

US EPA ARCHIVE DOCUMENT

CATALOG DOCUMENTATION
EMAP-ESTUARIES PROGRAM LEVEL DATABASE
1991 VIRGINIAN PROVINCE
SEDIMENT CHEMISTRY

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1. DATA SET IDENTIFICATION

1.1 Title of Catalog document

EMAP-Estuaries Program Level Database
1991 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

00025

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

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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 and AVS

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.

4.2 Data Set Objective

The objective of the Sediment Chemistry data set is to present the concentrations of a suite of analytes and compounds measured from an uncontaminated surface sediment sample collected at a station in the Virginian Province. The sample was an homogenate composed of several grabs. Only the randomly located Base Sampling Sites (BASE) are included in this data set.

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.

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.

EMAP monitoring efforts have focused on sediment contaminants rather than measurement of water column contaminants because concentrations of contaminants in sediments are less variable and the sediment integrates contaminant inputs to estuaries over time (i.e., months and years).

Metals in the sediment are derived from anthropogenic sources or from the natural geochemical processes of weathering and erosion of 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

The organic and inorganic compound concentrations measured included: 15 major and trace elements, 24 individual Poly-Aromatic Hydrocarbon (PAH) compounds, the pesticide DDT and its metabolites, 9 pesticides other than DDT, 18 individual Poly-Chlorinated Biphenyl (PCB) congeners, mono-, di- and tri-butyltin (MBT, DBT, TBT), Total Organic Carbon (TOC) and acid volatile sulfides (AVS). 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 include individual inorganic and organic compound concentrations and 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.

5.0 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, TOC and AVS. One sediment sample was expected to be collected at each station.

5.1.2 Sample Collection Methods Summary

The grab sampler was lowered through the water column such that travel through the last 5 meters was no faster than 1 m/sec. The grab penetrated

the sediment by gravity releasing a trigger allowing the jaws to close. 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 grabs were taken, the boat was moved five meters downstream by letting out the appropriate length of anchor line.

Stainless steel utensils were used to remove the top two cm of sediment from a grab. 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 glass jars (for organics) or plastic containers (for inorganics and AVS). The samples were immediately stored on ice following collection. The remainder of the sediment was split between grain size and sediment toxicity samples.

5.1.3 Beginning Sampling Date

22 July 1991

5.1.4 Ending Sampling Date

13 September 1991

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 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.

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

Field technicians were trained to follow Standard Operating Procedures to insure the collection of representative, uncontaminated and high quality samples. QA/QC measures were taken in the field to avoid or reduce contamination and insure the collection of representative samples. These included: use of stainless steel instruments, thorough cleaning of the sampler between grabs, use of pre-cleaned containers for sediment storage and ensuring that engines were shut down when a sample was exposed to the air.

A successful grab had relatively level, intact sediment over the entire area of the grab and a sediment depth of 7-10 centimeters. 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 oozing out of the hinged top, were also unacceptable.

5.1.11 Sample Collection Method Reference

Strobel, C. J. and S. C. Schimmel. 1991. Environmental Monitoring and Assessment Program Near Coastal Component: 1991 Virginian Province Field Operations and Safety Manual. U.S. Environmental Protection Agency, Office of Research and Development, NHEERL-AED, Narragansett, RI. June 1991.

5.1.12 Sample Collection Method Deviations

None

5.2 Data Preparation and Sample Processing

5.2.1 Sample Processing Objective

Process uncontaminated sediment samples for characterization of contaminants.

5.2.2 Sample Processing Methods Summary

Upon receipt at the laboratory, the samples were frozen pending analysis.

The frozen sediment samples were thawed and thoroughly homogenized prior to analysis. Separate aliquots of the homogenized sediment were removed.

The aliquots were processed for several types of chemical analyses. These included: inorganic analyses (major and trace elements; butyltins (MBT, TBT and DBT); organic analyses (PAHs, PCBs and pesticides) and acid volatile sulfides (AVS).

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.

ORGANIC

The analysis of organic contaminants involved 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 1991 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 1991 QA Plan required the laboratory's percent recovery (relative to the certified concentration in the reference material) to fall within the range of 80 to 120 % for each inorganic analyte and 70 to 130 % for each organic analyte. 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 and were flagged.

5.2.4 Sample Processing Quality Control

Each laboratory was required to analyze the following quality control (QC) samples along with every batch or "set" of field chemistry samples: laboratory reagent blank, calibration check standards, laboratory fortified sample matrix, laboratory 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 SAS Name	Type	Len	Format	Parameter 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 Analyte

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	Minmum Value
ACENTHE	0.08
ACENTHY	0.04
AG	0.01
AL	1760.00
ALDRIN	0.23
ANTHRA	0.07
AS	0.77
AVS	0.04
BENANTH	3.65
BENAPY	0.11
BENEPY	0.12
BENZOFL	1.17
BENZOP	0.06

BIPHENYL	1.43
CD	0.03
CHRYSENE	1.44
CISCHL	0.24
CR	1.88
CU	0.49
DBT	2.43
DDT_TOT	0.00
DIBENZ	0.07
DIELDRIN	0.25
DIMETH	1.34
FE	653.00
FLUORANT	1.25
FLUORENE	1.80
HEPTACHL	0.24
HEPTAEPO	0.20
HEXACHL	0.28
HG	0.00
INDENO	0.30
LINDANE	0.46
MBT	4.86
MENAP1	0.86
MENAP2	1.71
MEPHEN1	0.93
MIREX	0.23
MN	11.60
NAPH	0.96
NI	1.79
OPDDD	0.10
OPDDE	0.10
OPDDT	0.10
PAH_HMW	1.77
PAH_LMW	1.15
PAH_TOT	3.21
PB	2.17
PCB101	0.24
PCB105	0.13
PCB118	0.20
PCB128	0.23
PCB138	0.21
PCB153	0.2580
PCB170	0.2200
PCB18	0.2440
PCB180	0.2260
PCB187	0.2220
PCB195	0.1920
PCB206	0.2130
PCB209	0.2380
PCB28	0.2240
PCB44	0.2120
PCB52	0.2740
PCB66	0.2300
PCB8	0.2240
PCB_TOT	0.0000
PERYLENE	0.2220

PHENANTH	0.5350
PPDDD	0.1000
PPDDE	0.2200
PPDDT	0.1000
PYRENE	0.0514
SB	0.0534
SE	0.1170
SN	0.1290
TBT	2.9800
TNONCHL	0.2140
TOC	0.0650
TRIMETH	0.3790
ZN	3.6600

7.1.8 Maximum Value in Data Set by Analyte

ANALYTE	Maximum Value
ACENTHE	2960.00
ACENTHY	186.00
AG	9.69
AL	89300.00
ALDRIN	1.82
ANTHRA	6510.00
AS	34.90
AVS	156.00
BENANTH	10000.00
BENAPY	6040.00
BENEPY	3950.00
BENZOFL	11300.00
BENZOP	3780.00
BIPHENYL	240.00
CD	6.58
CHRYSENE	9770.00
CISCHL	7.32
CR	174.00
CU	263.00
DBT	50.30
DDT_TOT	124.00
DIBENZ	342.00
DIELDRIN	4.56
DIMETH	399.00
FE	54500.00
FLUORANT	22900.00
FLUORENE	3180.00
HEPTACHL	3.19
HEPTAEPO	0.96
HEXACHL	3.21
HG	1.96
INDENO	4080.00
LINDANE	0.46
MBT	73.30
MENAP1	386.00
MENAP2	459.00
MEPHEN1	2100.00

MIREX	0.62
MN	6430.00
NAPH	488.00
NI	70.10
OPDDD	13.10
OPDDE	12.90
OPDDT	12.70
PAH_HMW	132000.00
PAH_LMW	8280.00
PAH_TOT	141000.00
PB	323.00
PCB101	53.20
PCB105	34.80
PCB118	55.70
PCB128	8.94
PCB138	42.20
PCB153	31.10
PCB170	7.82
PCB18	50.70
PCB180	17.90
PCB187	14.30
PCB195	5.12
PCB206	10.30
PCB209	18.20
PCB28	346.00
PCB44	72.60
PCB52	107.00
PCB66	152.00
PCB8	35.40
PCB_TOT	1040.00
PERYLENE	2020.00
PHENANTH	25500.00
PPDDD	32.90
PPDDE	30.80
PPDDT	33.30
PYRENE	24600.00
SB	49.10
SE	1.76
SN	27.00
TBT	98.40
TNONCHL	3.83
TOC	3.98
TRIMETH	518.00
ZN	484.00

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

1. VA91-261	910803	AS		1.680000	ug/g
					METAL
2. VA91-261	910803	ALDRIN			ng/g
CH-A,CH-C			0.250000		PESTICIDE
3. VA91-261	910803	AVS	0.115000		umoles/g
CH-C					AVS

8. GEOGRAPHIC AND SPATIAL INFORMATION

8.1 Minimum Longitude

-77 Degrees 18 Minutes 58.80 Decimal Seconds

8.2 Maximum Longitude

-70 Degrees 01 Minutes 00.00 Decimal Seconds

8.3 Minimum Latitude

36 Degrees 56 Minutes 24.60 Decimal Seconds

8.4 Maximum Latitude

42 Degrees 08 Minutes 00.00 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 ASSURANCE

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 1991 Virginian Province sediment chemistry analyses were defined in the 1991 Virginian Province Quality Assurance Project Plan (Valente and Schoenherr, 1991). 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, laboratory fortified sample matrix, laboratory duplicate, and Laboratory Control Material (LCM). Results for these QC samples had to fall within certain pre-established control limits.

9.2 Quality Assurance/Quality Control Methods

If results for these QC samples did not fall within certain pre-established control limits, the analysis of a batch of samples was not considered acceptable. These and other quality control issues are coded in four data qualifier codes or "flags" used in the 1991 Virginian Province sediment chemistry data set:

CH-A CODE

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 method detection limit (DETLIMIT).

CH-B CODE

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.

CH-C CODE

The "SC-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. Values flagged with the "SC-C" code therefore are considered estimates only and should be used with discretion. It is important to note that values flagged with the SC-C code ARE included in the TOTALs. Excluding analytes would result in an artificially lowered concentration.

CH-D CODE

In 1991, 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, for all reported PCB congeners except PCB 195, the rate of confirmation was between 95% to 100% (PCB 195 rate of confirmation was 87%). The rate of confirmation exceeded 90% for all the chlorinated pesticides except the following: heptachlor (59%), heptachlor epoxide (57%), mirex (82%), p,p DDT (65%), and o,p DDT (72%).

Close inspection of the "confirmed" results for the DDT-series compounds revealed a number of instances where there was a significant discrepancy in the amount 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., 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 SC-D code has the following meaning: "Analyses were conducted using GC/ECD with dual column confirmation. Quantification on the two columns differed by more than a factor of three, and the lower of the two results is reported."

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 Virginian Province database and are available upon request. In the following sections, these results are summarized, and the data flags associated with the 1991 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 13 analytical 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 and Pb, 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 was slightly lower than acceptable, and the average percent recovery for Pb was slightly higher than acceptable. These results suggest that Cr may have been consistently "under-recovered" and Pb may have been consistently "over-recovered" in the actual samples.

Therefore, all reported values for these two metals were qualified with the SC-C code in the database.

The GFAA analyses included the metals Ag, As, Cd, Sb, Se, and Sn; a total of 19 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, making it difficult to assess laboratory accuracy and precision for this metal.

 Table 9-1. Summary results for CRM BCSS-1 (Estuarine Sediment) used as a set control for the 1991 EMAP-Estuaries sediment inorganic analyses.

ICP-AES METALS (n = 13 analysis sets or "batches"):

Element	Average ¹	Stdv ²	C.V. ³	Min. ⁴	Max. ⁵
Al	95	6.2	6.5	87	109
Cr	70	2.0	2.8	66	73
Cu	105	3.0	2.8	99	110
Fe	95	2.9	3.0	91	100
Mn	93	2.9	3.1	87	97
Ni	91	2.4	2.7	86	94
Pb	122	26.5	21.7	81	185
Zn	89	1.5	1.7	87	91

GFAA METALS (n = 19 analysis sets):

Element	Average ¹	Stdv ²	C.V. ³	Min. ⁴	Max. ⁵
Ag	na	na	na	na	na
As	94	9.0	9.6	76	114
Cd	91	23.6	26.1	39	157
Sb	98	15.4	15.6	78	137
Se	111	32.5	29.3	50	189
Sn	111	14.9	13.4	66	135

-
- 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 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 samples generally fell within control limits, although these recoveries tended to be highly variable between different batches. This in part reflects the fact that the spiked samples were chosen at random and sometimes had high "background" concentrations of the spiked analytes. In these cases it was difficult for the laboratory to accurately recover the spiked

amount relative to the high background, resulting in zero percent recovery in some samples. Furthermore, it is 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 on using the matrix spike results to assess the overall quality of the 1991 organics data, great emphasis was placed on the 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 $n = 14$ batches for PAHs and $n = 15$ 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 1991 database for that compound were flagged with the "SC-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 "SC-C" code in the 1991 database: PCB 101, PCB 138, PCB 153, PCB 18, PCB 187, acenaphthylene, chrysene, 1-methylphenanthrene and naphthalene. In addition, although the average percent recovery for ideno(1,2,3-c,d)pyrene was within limits (98%), all results for this compound were flagged with the SC-C code because the recoveries between batches exhibited relatively high variability (35% coefficient of variation). Although the average SRM percent recoveries for the compounds dieldrin, heptachlor epoxide and PCB 195 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.

In addition to the above, due to analytical difficulties, all 1991 pesticide results have been assigned the SC-C code and are considered estimates.

 Table 9-2. Results for SRM 1941 (Organics in Marine Sediment) used as the set control (Laboratory Control Material) for the 1991 sediment PAH analyses (n = 14 analysis sets or "batches").

Compound1	Average2	Stdv3	C.V.4	Min5	Max6
Acenaphthene	111	23.2	20.9	67	137
Acenaphthylene	41	10.6	25.9	27	61
Anthracene	95	26.4	27.7	59	142
Benz(a)anthracene	92	28.2	30.5	54	165
Benzo(a)pyrene	77	15.1	19.7	52	106
Benzo(e)pyrene	101	22.4	22.2	61	138
Benzo(b+k)fluoranthene	121	25.4	21.0	87	174
Benzo(g,h,i)perylene	105	21.1	20.1	64	141
Biphenyl	103	22.7	22.1	63	138
Chrysene	145	30.4	21.0	94	196
2,6-dimethylnaphthalene	113	24.2	21.3	70	145
Fluoranthene	93	20.2	21.7	64	134
Fluorene	105	32.3	30.7	62	179
Ideno(1,2,3-c,d)pyrene	98	34.1	34.7	21	150
1-methylnaphthalene	99	27.8	28.2	59	158
2-methylnaphthalene	109	33.6	30.8	53	158
1-methylphenanthrene	138	50.5	36.5	64	247
Naphthalene	69	27.3	39.5	8	126
Perylene	72	15.2	21.1	47	96
Phenanthrene	111	27.2	24.4	76	160
Pyrene	96	23.9	24.9	56	134

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- 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 14 analysis sets
 - 6 Maximum percent recovery for 14 analysis sets

Table 9-3. Results for SRM 1941 (Organics in Marine Sediment) used as the set control (Laboratory Control Material) for the 1991 sediment PCB/pesticide analyses (n = 15 analysis sets or "batches").

Compound1	Average2	Stdv3	C.V.4	Min5	Max6
PCB 18	32	10.0	31.2	20	50
PCB 28	77	11.7	15.2	58	95
PCB 52	102	14.1	13.8	85	122
PCB 66	87	12.8	14.7	68	104
PCB 101	68	10.4	15.2	48	86
PCB 118	93	28.0	29.9	58	170
PCB 153	66	5.2	7.9	55	76
PCB 105	128	19.1	15.0	99	165
PCB 138	68	5.5	8.1	60	77
PCB 187	64	7.7	11.9	52	84
PCB 180	96	9.9	10.3	80	110
PCB 170	75	6.4	8.6	68	89
PCB 195*	142	29.8	20.8	108	199
PCB 206*	76	10.4	13.7	62	92
PCB 209	82	9.7	11.8	69	98
Dieldrin*	143	29.3	20.6	85	182
Heptachlor epoxide*	139	27.3	19.6	99	184
cis-Chlordane*	96	12.7	13.3	71	122
trans-Nonachlor*	89	15.3	17.2	72	127
4,4'-DDE	91	9.5	10.5	75	109
4,4'-DDD	80	9.0	11.2	64	98
4,4'-DDT*	102	22.6	22.2	62	128

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 22 analysis sets

6 Maximum percent recovery for 22 analysis sets

9.3.3 Mercury analyses

For the 1991 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 = 9 sample batches). The average percent recovery of 92% for mercury in this reference material fell well within the acceptability range of 80% to 120%. In addition, an average percent recovery of 104% was achieved for the matrix spike samples analyzed in each batch. Overall, these results indicate acceptable accuracy for the mercury analyses, and no "SC-C" codes were used to qualify the data. The 1991 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 1991 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 = 11 batches of TOC samples (i.e., 11 separate analyses of CRM PACS-1) was 94.1%, with all values falling within the range 88% to 99%. 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 are expected to be below 100%. Based on the good overall percent recovery of organic carbon in the Certified Reference Material, the 1991 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 1991 sediment data set for butyltin compounds which might limit or preclude the use of these data. The laboratory's failure to detect the butyltin compounds of interest (TBT, DBT, MBT) in the majority of samples analyzed suggests a potential deficiency resulting from the method detection limits for the individual analytes. The MDLs established by the laboratory were 5 ng/g dry weight for both TBT and DBT, and 12 ng/g dry weight for MBT. Assuming these MDL's are valid, it is probable that contamination by butyltin compounds may be more widespread than indicated by these data.

It should be noted at this point 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 = 12 analysis sets were 79% for TBT, 89% for DBT and 115% for MBT. The percent recovery value for TBT falls slightly outside the acceptable accuracy limits of 80% to 120% and indicates that TBT may have been consistently under-recovered in this reference material. Average percent recoveries for matrix spike samples (98% for TBT, 66% for DBT and 70% for MBT) suggest the laboratory attained better accuracy for TBT than the SRM results indicate. Given these inconsistencies in the QC data, all values reported for TBT in samples where this compound was detected are considered estimates (SC-C code) and should be used with discretion.

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

Data can only be accessed from the WWW site.

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 when a Data Request Form is submitted.

10.5 Information Concerning Anonymous FTP

Not accessible

10.6 Information Concerning WWW

Data can be downloaded from the WWW.

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

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