

US EPA ARCHIVE DOCUMENT

CATALOG DOCUMENTATION  
EMAP-ESTUARIES PROGRAM LEVEL DATABASE  
1992 VIRGINIAN PROVINCE  
SEDIMENT CHEMISTRY

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1. DATA SET IDENTIFICATION

1.1 Title of Catalog document

EMAP-Estuaries Program Level Database  
1992 Virginian Province  
Sediment Chemistry Data

1.2 Authors of the Catalog entry

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1.3 Catalog revision date

20 March 1996

#### 1.4 Data set name

SED\_CHEM

#### 1.5 Task Group

Estuaries

#### 1.6 Data set identification code

00065

#### 1.7 Version

001

#### 1.8 Requested Acknowledgement

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

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### 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 1992 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 1992 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 (1) 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 1992

#### 5.1.4 Ending Sampling Date

31 August 1992

#### 5.15 Platform

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

#### 5.16 Sampling Equipment

A Kynar-coated stainless steel Young-modified Van Veen grab sampler was used to collect sediments. This grab sampled an area of 440 cm<sup>2</sup> 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.

#### 5.19 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., 1992) 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 S. C. Schimmel. 1992. EMAP-Estuaries 1992 Virginian Province Field Operations and Safety Manual. U.S. Environmental Protection Agency, Office of Research and Development, NHEERL-AED Narragansett, RI. June 1992.

## 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), 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/HNO<sub>3</sub> 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 HNO<sub>3</sub>/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.

## 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.

### 54.2.3 Sample Processing Method Calibration

For the 1992 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 1992 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

Not available

## 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	Length	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
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	0.1960
PCB180	0.3450
PCB187	0.2520
PCB195	0.1890
PCB206	0.1710
PCB209	0.1460
PCB28	0.3040
PCB44	0.2560
PCB52	0.2200
PCB66	0.3090
PCB8	0.1580
PCB_TOT	0.0000
PERYLENE	5.0000
PHENANTH	6.0000
PPDDD	0.1820
PPDDE	0.2760
PPDDT	0.1000
PYRENE	8.0000
SB	0.0597
SE	0.1190
SN	0.1270
TBT	4.0000
TNONCHL	0.1490
TOC	0.0119
TRIMETH	5.6400
ZN	3.1500

### 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
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
HEPTAEO	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
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	VA92-451	920810	ACENTHE	8.000000	ng/g
2	VA92-451	920810	ACENTHY	.	ng/g
3	VA92-451	920810	AG	0.235000	ug/g

  

OBS	QA_CODE	TOT_ANAL	DETLIMIT	ANAL_CAT
1	CH-B	.	.	PAH
2	CH-A,CH-C	.	10.000000	PAH
3		.	.	METAL

## 8. GEOGRAPHIC AND SPATIAL INFORMATION

### 8.1 Minimum Longitude

-77 Degrees 19 Minutes 30.00 Decimal Seconds

### 8.2 Maximum Longitude

-69 Degrees 65 Minutes 27.60 Decimal Seconds

### 8.3 Minimum Latitude

36 Degrees 51 Minutes 51.00 Decimal Seconds

### 8.4 Maximum Latitude

42 Degrees 05 Minutes 15.49 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 1992 Virginian Province sediment chemistry analyses were defined in the 1992 Virginian Province Quality Assurance Project Plan (Valente et. al. 1992). 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 1992 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 1992 Virginian Province sediment chemistry dataset:

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 1992 Virginian Province sediment chemistry dataset. 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 1992, 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 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 195 (75%), heptachlor (26%), heptachlor epoxide (42%), lindane (35%), o,p DDT (77%), and p,p DDT (79%).

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 1992 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 16 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 (71%) 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 16 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), and no results were flagged in the database. 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.

Table 9-1. Summary results for CRM BCSS-1 (Estuarine Sediment) used as a set control for the 1992 EMAP-Estuaries sediment inorganic analyses.

ICP-AES METALS (n = 16 analysis sets or "batches"):

Element	Average <sup>1</sup>	Stdv <sup>2</sup>	C.V. <sup>3</sup>	Min. <sup>4</sup>	Max. <sup>5</sup>
Al	82	3.7	4.5	78	93
Cr	71	3.3	4.7	66	80
Cu	101	3.7	3.7	94	107
Fe	87	3.6	4.2	80	92
Mn	91	3.2	3.5	83	96
Ni	86	2.8	3.3	79	90
Pb	103	15.3	14.9	72	137
Zn	85	3.5	4.1	80	92

GFAA METALS (n = 16 analysis sets):

Element	Average <sup>1</sup>	Stdv <sup>2</sup>	C.V. <sup>3</sup>	Min. <sup>4</sup>	Max. <sup>5</sup>
Ag	na	na	na	na	na
As	111	13.0	11.6	83	135
Cd	102	11.6	11.4	67	119
Sb	101	15.7	15.5	79	130
Se	85	20.8	24.4	45	123
Sn	99	9.8	10.0	83	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 Laboratory Control Material results. For both the PAH and PCB/pesticide analyses, SRM 1941 (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 1941 (this includes both "certified" and "non-certified" values), the average percent recovery achieved by the laboratory (based on  $n = 13$  batches for PAHs and  $n = 13$  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 1992 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 1992 database: PCB 101, PCB 105, PCB 18, PCB 187, acenaphthylene, benz(a)pyrene, chrysene, and 1-methylphenanthrene. In addition, although the average percent recovery for naphthalene was within limits (77%), all results for this compound were flagged with the CH-C code because the recoveries between batches exhibited relatively high variability (e.g., 47% coefficient of variation). Although the average SRM percent recoveries for the compounds heptachlor epoxide and PCB 195 also were outside the acceptability range of 70% to 130% (Table 8-3), these compounds occur in the SRM at concentrations less than 10 times the laboratory's detection limit. Therefore, the acceptability criteria do not apply.

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 1941 (Organics in Marine Sediment) used as the set control (Laboratory Control Material) for the 1992 sediment PAH analyses (n = 13 analysis sets or "batches").

Compound1	Average2	Stdv3	C.V.4	Min5	Max6
Acenaphthene	127	22.4	17.7	98	167
Acenaphthylene	57	12.5	21.9	38	79
Anthracene	93	27.8	29.8	59	145
Benz(a)anthracene	88	14.5	16.4	69	109
Benzo(a)pyrene	69	10.4	15.1	52	86
Benzo(e)pyrene	95	19.9	21.0	63	132
Benzo(b+k)fluoranthene	105	17.4	16.6	79	137
Benzo(g,h,i)perylene	111	15.2	13.8	95	146
Biphenyl	118	29.9	25.3	56	153
Chrysene	152	25.6	16.8	118	198
2,6-dimethylnaphthalene	128	32.0	25.0	66	177
Fluoranthene	100	21.5	21.5	70	143
Fluorene	126	21.4	17.0	91	176
Ideno(1,2,3-c,d)pyrene	114	16.2	14.2	84	140
1-methylnaphthalene	115	29.3	25.5	62	153
2-methylnaphthalene	126	40.5	32.0	52	190
1-methylphenanthrene	130	44.6	34.2	69	239
Naphthalene	77	35.9	46.6	8	131
Perylene	71	9.2	13.1	58	89
Phenanthrene	127	28.7	22.7	75	162
Pyrene	113	17.0	15.0	92	156

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

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 13 analysis sets

6 Maximum percent recovery for 13 analysis sets

Table 9-3. Results for SRM 1941 (Organics in Marine Sediment) used as the set control (Laboratory Control Material) for the 1992 sediment PCB/pesticide analyses (n = 13 analysis sets or "batches").

Compound1	Average2	Stdv3	C.V.4	Min5	Max6
PCB 18	47	9.8	20.9	30	57
PCB 28	74	12.0	16.1	49	94
PCB 52	121	21.2	17.5	90	157
PCB 66	94	15.5	16.4	74	122
PCB 101	69	10.4	15.0	56	90
PCB 118	78	11.2	14.2	64	101
PCB 153	71	6.1	8.6	61	80
PCB 105	146	24.1	16.5	102	183

PCB 138	70	6.6	9.4	61	81
PCB 187	67	5.4	8.1	58	77
PCB 180	100	10.1	10.1	88	118
PCB 170	80	7.3	9.2	69	89
PCB 195*	176	27.5	15.7	133	222
PCB 206*	82	11.5	14.0	54	95
PCB 209	86	15.3	17.7	57	104
Dieldrin*	125	52.2	41.9	63	255
Heptachlor epoxide*	160	72.6	45.3	58	281
cis-Chlordane*	108	24.9	23.0	74	150
trans-Nonachlor*	120	28.1	23.4	75	160
4,4'-DDE	91	17.9	19.6	69	125
4,4'-DDD	84	16.4	19.6	65	110
4,4'-DDT*	102	36.0	35.2	41	167

1 SRM 1941 only lists "non-certified" or informational values for this group of PCB congeners and pesticides (\* = 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 13 analysis sets

6 Maximum percent recovery for 13 analysis sets

### 9.3.3 Mercury analyses

For the 1992 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=8 sample batches). The average percent recovery of 88% for mercury in this reference material fell well within the acceptability range of 80% to 120%. In addition, an average percent recovery of 102% 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 1992 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 1992 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 97.4%, 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 1992 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 1992 sediment dataset for butyltin compounds which might limit or preclude the use of these data. The laboratory detected dibutyltin (DBT) in only 18% and monobutyltin (MBT) in only 3% of the samples analyzed in 1992, while tributyltin (TBT) was detected in 73% of the samples. The method detection limits (DETLIMIT) 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 = 10 analysis sets were 77% for TBT, 52% for DBT and 171% for MBT. These values fall outside the acceptable accuracy control limits of 80% to 120%. Average percent recoveries for matrix spike samples (115% for TBT, 82% 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 1992 samples, the laboratory utilized a laboratory fortified blank sample as the laboratory control material (LCM). The average percent recovery of AVS for n = 68 laboratory fortified blank samples was 93%, suggesting good overall analytical performance. Average percent recoveries for matrix spike samples were somewhat low (55% for n = 9 matrix spike duplicate sets); these low recoveries were attributed to possible matrix effects. In general, the 1992 AVS analyses were deemed acceptable, and no data qualifier codes were applied to these data.

## 10. DATA ACCESS

### 10.1 Data Access Procedures

A Data Request Package can be requested from a contact under Section 10.3. Data can be downloaded from the WWW site.

### 10.2 Data Access Restrictions

### 10.3 Data Access Contact Persons

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### 10.4 Data Set Format

Data can be transmitted in a variety of formats derived from SAS data sets.

### 10.5 Information Concerning Anonymous FTP

Not accessible

### 10.6 Information Concerning Gopher and WWW

Data can be downloaded from the WWW site.

### 10.7 EMAP CD-ROM Containing the Data Set

Data not available on CD-ROM.

## 11. REFERENCES

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Valente, R. M., C. S. Strobel and S. C. Schimmel. 1992. EMAP-Estuaries 1992 Virginian Province Quality Assurance Project Plan. U.S. Environmental Protection Agency, Office of Research and Development, NHEERL-AED, Narragansett, RI. July 1992.

## 12. LIST OF ACRONYMS

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