

CATALOG DOCUMENTATION
EMAP-ESTUARIES PROGRAM LEVEL DATABASE
1993 VIRGINIAN PROVINCE
SEDIMENT CHEMISTRY

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1. DATA SET IDENTIFICATION
 - 1.1 Title of Catalog document

EMAP-Estuaries Program Level Database
1993 Virginian Province
Sediment Chemistry Data
 - 1.2 Authors of the Catalog entry

Charles Strobel, U.S. EPA NHEERL-AED
Melissa Hughes, OAO Corp.
 - 1.3 Catalog revision date

25 March 1996
 - 1.4 Data set name

SED_CHEM
 - 1.5 Task Group

Estuaries

1.6 Data set identification code

00105

1.7 Version

001

1.8 Requested Acknowledgment

These data were produced as part of the U.S. EPA's Environmental Monitoring and Assessment Program (EMAP). If you plan to publish these data in any way, EPA requires a standard statement for work it has supported:

"Although the data described in this article has been funded wholly or in part by the U. S. Environmental Protection Agency through its EMAP-Estuaries Program, it has not been subjected to Agency review, and therefore, does not necessarily reflect the views of the Agency and no official endorsement should be inferred."

2. INVESTIGATOR INFORMATION

2.1 Principal Investigator

Darryl Keith
U.S. Environmental Protection Agency
NHEERL-AED

2.2 Investigation Participant-Sample Collection

Charles J. Strobel
U.S. Environmental Protection Agency
NHEERL-AED

2.3 Principal Investigator-Sample Processing

John Martinson
U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory-Cincinnati

3. DATA SET ABSTRACT

3.1 Abstract of the Data Set

The Sediment Chemistry data set presents a suite of chemical concentrations derived from analyses of a surface sediment sample collected at a station in the Virginian Province. Individual and summed analyte concentrations are presented.

A code for each compound is given under ANALYTE. These include 18 inorganic, 57 organic, five organic concentration sums, Total Organic Carbon (TOC) and acid volatile sulfides (AVS). Concentrations are recorded in dry weight. Units are reported under a separate attribute: ug/g, ng/g, % or umoles/g. Quality Assurance/Quality Control issues are coded. Depending on the QA code, only a detection limit may be reported.

3.2 Keywords for the Data Set

Contaminants, DDT, inorganic analytes, organic analytes, PAH, PCB, pesticides, QA Code, sediment, sediment chemistry, TOC, AVS, mono-butyltin, di-butyltin and tri-butyltin

4. OBJECTIVES AND INTRODUCTION

4.1 Program Objective

The Environmental Monitoring and Assessment Program (EMAP) was designed to periodically estimate the status and trends of the Nation's ecological resources on a regional basis. EMAP provides a strategy to identify and bound the extent, magnitude and location of environmental degradation and improvement on a regional scale based on station sites randomly located in estuaries. Only BASE Sampling Sites were included in this data set. The general objective of this project was to collect data to characterize the environmental condition of estuaries in the Virginian Province.

4.2 Data Set Objective

The specific objective of this investigation was to determine the concentrations of a suite of organic and inorganic contaminants measured in surface sediments collected during summer 1993 at sampling sites located in estuaries throughout the Virginian Province.

4.3 Data Set Background Discussion

The presence of contaminants in estuaries has been identified in both the scientific and popular press as a major problem contributing to degraded ecological resources and restricted harvest of fish and shellfish resources due to human health concerns. Reducing contaminant inputs and concentrations, therefore, is often a major focus of regulatory programs for estuaries. Contaminants include both inorganic (primarily metals) and organic forms originating from many sources, including atmospheric deposition, freshwater inputs, land runoff and point sources. These sources are poorly characterized, except in the most well-studied estuaries. Most contaminants that are potentially toxic to indigenous biological resources tend to bind to particles, which ultimately are deposited at the bottom of estuaries. This binding changes the form of contaminants and removes them from the water column; consequently, contaminants accumulate in estuarine sediments.

EMAP monitoring efforts have focused on sediment contaminants rather than measurement of contaminants in the water column. Concentrations of contaminants in sediments are less variable than those in the water column and the sediment integrates contaminant inputs to estuaries over months and years.

Sediment contaminant concentrations were measured to aid in the interpretation of the spatial patterns observed in the condition of biological resources in the estuaries of the Virginian Province.

Metals in the sediment may be derived from anthropogenic sources or from the natural geochemical processes of weathering and erosion of rocks, since metals occur naturally in the earth's crust. The difficulty arises in identifying which portion of the total metal content of the sediment was due to natural processes and which was due to human activities.

Several methods can be used to determine whether measured metal concentrations in estuarine sediments represent anthropogenically-enriched or natural conditions. A further discussion can be found in one of the EMAP-VP statistical summaries.

4.4 Summary of Data Set Parameters

Surface sediments collected at Virginian Province stations in 1993 were analyzed to determine the concentrations of the following: 15 major and trace elements, 24 individual PAH compounds, the pesticide DDT and its metabolites, 9 pesticides other than DDT, 18 individual PCB congeners, total organic carbon (TOC), acid volatile sulfides (AVS), and mono-, di- and tributyltin (MBT, DBT and TBT). A complete list of analytes can be found in the 1990 Near Coastal Program Plan (Holland et al., 1990). This suite of analytes is the same as that measured in the National Oceanic and Atmospheric Administration's (NOAA) National Status and Trends (NS&T) program. Values in this data set also include concentrations summed for several major groups: total PAHs, Low and High Molecular Weight PAHs, PCBs and DDTs.

Concentrations of all sediment chemistry analytes are reported on a dry weight basis.

5. DATA ACQUISITION AND PROCESSING METHODS

5.1 Data Acquisition

5.1.1 Sampling Objective

Collect sediment samples suitable for the analysis of organic and inorganic compounds and sediment constituents. One sediment sample was expected to be collected at each station.

5.1.2 Sample Collection Methods Summary

The sampler was attached to the end of a winch cable with a shackle. A pinger and a set of weights were attached to the grab. The grab was then cocked. The grab sampler was lowered through the water column. The grab penetrated the sediment by gravity releasing a trigger which kept the jaws of the grab open. When the grab was pulled from the sediment using the winch, the jaws closed, encapsulating the sediment sample. The chance of sampling the exact same location twice was minimized. After three (3) grabs were taken, the boat was moved five (5) meters downstream by letting out the appropriate length of anchor line.

Stainless steel utensils were used to remove the top two (2) cm of sediment from a grab. A margin of one (1) cm was left from the edge of the sample to reduce the possibility of contamination from the sampler. The sediment was removed to a stainless steel bowl and placed in a cooler of ice to remain cold, but unfrozen. The grab sampler was rinsed and re-deployed. This procedure was repeated until approximately 3,000 cc of sediment was collected. The sediment was mixed by hand until thoroughly homogenized, and aliquots were placed immediately into pre-cleaned jars (for organics) or plastic containers (for inorganics). The samples were immediately stored on ice following collection.

5.1.3 Beginning Sampling Date

27 July 1993

5.1.4 Ending Sampling Date

31 August 1993

5.1.5 Platform

Sampling was conducted from 8 m (24 ft), twin-engine Chesapeake style work boats.

5.1.6 Sampling Equipment

A 1/25 m², Kynar-coated stainless steel Young-modified Van Veen grab sampler was used to collect sediments. This grab sampled an area of 440 cm² and had a maximum depth of penetration in the sediment of 10 cm.

5.1.7 Manufacturer of Sampling Equipment

Young's Welding, Sandwich, MA

5.1.8 Key Variables

This data set does not contain any values which were measured at the time of collection. Chemical analyses produced data on organic and inorganic compounds and sediment constituents.

5.1.9 Sampling Method Calibration

The sampling gear does not require any calibration. It required inspection for deformities incurred due to mishandling or impact on rocky substrates.

5.1.10 Sample Collection Quality Control

Grabs were visually inspected at the time of collection; acceptable grabs were those that showed a uniform (i.e., undisturbed) sediment surface and that had penetrated the sediment to a depth between 7 and 10 cm. Unacceptable grabs included those: containing no sediments, which were partially filled or had shelly substrates or grossly slumped surfaces. Grabs completely filled to the top, where the sediment was in direct contact with the hinged top, were also unacceptable.

Field technicians were trained to follow Standard Operating Procedures (Reifsteck et al., 1993) to insure the collection of representative, uncontaminated, high quality samples. Examples of QA/QC measures taken in the field to avoid or reduce contamination and insure the collection of representative samples include the following: use of stainless steel implements for mixing and transferring sediments, thorough cleaning and rinsing of the grab sampler and implements between samples, use of pre-cleaned sample containers for sediment storage, assuring that all engines are shut down when the sample is exposed to the air, and immediate storage of samples on ice following collection.

4.1.9 Sample Collection Method Reference

Reifsteck, D.M., C.J. Strobel, and D. Keith. 1993. EMAP-Estuaries 1993 Virginian Province Field Operations and Safety Manual. U.S. Environmental Protection Agency, Office of Research and Development, NHEERL-AED, Narragansett, RI. June 1993.

5.2 Data Preparation and Sample Processing

5.2.1 Data Preparation Objective

Process uncontaminated sediment samples for characterization of contaminants.

5.2.2 Sample Processing Methods Summary

In the laboratory, the frozen sediment samples were thawed and thoroughly homogenized prior to analysis. Separate aliquots of the homogenized sediment were removed for the following analyses: inorganic analyses (major and trace elements both total and Simultaneously Extracted Metals (SEM)), organic analyses (PAHs, PCBs, and pesticides), total organic carbon (TOC), butyltins (MBT, DBT, and TBT), and acid volatile sulfides (AVS). A brief description of the method used for each of these analyses follows.

INORGANIC

Analysis of the sediment for major and trace elements involved a total digestion (i.e., complete dissolution) of the sediment matrix. For the metals Ag, Al, Cr, Cu, Fe, Mn, Ni, Pb and Zn, the total digestion was accomplished using HF/HNO₃ in an open beaker on a hot plate, followed by instrumental analyses using inductively-coupled plasma-atomic emission spectrometry (ICP-AES). For the metals As, Cd, Sb, Se, and Sn, a microwave digestion using HNO₃/HCl in a closed teflon-lined pressure vessel was followed by analysis using Zeeman-corrected, stabilized temperature graphite furnace atomic absorption (GFAA). Mercury (Hg) was analyzed by cold vapor atomic absorption spectrometry.

Sediment concentrations of butyltin compounds were determined using high resolution gas chromatography and flame photometric detection.

SEM analyses consisted of analyzing the AVS extract using ICP and GFAA, as described above.

ORGANIC

The analysis of organic contaminants in the sediment involved sample extraction and cleanup followed by instrumental analysis. This included the following basic steps: Soxhlet extraction, extract drying using sodium sulfate, extract concentration using Kuderna-Danish apparatus, removal of elemental sulfur with activated copper, removal of organic interferences with gel permeation chromatography (GPC) and/or alumina. Following extraction and cleanup, PAH compounds were analyzed using gas chromatography/mass spectrometry (GC/MS). The pesticides and PCB congeners were analyzed using gas chromatography/electron capture detection (GC/ECD) with second column confirmation.

OTHER CONSTITUENTS

The concentration of total organic carbon (TOC) in each sediment sample was determined by ultraviolet light-promoted persulfate oxidation. Acid volatile sulfides (AVS) were measured using a sulfide ion-specific electrode following reaction of the sediment with hydrochloric acid and subsequent trapping of the evolved hydrogen sulfide in solution.

5.2.3 Sample Processing Method Calibration

For the 1993 sediment analyses, a Standard or Certified Reference Material (SRM or CRM) typically was used as the Laboratory Control Material (LCM). SRMs and CRMs have known or "certified" concentrations of the analytes being measured and therefore are useful for assessing both accuracy and precision. The 1993 QA Plan required the laboratory's percent recovery (relative to the certified concentration in the reference material) to fall within a range of 80% to 120% for each inorganic analyte and 70% to 130% for at least 70% of the organic analytes. If the laboratory consistently failed to meet these accuracy goals for the CRM or SRM, the values reported for the failed analytes were considered to be suspect (biased) and were flagged in the database.

5.2.4 Sample Processing Quality Control

Each laboratory was required each laboratory to analyze the following quality control (QC) samples along with every batch or "set" of field chemistry samples: laboratory reagent blank, calibration check standards, matrix spike/matrix spike duplicate, and Laboratory Control Material (LCM). Results for these QC samples had to fall within certain pre-established control limits for the analysis of a batch of samples to be considered acceptable.

5.2.5 Sample Processing Method Reference

Valente, R.M. and C.S. Strobel. 1993. EMAP-Estuaries 1993 Virginian Province Quality Assurance Project Plan. U.S. Environmental Protection Agency, Office of Research and Development, NHEERL-AED, Narragansett, RI. May 1993.

6. DATA MANIPULATIONS

6.1 Name of New or Modified Values

TOT_PCB, TOT_PAH, PAH_LMW, PAH_HMW, TOT_DDT and TOT_ANAL

6.2 Data Manipulation Description

6.2.1 TOT_PCB, TOT_PAH, PAH_LMW, PAH_HMW, TOT_DDT

Summary values were calculated for groups of organic analytes. The values under a summed analyte are the sum of the concentrations of a specific set of compounds.

6.2.2 TOT_ANAL

The number of analytes under TOT_ANAL include only those with a concentration.

6.3 Data Manipulation Examples

The following groups must be summed in order to have consistency across Provinces:

6.3.1 Total Poly-aromatic Hydrocarbons

TOT_PAH = sum of concentrations of biphenyl, fluorene, 1-methylnaphthalene, 2-methylnaphthalene, naphthalene, 2,6-dimethylnaphthalene, acenaphthene, phenanthrene, anthracene, acenaphthylene, 2,3,5-trimethylnaphthalene, 1-methylphenanthrene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b,k)fluoranthene or individual compounds, ideno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene, perylene, benzo(a)pyrene, benzo(e)pyrene and dibenz(a,h)anthracene.

6.3.2 Low Molecular Weight PAHs

PAH_LMW = sum of concentrations of biphenyl, fluorene, 1-methylnaphthalene, 2-methylnaphthalene, naphthalene, 2,6-dimethylnaphthalene, anthracene, acenaphthylene, 2,3,5-trimethylnaphthalene.

6.3.3 High Molecular Weight PAHs

PAH_HMW = sum of concentrations of fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b,k)fluoranthene or individual compounds, ideno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene, perylene, benzo(a)pyrene, benzo(e)pyrene and dibenz(a,h)anthracene, acenaphthene, phenanthrene and 1-methylphenanthrene.

6.3.4 Total DDT

TOT_DDT = sum of concentrations of OPDDE, OPDDD, OPDDT, PPDDE, PPDDD, PPDDT.

6.3.5 Total Polychlorinated Biphenyls

TOT_PCB = sum of concentrations of the following PCB congeners: 8, 18, 28, 52, 44, 66, 101, 118, 153, 105, 138, 187, 128, 180, 170, 195, 206 and 209.

7. DATA DESCRIPTION

7.1 Description of Parameters

#	Parameter	Data			Parameter
	SAS Name	Type	Len	Format	Label
1	STA_NAME	Char	8	8.	The Station Identifier
2	VST_DATE	Num	8	YYMMDD6.	The Date the Sample was Collected
3	ANALYTE	Char	8	8.	Analyte Code
4	CONC	Num	8	13.6	Conc. of Analyte (dry wt.)
5	CHMUNITS	Char	15	12.	Concentration Units
6	QA_CODE	Char	15	15.	Quality Assurance Code for Data
7	TOT_ANAL	Num	8	3.	Analytes (#) Included in Summed Conc.
8	DETLIMIT	Num	8	13.6	Method Detection Limit for Analyte
9.	ANAL_CAT	Char	15	15.	General Category for Group of Analytes

7.1.6 Precision to which values are reported

The sediment chemistry concentrations presented are in a format of 6 decimal places. This format is necessary because some concentrations are in ug/g and some concentrations are in ng/g. However, the concentrations are only valid FOR THREE SIGNIFICANT FIGURES (not necessarily three decimal places), i.e., 345.67 ug/g is 346 ug/g but 0.00235 ng/g remains as 0.00235 ng/g.

7.1.7 Minimum Value in Data Set by Analyte

ANALYTE	Minimum Value
ACENTHE	5.99
ACENTHY	7.97
AG	0.01
AL	1890.00
ANTHRA	5.10
AS	0.42
AVS	0.03
BENANTH	7.00
BENAPY	7.00
BENEPY	7.00
BENZOFL	9.00
BENZOP	6.00
BIPHENYL	8.00
CD	0.04
CHRYSENE	6.00
CISCHL	0.31
CR	1.90
CU	1.05
DBT	3.00
DDT_TOT	0.00
DIBENZ	5.89
DIELDRIN	0.15
DIMETH	6.00
FE	1360.00
FLUORANT	12.20
FLUORENE	7.94
HEPTACHL	0.20
HEPTAEPO	0.10
HEXACHL	0.21
HG	0.00
INDENO	5.00
LINDANE	0.20
MBT	6.00
MENAP1	6.00
MENAP2	6.94
MEPHEN1	9.00
MIREX	0.61
MN	23.90
NAPH	8.00
NI	0.59
OPDDD	0.15
OPDDE	0.25
OPDDT	0.28
PAH_HMW	6.00
PAH_LMW	8.00

7.1.7 Minimum Value in Data Set by Analyte, continued

ANALYTE	Minimum Value
PAH_TOT	0.00
PB	1.66
PCB101	0.26
PCB105	0.36
PCB118	0.30
PCB128	0.14
PCB138	0.26
PCB153	0.26
PCB170	0.18
PCB18	0.196
PCB180	0.345
PCB187	0.252
PCB195	0.189
PCB206	0.171
PCB209	0.146
PCB28	0.304
PCB44	0.256
PCB52	0.220
PCB66	0.309
PCB8	0.158
PCB_TOT	0.000
PERYLENE	5.000
PHENANTH	6.000
PPDDD	0.182
PPDDE	0.276
PPDDT	0.100
PYRENE	8.000
SB	0.0597
SE	0.119
SN	0.127
TBT	4.000
TNONCHL	0.149
TOC	0.0119
TRIMETH	5.640
ZN	3.150

7.1.8 Maximum Value in Data Set by Analyte

ANALYTE	Maximum Value
ACENTHE	342.00
ACENTHY	209.00
AG	8.77
AL	83000.00
ANTHRA	447.00
AS	30.80
AVS	121.00
BENANTH	964.00
BENAPY	1150.00
BENEPY	925.00
BENZOFL	1790.00
BENZOP	876.00
BIPHENYL	292.00

7.1.8 Maximum Value in Data Set by Analyte, continued

ANALYTE	Maximum Value
CD	2.39
CHRYSENE	1120.00
CISCHL	7.03
CR	147.00
CU	201.00
DBT	25.10
DDT_TOT	48.80
DIBENZ	215.00
DIELDRIN	2.60
DIMETH	489.00
FE	64700.00
FLUORANT	2020.00
FLUORENE	501.00
HEPTACHL	0.52
HEPTAEPO	1.18
HEXACHL	1.47
HG	1.57
INDENO	933.00
LINDANE	0.63
MBT	37.00
MENAP1	477.00
MENAP2	1120.00
MEPHEN1	341.00
MIREX	0.95
MN	5850.00
NAPH	1500.00
NI	66.70
OPDDD	9.44
OPDDE	11.60
OPDDT	4.31
PAH_HMW	12000.00
PAH_LMW	5110.00
PAH_TOT	13200.00
PB	13600.00
PCB101	34.40
PCB105	22.80
PCB118	33.00
PCB128	3.87
PCB138	31.90
PCB153	25.40
PCB170	5.44
PCB18	44.70
PCB180	9.86
PCB187	7.23
PCB195	2.81
PCB206	21.60
PCB209	29.40
PCB28	156.00
PCB44	38.00
PCB52	57.10
PCB66	85.90
PCB8	32.60
PCB_TOT	578.00
PERYLENE	1670.00

7.1.8 Maximum Value in Data Set by Analyte, continued

ANALYTE	Maximum Value
PHENANTH	1120.00
PPDDD	21.70
PPDDE	21.80
PPDDT	4.80
PYRENE	2670.00
SB	152.00
SE	0.86
SN	30.40
TBT	194.00
TNONCHL	5.44
TOC	4.65
TRIMETH	182.00
ZN	402.00

7.2 Data Record Example

7.2.1 Column Names for Example Records

STA_NAME	VST_DATE	ANALYTE	CONC	CHMUNITS	QA_CODE	TOT_ANAL
DETLIMIT	ANAL_CAT					

7.2.2 Example Data Records

OBS	STA_NAME	VST_DATE	ANALYTE	CONC	CHMUNITS
1	VA93-601	930918	ACENTHE	.	ng/g
2	VA93-601	930918	ACENTHY	.	ng/g
3	VA93-601	930918	AG	0.054700	ug/g

OBS	QA_CODE	TOT_ANAL	DETLIMIT	ANAL_CAT
1	CH-A	.	9.900000	PAH
2	CH-A	.	9.900000	PAH
3		.	.	METAL

8. GEOGRAPHIC AND SPATIAL INFORMATION

8.1 Minimum Longitude

-77 Degrees 23 Minutes 37.20 Decimal Seconds

8.2 Maximum Longitude

-70 Degrees 01 Minutes 9.00 Decimal Seconds

8.3 Minimum Latitude

36 Degrees 56 Minutes 54.00 Decimal Seconds

8.4 Maximum Latitude

42 Degrees 11 Minutes 30.00 Decimal Seconds

8.5 Name of area or region

Virginian Province

Stations were located in estuaries along the East Coast of the United States from Cape Cod, Massachusetts, to Cape Henry, Virginia, at the mouth of the Chesapeake Bay. The area includes the District of Columbia and the States of Virginia, Maryland, New Jersey, Delaware, Pennsylvania, New York, Connecticut, Rhode Island and Massachusetts.

9. QUALITY CONTROL AND QUALITY ASSESSMENT

Because of the complexity and importance of sediment contaminant data, EMAP has expended a tremendous effort in the Quality Assurance of these data as is reflected in the detail provided in this section.

9.1 Measurement Quality Objectives

Measurement Quality Objectives (MQOs) for the 1993 Virginian Province sediment chemistry analyses were defined in the 1993 Virginian Province Quality Assurance Project Plan (Valente and Strobel, 1993). This plan required each laboratory to analyze the following quality control (QC) samples along with every batch or "set" of field chemistry samples: laboratory reagent blank, calibration check standards, matrix spike/matrix spike duplicate, and Laboratory Control Material (LCM). Results for these QC samples had to fall within certain pre-established control limits for the analysis of a batch of samples to be considered acceptable.

For the 1993 sediment analyses, a Standard or Certified Reference Material (SRM or CRM) typically was used as the Laboratory Control Material (LCM). If the laboratory consistently failed to meet these accuracy goals for the CRM or SRM (Section 5.2.4), the values reported for the failed analytes were considered to be suspect (biased) and were flagged in the database, as described in the following section.

9.2 Data Qualifier Codes

Four data qualifier codes or "flags" are used in the 1993 Virginian Province sediment chemistry data set:

The "CH-A" code indicates that an analyte was not detected. When the "CH-A" code is used, the concentration field is left blank and the detection limit for the analyte in that particular sample is reported under the variable "MDL" (method detection limit).

It is sometimes possible for a laboratory to detect an analyte and report its concentration at a level which is below the calculated method detection limit for the sample. In these situations, the analyst is confident that the analyte was present in the sample, but there is a high degree of uncertainty in the reported concentration. The "CH-B" code is used to flag reported values which are below the calculated method detection limit for the sample. Such values are considered estimates only and should be used with discretion.

The "CH-C" code is applied in situations where the laboratory failed to meet required control limits for one or more of the quality control samples analyzed along with each sample batch. In such situations, there

is reason to believe that the concentrations reported for an analyte or group of analytes may not accurately reflect the actual concentrations present in the samples. The "CH-C" code usually is applied when the Certified Reference Material results indicate that a laboratory experienced a consistent bias in the analysis of a particular analyte or group of analytes. The "CH-C" code is also applied whenever other QC sample results suggest a possible bias in the reported values (e.g., sample contamination detected in the laboratory reagent blank). Values flagged with the "CH-C" code therefore are considered estimates only and should be used with discretion.

The "CH-C" code used to flag suspect values is applied following a thorough QA review of the entire data package submitted by the laboratory for a given year. In many instances, best professional judgement must be used to decide which values should be qualified as estimates only. In the following sections, explanations are provided for the "CH-C" codes which appear in the 1993 Virginian Province sediment chemistry data set. Persons using these data may wish to perform their own review of the QC sample results to determine the acceptability of these data for their purposes.

In 1993, the laboratory used gas chromatography/electronic capture detection (GC/ECD) with dual column confirmation for the analysis of PCB congeners and chlorinated pesticides in the sediment samples. All values reported in the database for the PCBs and pesticides represent "confirmed" results (i.e., the analyte was detected and could be quantified on both the primary and secondary columns). In situations where an analyte was detected on one column, but was not confirmed on the second column, the result was treated as a "not detect" (i.e., the CH-A code is used to flag the result in the database).

In general, the rate of second-column confirmation for all reported PCB congeners and chlorinated pesticides was greater than 80%, with the following exceptions (confirmation rate in parenthesis): PCB 52 (78%), 2,4'-DDT (78%), 2,4-DDD (67%) and aldrin (74%).

While the rate of second-column confirmation generally was high for most compounds, in some instances there was a significant discrepancy in the amount of a particular PCB congener or pesticide detected on the two GC/ECD columns (i.e., greater than a factor of 3 difference). In these instances, it is difficult to ascertain which amount is more accurate (i.e., which is the "right" answer). A decision was made to take a "conservative" approach and report the lower of the two values in the database, and to flag these values using the "CH-D" code. The CH-D code has the following meaning: "Analyses were conducted using GC/ECD with dual column confirmation. Quantitation on the two columns differed by more than a factor of three, and the lower of the two results is reported."

Although this approach was deemed necessary, the user must be cautioned that the application of the "CH-D" code may invalidate investigations of the ratios of compounds. For example, if the concentrations of p,p'-DDT from the two columns were 6.1 and 2.0 ng/g respectively, the CH-D code would be applied and the lower value of 2.0 ng/g reported. However, if the values for p,p'-DDE were 6.0 and 2.1 ng/g, the CH-D code would NOT be applied and the original value of 6.0 ng/g would be reported. Most likely the ratio of these two compounds is approximately 1, but the results as reported would indicate a ratio of about 3. Therefore, ratios

of compounds should only be used when either all or none of the compounds are flagged with the CH-D code.

Values which are not flagged with the CH-B, CH-C or CH-D codes are considered valid and useful for most assessment purposes.

9.3 Quality Assessment Results

Results of QC sample analyses are stored in the EMAP-Estuaries database and are available upon request. In the following sections, these results are summarized, and the data flags associated with the 1993 Virginian Province sediment chemistry analyses are explained.

9.3.1 Major and trace element analyses (except mercury)

For the analysis of major and trace elements by ICP-AES and GFAA, the laboratory generally met the pre-established acceptability criteria (control limits) for the QC samples (e.g., calibration check samples, laboratory reagent blanks, matrix spikes, and Laboratory Control Materials). For the ICP-AES analyses, which included the metals Al, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, a total of 18 analytical sets or "batches" of samples were analyzed. The Certified Reference Material (CRM) "BCSS-1" (Estuarine Sediment, issued by the National Research Council of Canada) was analyzed along with every batch as the Laboratory Control Material. With the exception of Cr, the average percent recovery of each metal (relative to the certified concentration in BCSS-1) was within the acceptability range of 80% to 120% (Table 9-1). The average percent recovery for Cr (73%) was slightly lower than acceptable, suggesting that this metal may have been consistently "under-recovered" in the actual samples. Therefore, all reported values for this metal were qualified with the CH-C code in the database.

The GFAA analyses included the metals Ag, As, Cd, Sb, Se, and Sn; a total of 18 analytical sets or "batches" of samples were analyzed. The CRM BCSS-1 also was analyzed along with every sample batch as the Laboratory Control Material. Average CRM percent recoveries for all metals fell within the acceptability range of 80% to 120% (Table 9-1). The CRM BCSS-1 does not have a "certified" value for silver, but the average recovery for this metal in laboratory spiked samples (matrix spikes) was within quality control limits. Although the percent recovery of all metals fell within the acceptable range, all values for As, Sb, and Se were qualified with the CH-C code due to high variability of percent recovery in the matrix spiked samples for these metals.

Table 9-1. Summary results for CRM BCSS-1 (Estuarine Sediment) used as a set control for the 1993 EMAP-Estuaries sediment inorganic analyses.

ICP-AES METALS (n = 18 analysis sets or "batches"):

Element	Average ¹	Stdv ²	C.V. ³	Min. ⁴	Max. ⁵
Al	91	5.1	5.6	83	102
Cr	73	1.8	2.5	71	77
Cu	101	2.5	2.5	95	105
Fe	92	1.9	2.1	88	96
Mn	97	1.5	1.5	93	99
Ni	84	2.6	3.1	81	89
Pb	101	18.9	18.7	70	133
Zn	87	2.4	2.8	82	90

Table 9-1, continued

GFAA METALS (n = 18 analysis sets):

Element	Average ¹	Stdv ²	C.V. ³	Min. ⁴	Max. ⁵
Ag	na	na	na	na	na
As	108	10.9	10.0	84	123
Cd	98	12.6	12.9	71	123
Sb	102	21.2	20.7	67	139
Se	101	26.6	26.3	66	143
Sn	94	10.3	11.0	77	116

1 Average percent recovery relative to the SRM certified value.

2 Standard deviation of the percent recovery values.

3 Coefficient of variation of the percent recovery values.

4 Minimum percent recovery for n analysis sets

5 Maximum percent recovery for n analysis sets

9.3.2 Organic analyses

In general, results for reagent blanks and calibration check samples analyzed with each batch of field samples fell within control limits and serve to verify that sample contamination did not occur and that all instruments were calibrated properly throughout the analytical runs. Average recoveries of compounds in matrix spike/matrix spike duplicate samples generally fell within control limits, indicating acceptable analytical performance. However, matrix spike samples are not the most ideal quality control samples because the analytes of interest are not truly incorporated into the matrix in the same manner as an actual field sample.

In addition, it can be difficult to evaluate laboratory performance solely on the basis of matrix spike results because it is often equivocal whether low recoveries are due to flawed methodology, poor technique, or a true matrix interference.

Given the above limitations related to the use of matrix spike samples to assess analytical performance, great emphasis was placed on the Laboratory Control Material results. For both the PAH and PCB/pesticide analyses, SRM 1941a (Organics in Marine Sediment, issued by the National Institute of Standards and Technology) was analyzed as the Laboratory Control Material along with each batch of field samples. For most of the individual PAH compounds and PCB congeners with "known" concentrations in SRM 1941a (this includes both "certified" and "non-certified" values), the average percent recovery achieved by the laboratory (based on n = 10 batches for PAHs and n = 10 batches for PCB/pesticides) generally fell within the control limit range of 70% to 130% (Tables 9-2 and 9-3). Whenever the laboratory failed to achieve these average recovery rates for a particular compound, all the results in the 1993 database for that compound were flagged with the "CH-C" code to indicate the potential inaccuracy inferred from the SRM analysis. It is important to note that the 70% to 130% recovery criteria only applies to compounds having SRM concentrations greater than 10 times the laboratory's detection limit. When compounds occur at concentrations less than about 10 times the detection limit, a greater amount of analytical uncertainty is expected and the normal control limit "acceptability" criteria do not apply.

Based on the above, the results for the following organic compounds were flagged with the "CH-C" code in the 1993 database: PCB 101, PCB 18 and chrysene. Although the concentration of PCB 18 in the SRM was less than 10x the detection limit, the very high mean percent recovery (343%) and high variability (range of recoveries from 90% to 1,550% with a CV of 138%) resulted in the CH-C code being applied to all values for PCB 18. In addition, although the average percent recovery for PCB 206 was within limits (110%), all results for this compound were flagged with the CH-C code because the recoveries between batches exhibited relatively high variability (e.g., 78% coefficient of variation). The CH-C code was also applied to all aldrin values due to high recoveries in the matrix spiked samples (mean of 501% with a CV of 75%). Although the average SRM percent recoveries for the compounds dieldrin, cis-chlordane, 4,4'-DDT and 2,4'-DDE also were outside the acceptability range of 70% to 130% (Table 9-3), these compounds occur in the SRM at concentrations less than 10 times the laboratory's detection limit. Therefore, the acceptability criteria do not apply.

The CH-C code was also applied to several specific samples for which the data were suspect (e.g., poor agreement between field splits).

A detection limit of 0.25 ng/g (dry weight) generally was achieved for each PCB congener and pesticide and a detection of 10.0 ng/g (dry weight) was achieved for each PAH compound in the majority of samples analyzed.

Table 9-2. Results for SRM 1941a (Organics in Marine Sediment) used as the set control (Laboratory Control Material) for the 1993 sediment PAH analyses (n = 10 analysis sets or "batches").

Compound ¹	Average ²	Stdv ³	C.V. ⁴	Min ⁵	Max ⁶
Acenaphthene	118	16.6	14.1	100	133
Acenaphthylene	73	17.8	24.4	61	94
Anthracene	86	15.2	17.8	57	110
Benz(a)anthracene	119	11.4	9.6	101	137
Benzo(a)pyrene	93	22.7	24.4	68	137
Benzo(e)pyrene	104	22.4	21.5	80	147
Benzo(b+k)fluoranthene	129	23.5	18.2	97	176
Benzo(g,h,i)perylene	99	22.4	22.6	74	146
Biphenyl	73	17.9	24.7	60	112
Chrysene	136	9.7	7.2	120	153
2,6-dimethylnaphthalene	74	20.1	27.0	55	116
Fluoranthene	97	6.8	7.1	88	110
Fluorene	109	8.7	8.0	102	119
Ideno(1,2,3-c,d)pyrene	107	20.1	18.8	82	143
1-methylnaphthalene	70	17.2	24.4	47	106
2-methylnaphthalene	88	18.0	20.5	57	120
1-methylphenanthrene	92	17.4	19.0	69	120
Naphthalene	88	25.3	28.8	49	120
Perylene	84	21.5	25.6	63	131
Phenanthrene	102	10.7	10.5	88	120
Pyrene	93	9.5	10.2	82	109

1 Listed compounds include those having both "certified" and "non-certified" concentrations in SRM 1941a.

2 Average percent recovery relative to the SRM value.

- 3 Standard deviation of the percent recovery values.
- 4 Coefficient of variation of the percent recovery values.
- 5 Minimum percent recovery for 10 analysis sets
- 6 Maximum percent recovery for 10 analysis sets

Table 9-3. Results for SRM 1941a (Organics in Marine Sediment) used as the set control (Laboratory Control Material) for the 1993 sediment PCB/pesticide analyses (n = 10 analysis sets or "batches").

Compound ¹	Average ²	Stdv ³	C.V. ⁴	Min ⁵	Max ⁶
PCB 8*	106	51.6	48.5	39	218
PCB 18*	343	473	138	90	1550
PCB 28	77	13.4	17.3	61	99
PCB 44	84	26.0	30.8	59	129
PCB 52	93	22.7	24.4	68	125
PCB 66*	119	58.9	49.6	84	278
PCB 101	69	14.9	21.3	53	96
PCB 118	76	11.7	15.4	64	96
PCB 153	72	16.6	23.1	51	96
PCB 105	84	21.1	25.1	44	117
PCB 128*	77	24.9	32.4	40	113
PCB 138	91	21.9	23.9	66	144
PCB 187	91	23.6	26.1	65	134
PCB 180	121	24.0	19.8	86	172
PCB 170	96	31.5	32.7	38	132
PCB 206	110	86.2	78.4	50	310
PCB 209	81	13.8	17.0	64	101
Dieldrin*	136	94.8	69.6	49	370
cis-Chlordane*	164	66.9	40.7	97	259
trans-Nonachlor*	89	25.8	29.0	43	122
Hexachlorobenzene	76	21.2	27.9	48	114
2,4'-DDE*	250	123	49.1	112	466
4,4'-DDE	110	28.3	25.7	67	169
4,4'-DDD	99	21.0	21.3	72	145
4,4'-DDT*	137	168	122	12	582

- 1 Listed compounds include those having both "certified" and "non-certified" concentrations in SRM 1941a (* = concentration in the SRM is less than 10 times the target detection limit).
- 2 Average percent recovery relative to the SRM value.
- 3 Standard deviation of the percent recovery values.
- 4 Coefficient of variation of the percent recovery values.
- 5 Minimum percent recovery for 10 analysis sets
- 6 Maximum percent recovery for 10 analysis sets

9.3.3 Mercury analyses

For the 1993 mercury analyses, the Certified Reference Material BEST-1 (issued by the National Research Council of Canada) was analyzed along with every sample batch as the Laboratory Control Material (n = 7 sample batches). The average percent recovery of 97% for mercury in this reference material fell well within the acceptability range of 80% to 120%. In addition, an average percent recovery of 95% was achieved for the matrix spike samples analyzed in each batch. Overall, these results indicate

acceptable accuracy for the mercury analyses, and no "CH-C" codes were used to qualify the data. The 1993 mercury results were deemed acceptable for use without qualification.

9.3.4 Total Organic Carbon analyses

All QC results for the analysis of total organic carbon in the 1993 sediment samples fell within required control limits. The Certified Reference Material PACS-1 (issued by the National Research Council of Canada) was utilized as the Laboratory Control Material. The certified concentration of total carbon in this reference material is 3.69% (percent dry weight). The average percent recovery achieved by the laboratory for $n = 8$ batches of TOC samples (i.e., 8 separate analyses of CRM PACS-1) was 95.8%, with all values falling within the range 90% to 106%. Since the PACS-1 certified concentration includes both organic carbon and a very small fraction of inorganic carbon, the laboratory's percent recovery values for organic carbon generally are expected to be below 100%. Based on the good overall percent recovery of organic carbon in the Certified Reference Material, the 1993 sediment TOC data were deemed acceptable for use without qualification.

9.3.5 Butyltin analyses

Data users are cautioned that there are deficiencies in the 1993 sediment data set for butyltin compounds which might limit or preclude the use of these data. The method detection limits (MDLs) established by the laboratory were 5 ng/g dry weight for both TBT and DBT, and 12 ng/g dry weight for MBT. It is possible that the butyltin compounds of interest were present in many samples at concentrations below these detection limits, and, therefore, the occurrence of butyltin compounds in Virginian Province sediments may be more widespread than indicated by these data.

It should be noted that all butyltin results are reported as ng tin/g dry sediment. Appropriate multipliers must be applied to convert to nanograms of the ion per gram of sediment if that is the desired unit of measurement.

The Certified Reference Material PACS-1 (issued by the National Research Council of Canada) was utilized as the Laboratory Control Material for these analyses. Average percent recoveries relative to the certified value for $n = 11$ analysis sets were 74% for TBT, 74% for DBT and 188% for MBT. These values fall outside the acceptable accuracy control limits of 80% to 120%. Average percent recoveries for matrix spike samples (89% for TBT, 98% for DBT and 66% for MBT) suggest the laboratory attained better accuracy than the SRM results indicate. Given these inconsistencies in the QC data, all values reported for TBT, DBT and MBT in samples where these compounds were detected are considered estimates (CH-C code) and should be used with discretion.

9.3.6 Acid volatile sulfides analyses

At present there are no Certified Reference Materials available for acid volatile sulfides. For the 1993 samples, the laboratory utilized a laboratory fortified blank sample as the laboratory control material (LCM). The average percent recovery of AVS for $n = 60$ laboratory fortified blank samples was 94%, suggesting good overall analytical performance. In general, the 1993 AVS analyses were deemed acceptable, and no data qualifier codes were applied to these data.

10. DATA ACCESS

10.1 Data Access Procedures

Data can be downloaded from the WWW server.

10.2 Data Access Restrictions

10.3 Data Access Contact Persons

John Paul, Ph.D.
U.S. EPA NHEERL-AED
(401) 782-3037 (Tel.)
(401) 782-3030 (FAX)
paul.john@epa.gov

Data Librarian EMAP-Estuaries
U.S. EPA NHEERL-AED
(401) 782-3184 (Tel.)
(401) 782-3030 (FAX)
hughes.melissa@epa.gov

10.4 Data Set Format

Data can be downloaded in several formats from the web application and web site.

10.5 Information Concerning Anonymous FTP

Not accessible

10.6 Information Concerning WWW

Data can be downloaded from the WWW server.

10.7 EMAP CD-ROM Containing the Data Set

Data not available on CD-ROM.

11. REFERENCES

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12. LIST OF ACRONYMS

13. PERSONNEL INFORMATION

Virginian Province Manager
Darryl Keith
U.S. Environmental Protection Agency
NHEERL-AED
27 Tarzwell Drive
Narragansett, RI 02882-1197
(401)782-3135 (Tel.)
(401)782-3030 (FAX)
keith.darryl@epa.gov

Virginian Province QA Officer
Charles J. Strobel
U.S. Environmental Protection Agency
NHEERL-AED
27 Tarzwell Drive
Narragansett, RI 02882-1197
(401)782-3180 (Tel.)
(401)782-3030 (FAX)
strobel.charles@epa.gov

Sample Processing Contact
John Martinson
U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
26 W. Martin Luther King Drive
Cincinnati, OH 45268
(513)569-7286 (Tel.)

John Paul, Ph.D.
U.S. Environmental Protection Agency
NHEERL-AED
27 Tarzwell Drive
Narragansett, RI 02882-1197
(401) 782-3037 (Tel.)
(401) 782-3030 (FAX)
paul.john@epa.gov

Data Librarian, EMAP-Estuaries
Melissa M. Hughes
OAO Corporation
U.S. EPA NHEERL-AED
27 Tarzwell Drive
Narragansett, RI 02882-1197
(401) 782-3184 (Tel.)
(401) 782-3030 (FAX)
hughes.melissa@epa.gov