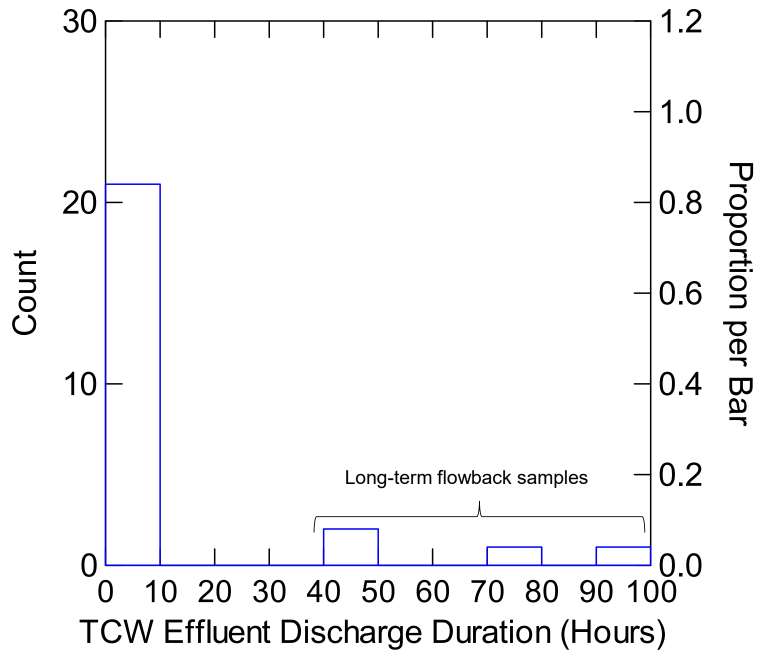

Figure J.1. Frequency distribution histogram of discharge duration (hours) for all TCW effluents (n=25). Long-term flowback samples contribute to the skewed distribution.

Descriptive Statistics

TCW effluent discharge duration ranges from 0.03 to 96 hours (**Table J.3**). Because the distribution is positively skewed, arithmetic mean discharge duration is 11.9 hours, and the median is 1 hour.

Table J.3. Descriptive statistics for TCW effluent discharge duration.	
Descriptive Statistic	**Value**
Sample Size	25
Minimum	0.03
Maximum	96
Range	96
Median	1
Mean	11
95% Confidence Interval Upper	21
95% Confidence Interval Lower	1
Standard Error	5
Standard Deviation	25
Variance	637
Coefficient of Variation	2

Out of the 25 discharges, 80% are $\leq$3 hours in duration (**Table J.4**); this is illustrated in **Figure J.2**. This result is consistent with the Year 1 characterization of TCW effluent discharge duration as short. The 75th percentile (upper quartile) is 2 hours, and the 25th percentile (lower quartile) is 0.4 hours. A 2-hour exposure duration for supplemental WET testing was selected as being reasonably reflective of actual operational practices.

Table J.4. TCW effluent discharge duration percentiles.	
Percentile	**Discharge Duration (Hours)**
10	0.1
20	0.4
25 (Lower Quartile)	0.4
50 (Median)	1
75 (Upper Quartile)	2
80	3
90	45
95	67
99	90

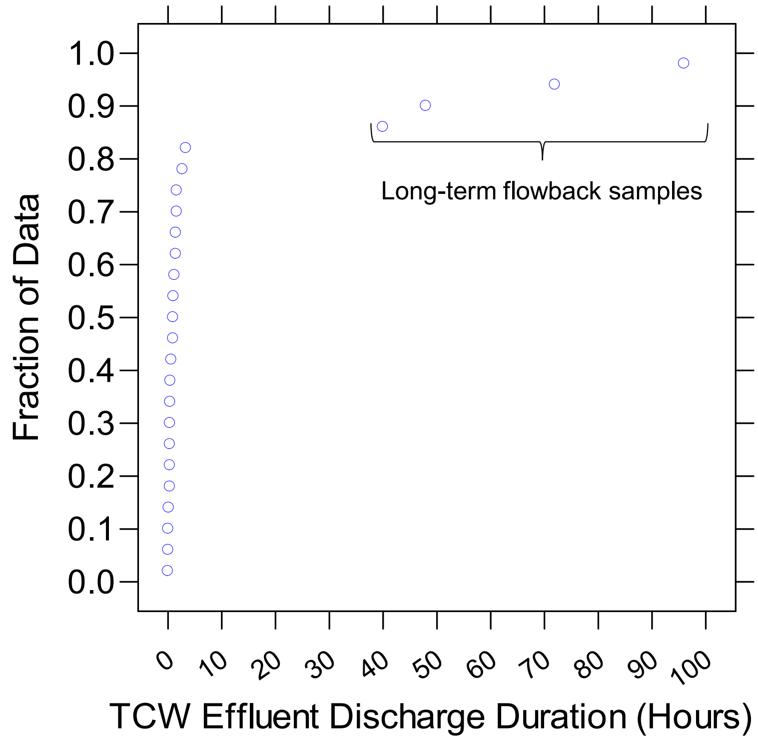

Figure J.2. Quantile plot of discharge duration (hours) for all TCW effluents (n=25).

References

U.S. Environmental Protection Agency (USEPA; Singh, A. and Maichle, R.). 2015. ProUCL Version 5.1 User Guide EPA/600/R-07/041 October 2015 accessed February 2, 2021 at https://www.epa.gov/sites/production/files/2016-05/documents/proucl_5.1_user-guide.pdf

Appendix K

ProUCL Documentation

UCL Statistics for Data Sets with Non-Detects

User Selected Options	
Date/Time of Computation	ProUCL 5.16/7/2021 11:16:15 AM
From File	WorkSheet.xls
Full Precision	OFF
Confidence Coefficient	95%
Number of Bootstrap Operations	2000

Arsenic,T

General Statistics			
Total Number of Observations	27	Number of Distinct Observations	5
Number of Detects	2	Number of Non-Detects	25
Number of Distinct Detects	2	Number of Distinct Non-Detects	3
Minimum Detect	0.111	Minimum Non-Detect	0.01
Maximum Detect	0.181	Maximum Non-Detect	0.15
Variance Detects	0.00245	Percent Non-Detects	92.59%
Mean Detects	0.146	SD Detects	0.0495
Median Detects	0.146	CV Detects	0.339
Skewness Detects	N/A	Kurtosis Detects	N/A
Mean of Logged Detects	-1.954	SD of Logged Detects	0.346

Warning: Data set has only 2 Detected Values.
This is not enough to compute meaningful or reliable statistics and estimates.

Normal GOF Test on Detects Only
Not Enough Data to Perform GOF Test

Kaplan-Meier (KM) Statistics using Normal Critical Values and other Nonparametric UCLs			
KM Mean	0.0202	KM Standard Error of Mean	0.0101
KM SD	0.037	95% KM (BCA) UCL	N/A
95% KM (t) UCL	0.0375	95% KM (Percentile Bootstrap) UCL	N/A
95% KM (z) UCL	0.0369	95% KM Bootstrap t UCL	N/A
90% KM Chebyshev UCL	0.0506	95% KM Chebyshev UCL	0.0644
97.5% KM Chebyshev UCL	0.0835	99% KM Chebyshev UCL	0.121

Gamma GOF Tests on Detected Observations Only
Not Enough Data to Perform GOF Test

Gamma Statistics on Detected Data Only			
k hat (MLE)	17.06	k star (bias corrected MLE)	N/A
Theta hat (MLE)	0.00856	Theta star (bias corrected MLE)	N/A
nu hat (MLE)	68.24	nu star (bias corrected)	N/A
Mean (detects)	0.146		

Estimates of Gamma Parameters using KM Estimates			
Mean (KM)	0.0202	SD (KM)	0.037
Variance (KM)	0.00137	SE of Mean (KM)	0.0101
k hat (KM)	0.298	k star (KM)	0.29
nu hat (KM)	16.1	nu star (KM)	15.65
theta hat (KM)	0.0678	theta star (KM)	0.0698
80% gamma percentile (KM)	0.0307	90% gamma percentile (KM)	0.0599
95% gamma percentile (KM)	0.0935	99% gamma percentile (KM)	0.181

Gamma Kaplan-Meier (KM) Statistics			
		Adjusted Level of Significance (β)	0.0401
Approximate Chi Square Value (15.65, α)	7.715	Adjusted Chi Square Value (15.65, β)	7.359

Arsenic,T

95% Gamma Approximate KM-UCL (use when n>=50	0.041	95% Gamma Adjusted KM-UCL (use when n<50)	0.043

Lognormal GOF Test on Detected Observations Only
Not Enough Data to Perform GOF Test

Lognormal ROS Statistics Using Imputed Non-Detects

Mean in Original Scale	0.0351	Mean in Log Scale	-3.737
SD in Original Scale	0.0376	SD in Log Scale	0.872
95% t UCL (assumes normality of ROS data)	0.0474	95% Percentile Bootstrap UCL	0.0472
95% BCA Bootstrap UCL	0.0503	95% Bootstrap t UCL	0.0565
95% H-UCL (Log ROS)	0.0522		

Statistics using KM estimates on Logged Data and Assuming Lognormal Distribution

KM Mean (logged)	-4.405	KM Geo Mean	0.0122
KM SD (logged)	0.703	95% Critical H Value (KM-Log)	2.163
KM Standard Error of Mean (logged)	0.193	95% H-UCL (KM -Log)	0.0211
KM SD (logged)	0.703	95% Critical H Value (KM-Log)	2.163
KM Standard Error of Mean (logged)	0.193		

DL/2 Statistics

DL/2 Normal		DL/2 Log-Transformed	
Mean in Original Scale	0.0514	Mean in Log Scale	-3.245
SD in Original Scale	0.0337	SD in Log Scale	0.92
95% t UCL (Assumes normality)	0.0624	95% H-Stat UCL	0.092

DL/2 is not a recommended method, provided for comparisons and historical reasons

Nonparametric Distribution Free UCL Statistics
Data do not follow a Discernible Distribution at 5% Significance Level

Suggested UCL to Use

95% KM (t) UCL	0.0375	KM H-UCL	0.0211
95% KM (BCA) UCL	N/A		

Warning: One or more Recommended UCL(s) not available!

Note: Suggestions regarding the selection of a 95% UCL are provided to help the user to select the most appropriate 95% UCL.
Recommendations are based upon data size, data distribution, and skewness.
These recommendations are based upon the results of the simulation studies summarized in Singh, Maichle, and Lee (2006).

However, simulations results will not cover all Real World data sets; for additional insight the user may want to consult a statistician.

Bromide,T

General Statistics			
Total Number of Observations	27	Number of Distinct Observations	25
		Number of Missing Observations	0
Minimum	24.7	Mean	560.8
Maximum	8850	Median	54.7
SD	1740	Std. Error of Mean	334.9
Coefficient of Variation	3.103	Skewness	4.539
Normal GOF Test			
Shapiro Wilk Test Statistic	0.34	Shapiro Wilk GOF Test	
5% Shapiro Wilk Critical Value	0.923	Data Not Normal at 5% Significance Level	
Lilliefors Test Statistic	0.4	Lilliefors GOF Test	
5% Lilliefors Critical Value	0.167	Data Not Normal at 5% Significance Level	
Data Not Normal at 5% Significance Level			
Assuming Normal Distribution			
95% Normal UCL		95% UCLs (Adjusted for Skewness)	
95% Student's-t UCL	1132	95% Adjusted-CLT UCL (Chen-1995)	1424
		95% Modified-t UCL (Johnson-1978)	1181
Gamma GOF Test			
A-D Test Statistic	4.4	Anderson-Darling Gamma GOF Test	
5% A-D Critical Value	0.833	Data Not Gamma Distributed at 5% Significance Level	
K-S Test Statistic	0.328	Kolmogorov-Smirnov Gamma GOF Test	
5% K-S Critical Value	0.181	Data Not Gamma Distributed at 5% Significance Level	
Data Not Gamma Distributed at 5% Significance Level			
Gamma Statistics			
k hat (MLE)	0.39	k star (bias corrected MLE)	0.371
Theta hat (MLE)	1440	Theta star (bias corrected MLE)	1512
nu hat (MLE)	21.03	nu star (bias corrected)	20.03
MLE Mean (bias corrected)	560.8	MLE Sd (bias corrected)	920.8
		Approximate Chi Square Value (0.05)	10.87
Adjusted Level of Significance	0.0401	Adjusted Chi Square Value	10.44
Assuming Gamma Distribution			
95% Approximate Gamma UCL (use when n>=50)	1033	95% Adjusted Gamma UCL (use when n<50)	1076
Lognormal GOF Test			
Shapiro Wilk Test Statistic	0.769	Shapiro Wilk Lognormal GOF Test	
5% Shapiro Wilk Critical Value	0.923	Data Not Lognormal at 5% Significance Level	
Lilliefors Test Statistic	0.237	Lilliefors Lognormal GOF Test	
5% Lilliefors Critical Value	0.167	Data Not Lognormal at 5% Significance Level	
Data Not Lognormal at 5% Significance Level			
Lognormal Statistics			
Minimum of Logged Data	3.207	Mean of logged Data	4.633
Maximum of Logged Data	9.088	SD of logged Data	1.472
Assuming Lognormal Distribution			
95% H-UCL	763.7	90% Chebyshev (MVUE) UCL	578.4
95% Chebyshev (MVUE) UCL	712.8	97.5% Chebyshev (MVUE) UCL	899.5
99% Chebyshev (MVUE) UCL	1266		

Bromide,T

Nonparametric Distribution Free UCL Statistics
Data do not follow a Discernible Distribution (0.05)

Nonparametric Distribution Free UCLs

95% CLT UCL	1112	95% Jackknife UCL	1132
95% Standard Bootstrap UCL	1100	95% Bootstrap-t UCL	3910
95% Hall's Bootstrap UCL	3056	95% Percentile Bootstrap UCL	1188
95% BCA Bootstrap UCL	1590		
90% Chebyshev(Mean, Sd) UCL	1566	95% Chebyshev(Mean, Sd) UCL	2021
97.5% Chebyshev(Mean, Sd) UCL	2652	99% Chebyshev(Mean, Sd) UCL	3893

Suggested UCL to Use

95% Chebyshev (Mean, Sd) UCL	2021

Note: Suggestions regarding the selection of a 95% UCL are provided to help the user to select the most appropriate 95% UCL.
Recommendations are based upon data size, data distribution, and skewness.
These recommendations are based upon the results of the simulation studies summarized in Singh, Maichle, and Lee (2006).
However, simulations results will not cover all Real World data sets; for additional insight the user may want to consult a statistician.

Calcium,T

General Statistics			
Total Number of Observations	27	Number of Distinct Observations	27
		Number of Missing Observations	0
Minimum	220	Mean	446.4
Maximum	2370	Median	284
SD	423.6	Std. Error of Mean	81.53
Coefficient of Variation	0.949	Skewness	3.908
Normal GOF Test			
Shapiro Wilk Test Statistic	0.507	Shapiro Wilk GOF Test	
5% Shapiro Wilk Critical Value	0.923	Data Not Normal at 5% Significance Level	
Lilliefors Test Statistic	0.297	Lilliefors GOF Test	
5% Lilliefors Critical Value	0.167	Data Not Normal at 5% Significance Level	
Data Not Normal at 5% Significance Level			
Assuming Normal Distribution			
95% Normal UCL		95% UCLs (Adjusted for Skewness)	
95% Student's-t UCL	585.4	95% Adjusted-CLT UCL (Chen-1995)	646
		95% Modified-t UCL (Johnson-1978)	595.6
Gamma GOF Test			
A-D Test Statistic	2.841	Anderson-Darling Gamma GOF Test	
5% A-D Critical Value	0.753	Data Not Gamma Distributed at 5% Significance Level	
K-S Test Statistic	0.287	Kolmogorov-Smirnov Gamma GOF Test	
5% K-S Critical Value	0.17	Data Not Gamma Distributed at 5% Significance Level	
Data Not Gamma Distributed at 5% Significance Level			
Gamma Statistics			
k hat (MLE)	2.697	k star (bias corrected MLE)	2.422
Theta hat (MLE)	165.5	Theta star (bias corrected MLE)	184.3
nu hat (MLE)	145.6	nu star (bias corrected)	130.8
MLE Mean (bias corrected)	446.4	MLE Sd (bias corrected)	286.8
		Approximate Chi Square Value (0.05)	105.4
Adjusted Level of Significance	0.0401	Adjusted Chi Square Value	103.9
Assuming Gamma Distribution			
95% Approximate Gamma UCL (use when n>=50)	554.1	95% Adjusted Gamma UCL (use when n<50)	561.8
Lognormal GOF Test			
Shapiro Wilk Test Statistic	0.772	Shapiro Wilk Lognormal GOF Test	
5% Shapiro Wilk Critical Value	0.923	Data Not Lognormal at 5% Significance Level	
Lilliefors Test Statistic	0.277	Lilliefors Lognormal GOF Test	
5% Lilliefors Critical Value	0.167	Data Not Lognormal at 5% Significance Level	
Data Not Lognormal at 5% Significance Level			
Lognormal Statistics			
Minimum of Logged Data	5.394	Mean of logged Data	5.904
Maximum of Logged Data	7.771	SD of logged Data	0.54
Assuming Lognormal Distribution			
95% H-UCL	524.8	90% Chebyshev (MVUE) UCL	559.7
95% Chebyshev (MVUE) UCL	622.2	97.5% Chebyshev (MVUE) UCL	709
99% Chebyshev (MVUE) UCL	879.4		
Nonparametric Distribution Free UCL Statistics			
Data do not follow a Discernible Distribution (0.05)			

Calcium,T

Nonparametric Distribution Free UCLs

95% CLT UCL	580.5	95% Jackknife UCL	585.4
95% Standard Bootstrap UCL	579.8	95% Bootstrap-t UCL	782
95% Hall's Bootstrap UCL	1052	95% Percentile Bootstrap UCL	584
95% BCA Bootstrap UCL	683.8		
90% Chebyshev(Mean, Sd) UCL	691	95% Chebyshev(Mean, Sd) UCL	801.8
97.5% Chebyshev(Mean, Sd) UCL	955.5	99% Chebyshev(Mean, Sd) UCL	1258

Suggested UCL to Use

95% Chebyshev (Mean, Sd) UCL	801.8

Note: Suggestions regarding the selection of a 95% UCL are provided to help the user to select the most appropriate 95% UCL.
Recommendations are based upon data size, data distribution, and skewness.
These recommendations are based upon the results of the simulation studies summarized in Singh, Maichle, and Lee (2006).
However, simulations results will not cover all Real World data sets; for additional insight the user may want to consult a statistician.

Copper,T

General Statistics

Total Number of Observations	27	Number of Distinct Observations	14
Number of Detects	14	Number of Non-Detects	13
Number of Distinct Detects	12	Number of Distinct Non-Detects	2
Minimum Detect	0.006	Minimum Non-Detect	0.03
Maximum Detect	0.055	Maximum Non-Detect	0.05
Variance Detects	2.47E-04	Percent Non-Detects	48.15%
Mean Detects	0.0321	SD Detects	0.0157
Median Detects	0.036	CV Detects	0.49
Skewness Detects	-0.632	Kurtosis Detects	-0.815
Mean of Logged Detects	-3.629	SD of Logged Detects	0.735

Normal GOF Test on Detects Only

Shapiro Wilk Test Statistic	0.887	Shapiro Wilk GOF Test
5% Shapiro Wilk Critical Value	0.874	Detected Data appear Normal at 5% Significance Level
Lilliefors Test Statistic	0.263	Lilliefors GOF Test
5% Lilliefors Critical Value	0.226	Detected Data Not Normal at 5% Significance Level

Detected Data appear Approximate Normal at 5% Significance Level

Kaplan-Meier (KM) Statistics using Normal Critical Values and other Nonparametric UCLs

KM Mean	0.0218	KM Standard Error of Mean	0.0034
KM SD	0.0159	95% KM (BCA) UCL	0.028
95% KM (t) UCL	0.0277	95% KM (Percentile Bootstrap) UCL	0.028
95% KM (z) UCL	0.0275	95% KM Bootstrap t UCL	0.0279
90% KM Chebyshev UCL	0.0321	95% KM Chebyshev UCL	0.0367
97.5% KM Chebyshev UCL	0.0432	99% KM Chebyshev UCL	0.0559

Gamma GOF Tests on Detected Observations Only

A-D Test Statistic	1.246	Anderson-Darling GOF Test
5% A-D Critical Value	0.743	Detected Data Not Gamma Distributed at 5% Significance Level
K-S Test Statistic	0.332	Kolmogorov-Smirnov GOF
5% K-S Critical Value	0.231	Detected Data Not Gamma Distributed at 5% Significance Level

Detected Data Not Gamma Distributed at 5% Significance Level

Gamma Statistics on Detected Data Only

k hat (MLE)	2.791	k star (bias corrected MLE)	2.241
Theta hat (MLE)	0.0115	Theta star (bias corrected MLE)	0.0143
nu hat (MLE)	78.16	nu star (bias corrected)	62.74
Mean (detects)	0.0321		

Gamma ROS Statistics using Imputed Non-Detects

GROS may not be used when data set has > 50% NDs with many tied observations at multiple DLs

GROS may not be used when kstar of detects is small such as <1.0, especially when the sample size is small (e.g., <15-20)

For such situations, GROS method may yield incorrect values of UCLs and BTVs

This is especially true when the sample size is small.

For gamma distributed detected data, BTVs and UCLs may be computed using gamma distribution on KM estimates

Minimum	0.006	Mean	0.0244
Maximum	0.055	Median	0.0205
SD	0.0142	CV	0.583
k hat (MLE)	2.945	k star (bias corrected MLE)	2.643
Theta hat (MLE)	0.00827	Theta star (bias corrected MLE)	0.0092
nu hat (MLE)	159	nu star (bias corrected)	142.7
Adjusted Level of Significance (β)	0.0401		
Approximate Chi Square Value (142.71, α)	116.1	Adjusted Chi Square Value (142.71, β)	114.6
95% Gamma Approximate UCL (use when n>=50)	0.0299	95% Gamma Adjusted UCL (use when n<50)	0.0303

Copper,T

Estimates of Gamma Parameters using KM Estimates			
Mean (KM)	0.0218	SD (KM)	0.0159
Variance (KM)	2.51E-04	SE of Mean (KM)	0.0034
k hat (KM)	1.896	k star (KM)	1.71
nu hat (KM)	102.4	nu star (KM)	92.34
theta hat (KM)	0.0115	theta star (KM)	0.0128
80% gamma percentile (KM)	0.0333	90% gamma percentile (KM)	0.0441
95% gamma percentile (KM)	0.0545	99% gamma percentile (KM)	0.0777
Gamma Kaplan-Meier (KM) Statistics			
Approximate Chi Square Value (92.34, α)	71.18	Adjusted Chi Square Value (92.34, β)	70
95% Gamma Approximate KM-UCL (use when n>=50)	0.0283	95% Gamma Adjusted KM-UCL (use when n<50)	0.0288
Lognormal GOF Test on Detected Observations Only			
Shapiro Wilk Test Statistic	0.785	Shapiro Wilk GOF Test	
5% Shapiro Wilk Critical Value	0.874	Detected Data Not Lognormal at 5% Significance Level	
Lilliefors Test Statistic	0.346	Lilliefors GOF Test	
5% Lilliefors Critical Value	0.226	Detected Data Not Lognormal at 5% Significance Level	
Detected Data Not Lognormal at 5% Significance Level			
Lognormal ROS Statistics Using Imputed Non-Detects			
Mean in Original Scale	0.0225	Mean in Log Scale	-4.042
SD in Original Scale	0.0154	SD in Log Scale	0.744
95% t UCL (assumes normality of ROS data)	0.0276	95% Percentile Bootstrap UCL	0.0274
95% BCA Bootstrap UCL	0.0278	95% Bootstrap t UCL	0.028
95% H-UCL (Log ROS)	0.0319		
Statistics using KM estimates on Logged Data and Assuming Lognormal Distribution			
KM Mean (logged)	-4.117	KM Geo Mean	0.0163
KM SD (logged)	0.782	95% Critical H Value (KM-Log)	2.253
KM Standard Error of Mean (logged)	0.191	95% H-UCL (KM -Log)	0.0312
KM SD (logged)	0.782	95% Critical H Value (KM-Log)	2.253
KM Standard Error of Mean (logged)	0.191		
DL/2 Statistics			
DL/2 Normal		DL/2 Log-Transformed	
Mean in Original Scale	0.0242	Mean in Log Scale	-3.885
SD in Original Scale	0.014	SD in Log Scale	0.593
95% t UCL (Assumes normality)	0.0288	95% H-Stat UCL	0.0311
DL/2 is not a recommended method, provided for comparisons and historical reasons			
Nonparametric Distribution Free UCL Statistics			
Detected Data appear Approximate Normal Distributed at 5% Significance Level			

Suggested UCL to Use

95% KM (t) UCL	0.0277

When a data set follows an approximate (e.g., normal) distribution passing one of the GOF test
When applicable, it is suggested to use a UCL based upon a distribution (e.g., gamma) passing both GOF tests in ProUCL

Note: Suggestions regarding the selection of a 95% UCL are provided to help the user to select the most appropriate 95% UCL.
Recommendations are based upon data size, data distribution, and skewness.
These recommendations are based upon the results of the simulation studies summarized in Singh, Maichle, and Lee (2006).
However, simulations results will not cover all Real World data sets; for additional insight the user may want to consult a statistician.

Selenium,T

General Statistics			
Total Number of Observations	27	Number of Distinct Observations	17
Number of Detects	15	Number of Non-Detects	12
Number of Distinct Detects	15	Number of Distinct Non-Detects	2
Minimum Detect	0.143	Minimum Non-Detect	0.2
Maximum Detect	0.473	Maximum Non-Detect	0.3
Variance Detects	0.012	Percent Non-Detects	44.44%
Mean Detects	0.294	SD Detects	0.11
Median Detects	0.327	CV Detects	0.373
Skewness Detects	-0.00932	Kurtosis Detects	-1.09
Mean of Logged Detects	-1.298	SD of Logged Detects	0.412
Normal GOF Test on Detects Only			
Shapiro Wilk Test Statistic	0.915	Shapiro Wilk GOF Test	
5% Shapiro Wilk Critical Value	0.881	Detected Data appear Normal at 5% Significance Level	
Lilliefors Test Statistic	0.173	Lilliefors GOF Test	
5% Lilliefors Critical Value	0.22	Detected Data appear Normal at 5% Significance Level	
Detected Data appear Normal at 5% Significance Level			
Kaplan-Meier (KM) Statistics using Normal Critical Values and other Nonparametric UCLs			
KM Mean	0.232	KM Standard Error of Mean	0.0211
KM SD	0.105	95% KM (BCA) UCL	0.265
95% KM (t) UCL	0.268	95% KM (Percentile Bootstrap) UCL	0.268
95% KM (z) UCL	0.267	95% KM Bootstrap t UCL	0.271
90% KM Chebyshev UCL	0.295	95% KM Chebyshev UCL	0.324
97.5% KM Chebyshev UCL	0.364	99% KM Chebyshev UCL	0.442
Gamma GOF Tests on Detected Observations Only			
A-D Test Statistic	0.687	Anderson-Darling GOF Test	
5% A-D Critical Value	0.738	Detected data appear Gamma Distributed at 5% Significance Level	
K-S Test Statistic	0.219	Kolmogorov-Smirnov GOF	
5% K-S Critical Value	0.222	Detected data appear Gamma Distributed at 5% Significance Level	
Detected data appear Gamma Distributed at 5% Significance Level			
Gamma Statistics on Detected Data Only			
k hat (MLE)	6.931	k star (bias corrected MLE)	5.589
Theta hat (MLE)	0.0424	Theta star (bias corrected MLE)	0.0526
nu hat (MLE)	207.9	nu star (bias corrected)	167.7
Mean (detects)	0.294		
Gamma ROS Statistics using Imputed Non-Detects			
GROS may not be used when data set has > 50% NDs with many tied observations at multiple DLs			
GROS may not be used when kstar of detects is small such as <1.0, especially when the sample size is small (e.g., <15-20)			
For such situations, GROS method may yield incorrect values of UCLs and BTVs			
This is especially true when the sample size is small.			
For gamma distributed detected data, BTVs and UCLs may be computed using gamma distribution on KM estimates			
Minimum	0.0669	Mean	0.234
Maximum	0.473	Median	0.203
SD	0.11	CV	0.472
k hat (MLE)	4.68	k star (bias corrected MLE)	4.185
Theta hat (MLE)	0.05	Theta star (bias corrected MLE)	0.0559
nu hat (MLE)	252.7	nu star (bias corrected)	226
Adjusted Level of Significance (β)	0.0401		
Approximate Chi Square Value (225.98, α)	192.2	Adjusted Chi Square Value (225.98, β)	190.2
95% Gamma Approximate UCL (use when n>=50)	0.275	95% Gamma Adjusted UCL (use when n<50)	0.278

Selenium,T

Estimates of Gamma Parameters using KM Estimates

Mean (KM)	0.232	SD (KM)	0.105
Variance (KM)	0.0111	SE of Mean (KM)	0.0211
k hat (KM)	4.855	k star (KM)	4.34
nu hat (KM)	262.2	nu star (KM)	234.4
theta hat (KM)	0.0478	theta star (KM)	0.0534
80% gamma percentile (KM)	0.317	90% gamma percentile (KM)	0.381
95% gamma percentile (KM)	0.44	99% gamma percentile (KM)	0.565

Gamma Kaplan-Meier (KM) Statistics

Approximate Chi Square Value (234.37, α)	199.9	Adjusted Chi Square Value (234.37, β)	197.9
95% Gamma Approximate KM-UCL (use when n>=50)	0.272	95% Gamma Adjusted KM-UCL (use when n<50)	0.275

Lognormal GOF Test on Detected Observations Only

Shapiro Wilk Test Statistic	0.887	Shapiro Wilk GOF Test
5% Shapiro Wilk Critical Value	0.881	Detected Data appear Lognormal at 5% Significance Level
Lilliefors Test Statistic	0.233	Lilliefors GOF Test
5% Lilliefors Critical Value	0.22	Detected Data Not Lognormal at 5% Significance Level

Detected Data appear Approximate Lognormal at 5% Significance Level

Lognormal ROS Statistics Using Imputed Non-Detects

Mean in Original Scale	0.236	Mean in Log Scale	-1.536
SD in Original Scale	0.107	SD in Log Scale	0.437
95% t UCL (assumes normality of ROS data)	0.271	95% Percentile Bootstrap UCL	0.271
95% BCA Bootstrap UCL	0.273	95% Bootstrap t UCL	0.275
95% H-UCL (Log ROS)	0.279		

Statistics using KM estimates on Logged Data and Assuming Lognormal Distribution

KM Mean (logged)	-1.553	KM Geo Mean	0.212
KM SD (logged)	0.413	95% Critical H Value (KM-Log)	1.9
KM Standard Error of Mean (logged)	0.0838	95% H-UCL (KM -Log)	0.269
KM SD (logged)	0.413	95% Critical H Value (KM-Log)	1.9
KM Standard Error of Mean (logged)	0.0838		

DL/2 Statistics

DL/2 Normal		DL/2 Log-Transformed	
Mean in Original Scale	0.21	Mean in Log Scale	-1.73
SD in Original Scale	0.126	SD in Log Scale	0.582
95% t UCL (Assumes normality)	0.251	95% H-Stat UCL	0.265

DL/2 is not a recommended method, provided for comparisons and historical reasons

Nonparametric Distribution Free UCL Statistics

Detected Data appear Normal Distributed at 5% Significance Level

Suggested UCL to Use

95% KM (t) UCL	0.268

Note: Suggestions regarding the selection of a 95% UCL are provided to help the user to select the most appropriate 95% UCL.
Recommendations are based upon data size, data distribution, and skewness.
These recommendations are based upon the results of the simulation studies summarized in Singh, Maichle, and Lee (2006).
However, simulations results will not cover all Real World data sets; for additional insight the user may want to consult a statistician.

Zinc,T

General Statistics			
Total Number of Observations	27	Number of Distinct Observations	9
Number of Detects	7	Number of Non-Detects	20
Number of Distinct Detects	7	Number of Distinct Non-Detects	2
Minimum Detect	0.014	Minimum Non-Detect	0.1
Maximum Detect	0.226	Maximum Non-Detect	0.608
Variance Detects	0.00565	Percent Non-Detects	74.07%
Mean Detects	0.107	SD Detects	0.0752
Median Detects	0.105	CV Detects	0.7
Skewness Detects	0.172	Kurtosis Detects	-0.469
Mean of Logged Detects	-2.591	SD of Logged Detects	1.069

Normal GOF Test on Detects Only			
Shapiro Wilk Test Statistic	0.947	Shapiro Wilk GOF Test	
5% Shapiro Wilk Critical Value	0.803	Detected Data appear Normal at 5% Significance Level	
Lilliefors Test Statistic	0.163	Lilliefors GOF Test	
5% Lilliefors Critical Value	0.304	Detected Data appear Normal at 5% Significance Level	
Detected Data appear Normal at 5% Significance Level			

Kaplan-Meier (KM) Statistics using Normal Critical Values and other Nonparametric UCLs			
KM Mean	0.0596	KM Standard Error of Mean	0.021
KM SD	0.0554	95% KM (BCA) UCL	0.107
95% KM (t) UCL	0.0954	95% KM (Percentile Bootstrap) UCL	0.106
95% KM (z) UCL	0.0941	95% KM Bootstrap t UCL	0.128
90% KM Chebyshev UCL	0.123	95% KM Chebyshev UCL	0.151
97.5% KM Chebyshev UCL	0.191	99% KM Chebyshev UCL	0.268

Gamma GOF Tests on Detected Observations Only			
A-D Test Statistic	0.465	Anderson-Darling GOF Test	
5% A-D Critical Value	0.721	Detected data appear Gamma Distributed at 5% Significance Level	
K-S Test Statistic	0.249	Kolmogorov-Smirnov GOF	
5% K-S Critical Value	0.317	Detected data appear Gamma Distributed at 5% Significance Level	
Detected data appear Gamma Distributed at 5% Significance Level			

Gamma Statistics on Detected Data Only			
k hat (MLE)	1.534	k star (bias corrected MLE)	0.972
Theta hat (MLE)	0.07	Theta star (bias corrected MLE)	0.111
nu hat (MLE)	21.48	nu star (bias corrected)	13.61
Mean (detects)	0.107		

Gamma ROS Statistics using Imputed Non-Detects
GROS may not be used when data set has > 50% NDs with many tied observations at multiple DLs
GROS may not be used when kstar of detects is small such as <1.0, especially when the sample size is small (e.g., <15-20)
For such situations, GROS method may yield incorrect values of UCLs and BTVs
This is especially true when the sample size is small.
For gamma distributed detected data, BTVs and UCLs may be computed using gamma distribution on KM estimates

Minimum	0.01	Mean	0.0578
Maximum	0.226	Median	0.0433
SD	0.0529	CV	0.916
k hat (MLE)	1.369	k star (bias corrected MLE)	1.241
Theta hat (MLE)	0.0422	Theta star (bias corrected MLE)	0.0465
nu hat (MLE)	73.92	nu star (bias corrected)	67.04
Adjusted Level of Significance (β)	0.0401		
Approximate Chi Square Value (67.04, α)	49.2	Adjusted Chi Square Value (67.04, β)	48.22
95% Gamma Approximate UCL (use when n>=50)	0.0787	95% Gamma Adjusted UCL (use when n<50)	0.0803

Zinc,T

Estimates of Gamma Parameters using KM Estimates			
Mean (KM)	0.0596	SD (KM)	0.0554
Variance (KM)	0.00307	SE of Mean (KM)	0.021
k hat (KM)	1.16	k star (KM)	1.055
nu hat (KM)	62.62	nu star (KM)	56.99
theta hat (KM)	0.0514	theta star (KM)	0.0565
80% gamma percentile (KM)	0.0955	90% gamma percentile (KM)	0.135
95% gamma percentile (KM)	0.175	99% gamma percentile (KM)	0.267
Gamma Kaplan-Meier (KM) Statistics			
Approximate Chi Square Value (56.99, α)	40.64	Adjusted Chi Square Value (56.99, β)	39.76
95% Gamma Approximate KM-UCL (use when n>=50)	0.0836	95% Gamma Adjusted KM-UCL (use when n<50)	0.0855
Lognormal GOF Test on Detected Observations Only			
Shapiro Wilk Test Statistic	0.848	Shapiro Wilk GOF Test	
5% Shapiro Wilk Critical Value	0.803	Detected Data appear Lognormal at 5% Significance Level	
Lilliefors Test Statistic	0.29	Lilliefors GOF Test	
5% Lilliefors Critical Value	0.304	Detected Data appear Lognormal at 5% Significance Level	
Detected Data appear Lognormal at 5% Significance Level			
Lognormal ROS Statistics Using Imputed Non-Detects			
Mean in Original Scale	0.0527	Mean in Log Scale	-3.355
SD in Original Scale	0.0524	SD in Log Scale	0.934
95% t UCL (assumes normality of ROS data)	0.0699	95% Percentile Bootstrap UCL	0.0694
95% BCA Bootstrap UCL	0.0723	95% Bootstrap t UCL	0.0766
95% H-UCL (Log ROS)	0.0844		
Statistics using KM estimates on Logged Data and Assuming Lognormal Distribution			
KM Mean (logged)	-3.271	KM Geo Mean	0.0379
KM SD (logged)	0.96	95% Critical H Value (KM-Log)	2.469
KM Standard Error of Mean (logged)	0.449	95% H-UCL (KM -Log)	0.0957
KM SD (logged)	0.96	95% Critical H Value (KM-Log)	2.469
KM Standard Error of Mean (logged)	0.449		
DL/2 Statistics			
DL/2 Normal		DL/2 Log-Transformed	
Mean in Original Scale	0.0743	Mean in Log Scale	-2.824
SD in Original Scale	0.0637	SD in Log Scale	0.634
95% t UCL (Assumes normality)	0.0952	95% H-Stat UCL	0.0942
DL/2 is not a recommended method, provided for comparisons and historical reasons			
Nonparametric Distribution Free UCL Statistics			
Detected Data appear Normal Distributed at 5% Significance Level			

Suggested UCL to Use

95% KM (t) UCL	0.0954

Note: Suggestions regarding the selection of a 95% UCL are provided to help the user to select the most appropriate 95% UCL.
Recommendations are based upon data size, data distribution, and skewness.
These recommendations are based upon the results of the simulation studies summarized in Singh, Maichle, and Lee (2006).
However, simulations results will not cover all Real World data sets; for additional insight the user may want to consult a statistician.

UCL Statistics for Data Sets with Non-Detects

User Selected Options	
Date/Time of Computation	ProUCL 5.16/7/2021 11:30:09 AM
From File	WorkSheet.xls
Full Precision	OFF
Confidence Coefficient	95%
Number of Bootstrap Operation:	2000

Arsenic,D

General Statistics

Total Number of Observations	27	Number of Distinct Observations	5
Number of Detects	2	Number of Non-Detects	25
Number of Distinct Detects	2	Number of Distinct Non-Detects	3
Minimum Detect	0.0139	Minimum Non-Detect	0.01
Maximum Detect	0.288	Maximum Non-Detect	0.15
Variance Detects	0.0376	Percent Non-Detects	92.59%
Mean Detects	0.151	SD Detects	0.194
Median Detects	0.151	CV Detects	1.284
Skewness Detects	N/A	Kurtosis Detects	N/A
Mean of Logged Detects	-2.76	SD of Logged Detects	2.143

Warning: Data set has only 2 Detected Values.
This is not enough to compute meaningful or reliable statistics and estimates.

Normal GOF Test on Detects Only
Not Enough Data to Perform GOF Test

Kaplan-Meier (KM) Statistics using Normal Critical Values and other Nonparametric UCLs

KM Mean	0.0212	KM Standard Error of Mean	0.0143
KM SD	0.0523	95% KM (BCA) UCL	N/A
95% KM (t) UCL	0.0456	95% KM (Percentile Bootstrap) UCL	N/A
95% KM (z) UCL	0.0447	95% KM Bootstrap t UCL	N/A
90% KM Chebyshev UCL	0.0641	95% KM Chebyshev UCL	0.0835
97.5% KM Chebyshev UCL	0.11	99% KM Chebyshev UCL	0.163

Gamma GOF Tests on Detected Observations Only
Not Enough Data to Perform GOF Test

Gamma Statistics on Detected Data Only

k hat (MLE)	0.696	k star (bias corrected MLE)	N/A
Theta hat (MLE)	0.217	Theta star (bias corrected MLE)	N/A
nu hat (MLE)	2.783	nu star (bias corrected)	N/A
Mean (detects)	0.151		

Estimates of Gamma Parameters using KM Estimates

Mean (KM)	0.0212	SD (KM)	0.0523
Variance (KM)	0.00274	SE of Mean (KM)	0.0143
k hat (KM)	0.165	k star (KM)	0.171
nu hat (KM)	8.888	nu star (KM)	9.233
theta hat (KM)	0.129	theta star (KM)	0.124
80% gamma percentile (KM)	0.0255	90% gamma percentile (KM)	0.0638
95% gamma percentile (KM)	0.114	99% gamma percentile (KM)	0.255

Gamma Kaplan-Meier (KM) Statistics

		Adjusted Level of Significance (β)	[illegible]
Approximate Chi Square Value (9.23, α)	3.469	Adjusted Chi Square Value (9.23, β)	3.245

Arsenic,D

95% Gamma Approximate KM-UCL (use when n>=50)	0.0565	95% Gamma Adjusted KM-UCL (use when n<50)	0.0604

Lognormal GOF Test on Detected Observations Only
Not Enough Data to Perform GOF Test

Lognormal ROS Statistics Using Imputed Non-Detects

Mean in Original Scale	0.015	Mean in Log Scale	-7.054
SD in Original Scale	0.0553	SD in Log Scale	2.495
95% t UCL (assumes normality of ROS data)	0.0332	95% Percentile Bootstrap UCL	0.0358
95% BCA Bootstrap UCL	0.0479	95% Bootstrap t UCL	0.156
95% H-UCL (Log ROS)	0.211		

Statistics using KM estimates on Logged Data and Assuming Lognormal Distribution

KM Mean (logged)	-4.401	KM Geo Mean	0.0123
KM SD (logged)	0.635	95% Critical H Value (KM-Log)	2.095
KM Standard Error of Mean (logged)	0.194	95% H-UCL (KM -Log)	0.0195
KM SD (logged)	0.635	95% Critical H Value (KM-Log)	2.095
KM Standard Error of Mean (logged)	0.194		

DL/2 Statistics

DL/2 Normal		DL/2 Log-Transformed	
Mean in Original Scale	0.0534	Mean in Log Scale	-3.219
SD in Original Scale	0.0497	SD in Log Scale	0.864
95% t UCL (Assumes normality)	0.0697	95% H-Stat UCL	0.0866

DL/2 is not a recommended method, provided for comparisons and historical reasons

Nonparametric Distribution Free UCL Statistics
Data do not follow a Discernible Distribution at 5% Significance Level

Suggested UCL to Use

97.5% KM (Chebyshev) UCL	0.11

Note: Suggestions regarding the selection of a 95% UCL are provided to help the user to select the most appropriate 95% UCL.
Recommendations are based upon data size, data distribution, and skewness.

These recommendations are based upon the results of the simulation studies summarized in Singh, Maichle, and Lee (2006).

However, simulations results will not cover all Real World data sets; for additional insight the user may want to consult a statistician.

Calcium,D

General Statistics			
Total Number of Observations	27	Number of Distinct Observations	25
		Number of Missing Observations	0
Minimum	216	Mean	438.9
Maximum	2140	Median	301
SD	378.9	Std. Error of Mean	72.91
Coefficient of Variation	0.863	Skewness	3.787
Normal GOF Test			
Shapiro Wilk Test Statistic	0.53	Shapiro Wilk GOF Test	
5% Shapiro Wilk Critical Value	0.923	Data Not Normal at 5% Significance Level	
Lilliefors Test Statistic	0.298	Lilliefors GOF Test	
5% Lilliefors Critical Value	0.167	Data Not Normal at 5% Significance Level	
Data Not Normal at 5% Significance Level			
Assuming Normal Distribution			
95% Normal UCL		95% UCLs (Adjusted for Skewness)	
95% Student's-t UCL	563.2	95% Adjusted-CLT UCL (Chen-1995)	615.6
		95% Modified-t UCL (Johnson-1978)	572.1
Gamma GOF Test			
A-D Test Statistic	2.638	Anderson-Darling Gamma GOF Test	
5% A-D Critical Value	0.751	Data Not Gamma Distributed at 5% Significance Level	
K-S Test Statistic	0.259	Kolmogorov-Smirnov Gamma GOF Test	
5% K-S Critical Value	0.169	Data Not Gamma Distributed at 5% Significance Level	
Data Not Gamma Distributed at 5% Significance Level			
Gamma Statistics			
k hat (MLE)	3.068	k star (bias corrected MLE)	2.752
Theta hat (MLE)	143	Theta star (bias corrected MLE)	159.5
nu hat (MLE)	165.7	nu star (bias corrected)	148.6
MLE Mean (bias corrected)	438.9	MLE Sd (bias corrected)	264.6
		Approximate Chi Square Value (0.05)	121.4
Adjusted Level of Significance	0.0401	Adjusted Chi Square Value	119.9
Assuming Gamma Distribution			
95% Approximate Gamma UCL (use when n>=50)	537.1	95% Adjusted Gamma UCL (use when n<50)	544.1
Lognormal GOF Test			
Shapiro Wilk Test Statistic	0.792	Shapiro Wilk Lognormal GOF Test	
5% Shapiro Wilk Critical Value	0.923	Data Not Lognormal at 5% Significance Level	
Lilliefors Test Statistic	0.241	Lilliefors Lognormal GOF Test	
5% Lilliefors Critical Value	0.167	Data Not Lognormal at 5% Significance Level	
Data Not Lognormal at 5% Significance Level			
Lognormal Statistics			
Minimum of Logged Data	5.375	Mean of logged Data	5.913
Maximum of Logged Data	7.669	SD of logged Data	0.511
Assuming Lognormal Distribution			
95% H-UCL	513.5	90% Chebyshev (MVUE) UCL	547.8
95% Chebyshev (MVUE) UCL	606.2	97.5% Chebyshev (MVUE) UCL	687.3
99% Chebyshev (MVUE) UCL	846.5		
Nonparametric Distribution Free UCL Statistics			
Data do not follow a Discernible Distribution (0.05)			

Calcium,D

Nonparametric Distribution Free UCLs

95% CLT UCL	558.8	95% Jackknife UCL	563.2
95% Standard Bootstrap UCL	555.7	95% Bootstrap-t UCL	733
95% Hall's Bootstrap UCL	985.9	95% Percentile Bootstrap UCL	570.9
95% BCA Bootstrap UCL	631.6		
90% Chebyshev(Mean, Sd) UCL	657.6	95% Chebyshev(Mean, Sd) UCL	756.7
97.5% Chebyshev(Mean, Sd) UCL	894.2	99% Chebyshev(Mean, Sd) UCL	1164

Suggested UCL to Use

95% Chebyshev (Mean, Sd) UCL	756.7

Note: Suggestions regarding the selection of a 95% UCL are provided to help the user to select the most appropriate 95% UCL. Recommendations are based upon data size, data distribution, and skewness.

These recommendations are based upon the results of the simulation studies summarized in Singh, Maichle, and Lee (2006).

However, simulations results will not cover all Real World data sets; for additional insight the user may want to consult a statistician.

Copper,D

General Statistics			
Total Number of Observations	27	Number of Distinct Observations	9
Number of Detects	7	Number of Non-Detects	20
Number of Distinct Detects	7	Number of Distinct Non-Detects	2
Minimum Detect	0.0058	Minimum Non-Detect	0.03
Maximum Detect	0.0532	Maximum Non-Detect	0.05
Variance Detects	4.18E-04	Percent Non-Detects	74.07%
Mean Detects	0.0257	SD Detects	0.0204
Median Detects	0.0132	CV Detects	0.797
Skewness Detects	0.421	Kurtosis Detects	-2.352
Mean of Logged Detects	-3.996	SD of Logged Detects	0.918
Normal GOF Test on Detects Only			
Shapiro Wilk Test Statistic	0.822	Shapiro Wilk GOF Test	
5% Shapiro Wilk Critical Value	0.803	Detected Data appear Normal at 5% Significance Level	
Lilliefors Test Statistic	0.3	Lilliefors GOF Test	
5% Lilliefors Critical Value	0.304	Detected Data appear Normal at 5% Significance Level	
Detected Data appear Normal at 5% Significance Level			
Kaplan-Meier (KM) Statistics using Normal Critical Values and other Nonparametric UCLs			
KM Mean	0.0207	KM Standard Error of Mean	0.00636
KM SD	0.0167	95% KM (BCA) UCL	0.0321
95% KM (t) UCL	0.0315	95% KM (Percentile Bootstrap) UCL	0.0318
95% KM (z) UCL	0.0311	95% KM Bootstrap t UCL	0.0513
90% KM Chebyshev UCL	0.0398	95% KM Chebyshev UCL	0.0484
97.5% KM Chebyshev UCL	0.0604	99% KM Chebyshev UCL	0.084
Gamma GOF Tests on Detected Observations Only			
A-D Test Statistic	0.57	Anderson-Darling GOF Test	
5% A-D Critical Value	0.719	Detected data appear Gamma Distributed at 5% Significance Level	
K-S Test Statistic	0.261	Kolmogorov-Smirnov GOF	
5% K-S Critical Value	0.316	Detected data appear Gamma Distributed at 5% Significance Level	
Detected data appear Gamma Distributed at 5% Significance Level			
Gamma Statistics on Detected Data Only			
k hat (MLE)	1.646	k star (bias corrected MLE)	1.036
Theta hat (MLE)	0.0156	Theta star (bias corrected MLE)	0.0248
nu hat (MLE)	23.05	nu star (bias corrected)	14.5
Mean (detects)	0.0257		
Gamma ROS Statistics using Imputed Non-Detects			
GROS may not be used when data set has > 50% NDs with many tied observations at multiple DLs			
GROS may not be used when kstar of detects is small such as <1.0, especially when the sample size is small (e.g., <15-20)			
For such situations, GROS method may yield incorrect values of UCLs and BTVs			
This is especially true when the sample size is small.			
For gamma distributed detected data, BTVs and UCLs may be computed using gamma distribution on KM estimates			
Minimum	0.0058	Mean	0.0208
Maximum	0.0532	Median	0.0153
SD	0.0131	CV	0.632
k hat (MLE)	2.986	k star (bias corrected MLE)	2.679
Theta hat (MLE)	0.00696	Theta star (bias corrected MLE)	0.00776
nu hat (MLE)	161.2	nu star (bias corrected)	144.7
Adjusted Level of Significance (β)	0.0401		
Approximate Chi Square Value (144.66, α)	117.9	Adjusted Chi Square Value (144.66, β)	116.3

Copper,D

95% Gamma Approximate UCL (use when n>=50)	0.0255	95% Gamma Adjusted UCL (use when n<50)	0.0258
Estimates of Gamma Parameters using KM Estimates			
Mean (KM)	0.0207	SD (KM)	0.0167
Variance (KM)	2.80E-04	SE of Mean (KM)	0.00636
k hat (KM)	1.525	k star (KM)	1.38
nu hat (KM)	82.35	nu star (KM)	74.53
theta hat (KM)	0.0136	theta star (KM)	0.015
80% gamma percentile (KM)	0.0323	90% gamma percentile (KM)	0.044
95% gamma percentile (KM)	0.0554	99% gamma percentile (KM)	0.0813
Gamma Kaplan-Meier (KM) Statistics			
Approximate Chi Square Value (74.53, α)	55.65	Adjusted Chi Square Value (74.53, β)	54.61
95% Gamma Approximate KM-UCL (use when n>=5(	0.0277	95% Gamma Adjusted KM-UCL (use when n<5(	0.0282
Lognormal GOF Test on Detected Observations Only			
Shapiro Wilk Test Statistic	0.874	Shapiro Wilk GOF Test	
5% Shapiro Wilk Critical Value	0.803	Detected Data appear Lognormal at 5% Significance Level	
Lilliefors Test Statistic	0.245	Lilliefors GOF Test	
5% Lilliefors Critical Value	0.304	Detected Data appear Lognormal at 5% Significance Level	
Detected Data appear Lognormal at 5% Significance Level			
Lognormal ROS Statistics Using Imputed Non-Detects			
Mean in Original Scale	0.0187	Mean in Log Scale	-4.235
SD in Original Scale	0.014	SD in Log Scale	0.726
95% t UCL (assumes normality of ROS data)	0.0232	95% Percentile Bootstrap UCL	0.0232
95% BCA Bootstrap UCL	0.024	95% Bootstrap t UCL	0.0246
95% H-UCL (Log ROS)	0.0258		
Statistics using KM estimates on Logged Data and Assuming Lognormal Distribution			
KM Mean (logged)	-4.2	KM Geo Mean	0.015
KM SD (logged)	0.789	95% Critical H Value (KM-Log)	2.262
KM Standard Error of Mean (logged)	0.309	95% H-UCL (KM -Log)	0.0291
KM SD (logged)	0.789	95% Critical H Value (KM-Log)	2.262
KM Standard Error of Mean (logged)	0.309		
DL/2 Statistics			
DL/2 Normal		DL/2 Log-Transformed	
Mean in Original Scale	0.0248	Mean in Log Scale	-3.788
SD in Original Scale	0.01	SD in Log Scale	0.469
95% t UCL (Assumes normality)	0.0281	95% H-Stat UCL	0.0302
DL/2 is not a recommended method, provided for comparisons and historical reasons			
Nonparametric Distribution Free UCL Statistics			
Detected Data appear Normal Distributed at 5% Significance Level			

Suggested UCL to Use

95% KM (t) UCL	0.0315

Note: Suggestions regarding the selection of a 95% UCL are provided to help the user to select the most appropriate 95% UCL.
Recommendations are based upon data size, data distribution, and skewness.

These recommendations are based upon the results of the simulation studies summarized in Singh, Maichle, and Lee (2006).

However, simulations results will not cover all Real World data sets; for additional insight the user may want to consult a statistician.

Selenium,D

General Statistics			
Total Number of Observations	27	Number of Distinct Observations	20
Number of Detects	17	Number of Non-Detects	10
Number of Distinct Detects	17	Number of Distinct Non-Detects	3
Minimum Detect	0.147	Minimum Non-Detect	0.2
Maximum Detect	0.465	Maximum Non-Detect	0.4
Variance Detects	0.0105	Percent Non-Detects	37.04%
Mean Detects	0.299	SD Detects	0.102
Median Detects	0.317	CV Detects	0.342
Skewness Detects	-0.185	Kurtosis Detects	-1.084
Mean of Logged Detects	-1.27	SD of Logged Detects	0.384
Normal GOF Test on Detects Only			
Shapiro Wilk Test Statistic	0.932	Shapiro Wilk GOF Test	
5% Shapiro Wilk Critical Value	0.892	Detected Data appear Normal at 5% Significance Level	
Lilliefors Test Statistic	0.141	Lilliefors GOF Test	
5% Lilliefors Critical Value	0.207	Detected Data appear Normal at 5% Significance Level	
Detected Data appear Normal at 5% Significance Level			
Kaplan-Meier (KM) Statistics using Normal Critical Values and other Nonparametric UCLs			
KM Mean	0.254	KM Standard Error of Mean	0.0214
KM SD	0.104	95% KM (BCA) UCL	0.289
95% KM (t) UCL	0.29	95% KM (Percentile Bootstrap) UCL	0.288
95% KM (z) UCL	0.289	95% KM Bootstrap t UCL	0.294
90% KM Chebyshev UCL	0.318	95% KM Chebyshev UCL	0.347
97.5% KM Chebyshev UCL	0.388	99% KM Chebyshev UCL	0.467
Gamma GOF Tests on Detected Observations Only			
A-D Test Statistic	0.672	Anderson-Darling GOF Test	
5% A-D Critical Value	0.74	Detected data appear Gamma Distributed at 5% Significance Level	
K-S Test Statistic	0.159	Kolmogorov-Smirnov GOF	
5% K-S Critical Value	0.209	Detected data appear Gamma Distributed at 5% Significance Level	
Detected data appear Gamma Distributed at 5% Significance Level			
Gamma Statistics on Detected Data Only			
k hat (MLE)	7.98	k star (bias corrected MLE)	6.611
Theta hat (MLE)	0.0375	Theta star (bias corrected MLE)	0.0453
nu hat (MLE)	271.3	nu star (bias corrected)	224.8
Mean (detects)	0.299		
Gamma ROS Statistics using Imputed Non-Detects			
GROS may not be used when data set has > 50% NDs with many tied observations at multiple DLs			
GROS may not be used when kstar of detects is small such as <1.0, especially when the sample size is small (e.g., <15-20)			
For such situations, GROS method may yield incorrect values of UCLs and BTVs			
This is especially true when the sample size is small.			
For gamma distributed detected data, BTVs and UCLs may be computed using gamma distribution on KM estimates			
Minimum	0.112	Mean	0.259
Maximum	0.465	Median	0.224
SD	0.101	CV	0.389
k hat (MLE)	6.904	k star (bias corrected MLE)	6.162
Theta hat (MLE)	0.0375	Theta star (bias corrected MLE)	0.042
nu hat (MLE)	372.8	nu star (bias corrected)	332.7
Adjusted Level of Significance (β)	0.0401		
Approximate Chi Square Value (332.73, α)	291.5	Adjusted Chi Square Value (332.73, β)	289

Selenium,D

95% Gamma Approximate UCL (use when n>=50)	0.295	95% Gamma Adjusted UCL (use when n<50)	0.298

Estimates of Gamma Parameters using KM Estimates

Mean (KM)	0.254	SD (KM)	0.104
Variance (KM)	0.0109	SE of Mean (KM)	0.0214
k hat (KM)	5.932	k star (KM)	5.297
nu hat (KM)	320.3	nu star (KM)	286.1
theta hat (KM)	0.0428	theta star (KM)	0.0479
80% gamma percentile (KM)	0.339	90% gamma percentile (KM)	0.401
95% gamma percentile (KM)	0.458	99% gamma percentile (KM)	0.577

Gamma Kaplan-Meier (KM) Statistics

Approximate Chi Square Value (286.06, α)	247.9	Adjusted Chi Square Value (286.06, β)	245.6
95% Gamma Approximate KM-UCL (use when n>=50)	0.293	95% Gamma Adjusted KM-UCL (use when n<50)	0.295

Lognormal GOF Test on Detected Observations Only

Shapiro Wilk Test Statistic	0.889	Shapiro Wilk GOF Test
5% Shapiro Wilk Critical Value	0.892	Detected Data Not Lognormal at 5% Significance Level
Lilliefors Test Statistic	0.172	Lilliefors GOF Test
5% Lilliefors Critical Value	0.207	Detected Data appear Lognormal at 5% Significance Level

Detected Data appear Approximate Lognormal at 5% Significance Level

Lognormal ROS Statistics Using Imputed Non-Detects

Mean in Original Scale	0.258	Mean in Log Scale	-1.43
SD in Original Scale	0.101	SD in Log Scale	0.391
95% t UCL (assumes normality of ROS data)	0.291	95% Percentile Bootstrap UCL	0.29
95% BCA Bootstrap UCL	0.289	95% Bootstrap t UCL	0.295
95% H-UCL (Log ROS)	0.298		

Statistics using KM estimates on Logged Data and Assuming Lognormal Distribution

KM Mean (logged)	-1.455	KM Geo Mean	0.233
KM SD (logged)	0.407	95% Critical H Value (KM-Log)	1.896
KM Standard Error of Mean (logged)	0.0845	95% H-UCL (KM -Log)	0.295
KM SD (logged)	0.407	95% Critical H Value (KM-Log)	1.896
KM Standard Error of Mean (logged)	0.0845		

DL/2 Statistics

DL/2 Normal		DL/2 Log-Transformed	
Mean in Original Scale	0.235	Mean in Log Scale	-1.586
SD in Original Scale	0.12	SD in Log Scale	0.546
95% t UCL (Assumes normality)	0.274	95% H-Stat UCL	0.295

DL/2 is not a recommended method, provided for comparisons and historical reasons

Nonparametric Distribution Free UCL Statistics
Detected Data appear Normal Distributed at 5% Significance Level

Suggested UCL to Use

95% KM (t) UCL	0.29

Note: Suggestions regarding the selection of a 95% UCL are provided to help the user to select the most appropriate 95% UCL.
Recommendations are based upon data size, data distribution, and skewness.

These recommendations are based upon the results of the simulation studies summarized in Singh, Maichle, and Lee (2006).

However, simulations results will not cover all Real World data sets; for additional insight the user may want to consult a statistician.

Zinc,D

General Statistics			
Total Number of Observations	27	Number of Distinct Observations	7
Number of Detects	5	Number of Non-Detects	22
Number of Distinct Detects	5	Number of Distinct Non-Detects	2
Minimum Detect	0.0307	Minimum Non-Detect	0.01
Maximum Detect	0.51	Maximum Non-Detect	0.1
Variance Detects	0.0404	Percent Non-Detects	81.48%
Mean Detects	0.228	SD Detects	0.201
Median Detects	0.166	CV Detects	0.882
Skewness Detects	0.677	Kurtosis Detects	-1.371
Mean of Logged Detects	-1.911	SD of Logged Detects	1.142
Normal GOF Test on Detects Only			
Shapiro Wilk Test Statistic	0.922	Shapiro Wilk GOF Test	
5% Shapiro Wilk Critical Value	0.762	Detected Data appear Normal at 5% Significance Level	
Lilliefors Test Statistic	0.221	Lilliefors GOF Test	
5% Lilliefors Critical Value	0.343	Detected Data appear Normal at 5% Significance Level	
Detected Data appear Normal at 5% Significance Level			
Kaplan-Meier (KM) Statistics using Normal Critical Values and other Nonparametric UCLs			
KM Mean	0.073	KM Standard Error of Mean	0.028
KM SD	0.11	95% KM (BCA) UCL	0.127
95% KM (t) UCL	0.121	95% KM (Percentile Bootstrap) UCL	0.128
95% KM (z) UCL	0.119	95% KM Bootstrap t UCL	0.114
90% KM Chebyshev UCL	0.157	95% KM Chebyshev UCL	0.195
97.5% KM Chebyshev UCL	0.248	99% KM Chebyshev UCL	0.351
Gamma GOF Tests on Detected Observations Only			
A-D Test Statistic	0.216	Anderson-Darling GOF Test	
5% A-D Critical Value	0.688	Detected data appear Gamma Distributed at 5% Significance Level	
K-S Test Statistic	0.198	Kolmogorov-Smirnov GOF	
5% K-S Critical Value	0.363	Detected data appear Gamma Distributed at 5% Significance Level	
Detected data appear Gamma Distributed at 5% Significance Level			
Gamma Statistics on Detected Data Only			
k hat (MLE)	1.3	k star (bias corrected MLE)	0.653
Theta hat (MLE)	0.175	Theta star (bias corrected MLE)	0.349
nu hat (MLE)	13	nu star (bias corrected)	6.532
Mean (detects)	0.228		
Gamma ROS Statistics using Imputed Non-Detects			
GROS may not be used when data set has > 50% NDs with many tied observations at multiple DLs			
GROS may not be used when kstar of detects is small such as <1.0, especially when the sample size is small (e.g., <15-20)			
For such situations, GROS method may yield incorrect values of UCLs and BTVs			
This is especially true when the sample size is small.			
For gamma distributed detected data, BTVs and UCLs may be computed using gamma distribution on KM estimates			
Minimum	0.01	Mean	0.0746
Maximum	0.51	Median	0.01
SD	0.118	CV	1.586
k hat (MLE)	0.662	k star (bias corrected MLE)	0.613
Theta hat (MLE)	0.113	Theta star (bias corrected MLE)	0.122
nu hat (MLE)	35.74	nu star (bias corrected)	33.1
Adjusted Level of Significance (β)	0.0401		
Approximate Chi Square Value (33.10, α)	20.95	Adjusted Chi Square Value (33.10, β)	20.33

Zinc,D

95% Gamma Approximate UCL (use when n>=50)	0.118	95% Gamma Adjusted UCL (use when n<50)	0.121

Estimates of Gamma Parameters using KM Estimates

Mean (KM)	0.073	SD (KM)	0.11
Variance (KM)	0.0121	SE of Mean (KM)	0.028
k hat (KM)	0.442	k star (KM)	0.417
nu hat (KM)	23.85	nu star (KM)	22.53
theta hat (KM)	0.165	theta star (KM)	0.175
80% gamma percentile (KM)	0.118	90% gamma percentile (KM)	0.205
95% gamma percentile (KM)	0.299	99% gamma percentile (KM)	0.535

Gamma Kaplan-Meier (KM) Statistics

Approximate Chi Square Value (22.53, α)	12.74	Adjusted Chi Square Value (22.53, β)	12.27
95% Gamma Approximate KM-UCL (use when n>=5(	0.129	95% Gamma Adjusted KM-UCL (use when n<5(	0.134

Lognormal GOF Test on Detected Observations Only

Shapiro Wilk Test Statistic	0.959	Shapiro Wilk GOF Test
5% Shapiro Wilk Critical Value	0.762	Detected Data appear Lognormal at 5% Significance Level
Lilliefors Test Statistic	0.179	Lilliefors GOF Test
5% Lilliefors Critical Value	0.343	Detected Data appear Lognormal at 5% Significance Level

Detected Data appear Lognormal at 5% Significance Level

Lognormal ROS Statistics Using Imputed Non-Detects

Mean in Original Scale	0.0737	Mean in Log Scale	-3.4
SD in Original Scale	0.114	SD in Log Scale	1.288
95% t UCL (assumes normality of ROS data)	0.111	95% Percentile Bootstrap UCL	0.111
95% BCA Bootstrap UCL	0.126	95% Bootstrap t UCL	0.159
95% H-UCL (Log ROS)	0.16		

Statistics using KM estimates on Logged Data and Assuming Lognormal Distribution

KM Mean (logged)	-3.287	KM Geo Mean	0.0374
KM SD (logged)	1.097	95% Critical H Value (KM-Log)	2.65
KM Standard Error of Mean (logged)	0.506	95% H-UCL (KM -Log)	0.121
KM SD (logged)	1.097	95% Critical H Value (KM-Log)	2.65
KM Standard Error of Mean (logged)	0.506		

DL/2 Statistics

DL/2 Normal		DL/2 Log-Transformed	
Mean in Original Scale	0.0813	Mean in Log Scale	-2.88
SD in Original Scale	0.107	SD in Log Scale	0.786
95% t UCL (Assumes normality)	0.116	95% H-Stat UCL	0.108

DL/2 is not a recommended method, provided for comparisons and historical reasons

Nonparametric Distribution Free UCL Statistics

Detected Data appear Normal Distributed at 5% Significance Level

Suggested UCL to Use

95% KM (t) UCL	0.121

Note: Suggestions regarding the selection of a 95% UCL are provided to help the user to select the most appropriate 95% UCL.
Recommendations are based upon data size, data distribution, and skewness.

These recommendations are based upon the results of the simulation studies summarized in Singh, Maichle, and Lee (2006).

However, simulations results will not cover all Real World data sets; for additional insight the user may want to consult a statistician.