CATALOG DOCUMENTATION
EMAP-ESTUARIES PROGRAM LEVEL DATABASE
1990 VIRGINIAN PROVINCE
SEDIMENT CHEMISTRY DATA

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1. Data Set Identification

1.1 Title of Catalog document

EMAP-Estuaries Program Level Database
1990 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

00005

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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2.3 Principal Investigator-Sample Processing

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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 and Total Organic Carbon (TOC). 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

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 specific objective of this investigation was to determine the concentrations of a suite of organic and inorganic contaminants and sediment components in surface sediments collected in 1990 at sampling sites located in estuaries throughout the Virginian Province. The analytes were measured in a sediment homogenate composed of several grabs.

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.

Sites that have experienced anthropogenic enrichment with organic contaminants can be defined operationally as any site where there are organic contaminants. Synthetic organics such as pesticides and PCBs only have human origins; human activities are also the main source of most PAHs.

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 Investigation 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) and Total Organic Carbon (TOC). 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. 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 sediment chemistry sample was a composite of surface sediments (top 2 cm) taken from multiple grabs at each station, as follows. With the boat anchored at the site, the grab sampler was deployed and retrieved, brought on deck and inspected. If the grab was judged to be acceptable, the top 2 cm of sediment was removed and placed into a stainless steel mixing bowl. The grab sampler then was rinsed and re-deployed. Sampling continued in this manner until a sufficient volume of sediment had been added to the mixing bowl. The sediment in the bowl then was mixed by hand with a stainless steel spoon until it was thoroughly homogenized, and an aliquot was placed immediately into a pre-cleaned glass jar for later chemical analysis.

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 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 sample collection. Chemical analyses produced data on organic and inorganic compounds.

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, 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.

A successful grab had relatively level, intact sediment over the entire area of the grab and a sediment depth of 5 cm, at minimum. 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.

All sediment chemistry samples were held in the field at 4C and shipped on ice to the laboratory by overnight mail. Upon receipt at the laboratory, the samples were frozen pending analysis.

5.1.11 Sample Collection Method Reference

Strobel, C. J. 1990. Environmental Monitoring and Assessment Program Near Coastal Component 1990 Demonstration Project Field Operations Manual. U.S. Environmental Protection Agency, Office of Research and Development, NHEERL-AED, Narragansett, RI.

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

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), and butyltins (MBT, DBT, and TBT). 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.

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 interferents 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.

TOTAL ORGANIC CARBON

The concentration of total organic carbon in each sediment sample was determined by ultraviolet light-promoted persulfate oxidation. Sediment concentrations of butyltin compounds were determined using high resolution gas chromatography and flame photometric detection.

5.2.3 Sample Processing Method Calibration

For the 1990 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 1990 QA Plan required the laboratory's percent recovery (relative to the certified concentration in the reference material) to fall within a range of 85% to 115% 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 (biased) and were flagged in the database, as described in the following section.

5.2.4 Sample Processing Quality Control

For the 1990 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 1990 QA Plan required the laboratory's percent recovery (relative to the certified concentration in the reference material) to fall within a range of 85% to 115% 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 (biased) and were flagged in the database.

5.2.5 Sample Processing Method Reference

Valente, R.M., C.J. Strobel, J.E. Pollard, K.M. Peres, T.C. Chiang and J.R. Rosen. 1990. Environmental Monitoring and Assessment Program Near Coastal Demonstration Project Quality Assurance Project Plan. U.S. Environmental Protection Agency, Office of Research and Development, NHEERL-AED, Narragansett, RI.

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, acenaphthlyene, 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, acenaphthene, phenanthrene, anthracene, acenaphthlyene, 2,3,5-trimethylnaphthalene, 1-methylphenanthrene.

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.

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.

6.3.6 Total Analytes

TOT_ANAL = Count of the number of concentrations summed for a 'total' concentration.

7. DATA DESCRIPTION

7.1 Description of Parameters

#	Parameter SAS Name	Data 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 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	0.41
ACENTHY	0.34
AG	1.00
AL	3110.00
ANTHRA	0.39
AS	0.11
BENANTH	0.81
BENAPY	0.71
BENEPY	0.61
BENZOFL	0.76
BENZOP	0.64

7.1.7 Minimum Value in Data Set by Analyte, continued

ANALYTE	Minimum Value
BIPHENYL	0.39
CD	0.01
CHRYSENE	0.71
CR	2.90
CU	0.60
DBT	5.00
DIBENZ	0.63
DIMETH	0.63
FE	1330.00
FLUORANT	0.71
FLUORENE	0.61
HG	0.01
INDENO	0.78
MBT	51.00
MENAP1	0.61
MENAP2	0.43
MEPHEN1	0.38
MN	27.00
NAPH	0.40
NI	3.00
PAH_HMW	1.58
PAH_LMW	1.20
PAH_TOT	5.20
PB	4.30
PERYLENE	0.76
PHENANTH	0.47
PYRENE	0.38
SB	0.01
SE	0.03
SN	0.06
TBT	8.80
TOC	0.01
TRIMETH	0.38
ZN	4.00

7.1.8 Maximum Value in Data Set by Analyte

ANALYTE	Maximum Value
ACENTHE	5120.00
ACENTHY	803.00
AG	4.50
AL	98300.00
ANTHRA	6010.00
AS	36.20
BENANTH	29100.00
BENAPY	6010.00
BENEPY	13500.00
BENZOFL	35000.00
BENZOP	9080.00
BIPHENYL	123.00
CD	7.99
CHRYSENE	18400.00
CR	856.00
CU	1500.00

7.1.8 Maximum Value in Data Set by Analyte

ANALYTE	Maximum Value
DBT	100.00
DIBENZ	5740.00
DIMETH	341.00
FE	57200.00
FLUORANT	42200.00
FLUORENE	1280.00
HG	3.27
INDENO	15100.00
MBT	51.00
MENAP1	255.00
MENAP2	316.00
MEPHEN1	2940.00
MN	2620.00
NAPH	1120.00
NI	136.00
PAH_HMW	231000.00
PAH_LMW	10000.00
PAH_TOT	241000.00
PB	282.00
PERYLENE	2940.00
PHENANTH	12800.00
PYRENE	31800.00
SB	3.92
SE	6.87
SN	47.60
TBT	313.00
TOC	4.08
TRIMETH	719.00
ZN	845.00

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

```
STA_NAME  VST_DATE  ANALYTE       CONC     CHMUNITS  QA_CODE  TOT_ANAL

VA90-021   900913   ACENTHE      1.750000     ng/g    CH-B,CH-C    .
VA90-021   900913   ACENTHY      3.490000     ng/g    CH-B,CH-C    .
VA90-021   900913     AG           .          ug/g    CH-A         .


DETLIMIT  ANAL_CAT

   .         PAH
   .         PAH
1.000000    METAL
```

8. GEOGRAPHIC AND SPATIAL INFORMATION

8.1 Minimum Longitude

-77 Degrees 17 Minutes 4.80 Decimal Seconds

8.2 Maximum Longitude

-70 Degrees 04 Minutes 18.60 Decimal Seconds

8.3 Minimum Latitude

36 Degrees 49 Minutes 54.60 Decimal Seconds

8.4 Maximum Latitude

41 Degrees 38 Minutes 33.00 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

9.1 Background

Measurement Quality Objectives (MQOs) for the 1990 Virginian Province sediment chemistry analyses were defined in the 1990 Demonstration Project Quality Assurance Project Plan for EMAP-Near Coastal (Valente et al. 1990). 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 for the analysis of a batch of samples to be considered acceptable.

9.2 Quality Assurance/Quality Control Methods

If the laboratory consistently failed to meet the 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 below.

Three data qualifier codes or "flags" are used in the 1990 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 "DETLIMIT".

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 1990 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.

Values which are not flagged with the CH-A, CH-B or CH-C 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 data flags associated with the 1990 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 Ag, Al, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, a total of 18 analytical sets or "batches" of samples were analyzed. SRM 2704 (Buffalo River Sediment, issued by the National Institute of Standards and Technology) was analyzed along with every batch as the Laboratory Control Material. Except for silver, the average percent recovery of each metal (relative to the certified concentration in SRM 2704) was within the acceptability range of 85% to 115% (Table 9-1), and no "CH-C" codes were applied.

Table 9-1. Summary results for SRM 2704 (Buffalo River Sediment) used as a set control for the 1990 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	96	1.8	1.9	92	99
Cr	87	2.7	3.1	80	91
Cu	95	2.4	2.5	90	99
Fe	88	1.6	1.8	83	90
Mn	96	2.2	2.3	92	99
Ni	90	5.5	6.2	84	110
Pb	93	4.5	4.8	85	99
Zn	96	1.6	1.7	93	99

GFAA METALS (n = 18 analysis sets):

Element	Average[1]	Stdv[2]	C.V.[3]	Min.[4]	Max.[5]
As	78	4.1	5.3	70	89
Cd	100	7.0	7.0	87	111
Sb	79	11.9	15.1	51	99
Se	97	12.4	12.8	70	119
Sn	80	30.0	37.5	29	144

[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 18 analysis sets
[5] Maximum percent recovery for 18 analysis sets

Silver was not detected in most of the 1990 samples; however, the laboratory's detection limit of 1 ppm was well above the target detection limit of 0.01 ppm specified in the QA Plan. If the target detection limit had been achieved, silver probably would have been detected and quantified in a much higher number of samples. Therefore, the 1990 results are not reliable for assessing silver concentrations in Virginian Province sediments.

The GFAA analyses included the metals As, Cd, Sb, Se, and Sn; a total of 18 analytical sets or "batches" of samples were analyzed. SRM 2704 (Buffalo River Sediment, issued by the National Institute of Standards and Technology) was analyzed along with every sample batch as the Laboratory Control Material. Average SRM percent recoveries fell outside the acceptability range of 85% to 115% for the following metals: As (78%), Sb (79%) and Sn (80%) (Table 9-1). In addition, matrix spike recoveries for these metals were highly variable. These low and variable recoveries are attributed to both the low concentrations of these metals in SRM 2704 (i.e., close to the detection limit) and the less rigorous digestion procedure used (i.e., hydrofluoric acid was not employed). Therefore, data users are cautioned that the reported concentrations for As, Sb, and Sn may underestimate the true amount present in each sample, but this bias is not considered severe given that the recoveries of these metals from SRM 2704 ranged between 78% and 80%. Given this slight low bias in the SRM results, all reported concentrations for As, Sb and Sn in the data set are qualified with the "CH-C" code.

9.3.2 Organic analyses

As a result of the QA/QC procedures, PCB and pesticide data are not releaseable. Users are cautioned that there are several major deficiencies in the 1990 sediment PAH data set that might limit or preclude the use of these data. These deficiencies, described below, were the result of numerous methodological and QA/QC problems experienced by the laboratory responsible for the 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. However, the matrix spike results are of limited use in assessing overall data quality because the spiking solutions used by the laboratory for the PAH and PCB/pesticide analyses contained only a small subset of the analytes of interest and not the full suite as originally specified in the QA Plan. 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.

Results for laboratory duplicate samples, intended to serve as a check on precision, also are of limited value in assessing the quality of the 1990 organics data because the laboratory usually failed to detect the analytes of interest in the sample chosen at random for duplicate analysis (i.e., most of the analytes in laboratory duplicate samples were reported as "not detected").

Given the above limitations on using the matrix spike and laboratory duplicate results to assess the overall quality of the 1990 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, the average percent recovery achieved by the laboratory (based on n=20 batches for PAHs and n=22 batches for PCB/pesticides) consistently fell within the control limit range of 70% to 130% (Tables 9-2 and 9-3). Whenever the laboratory failed to achieve these recovery rates for a particular compound, all the results obtained for that compound in the associated batch of samples were flagged with the "CH-C" code to indicate the potential inaccuracy inferred from the SRM analysis. All PAH data were flagged with the "CH-C" code.

Very high and variable SRM 1941 recovery rates were experienced for the pesticides heptachlor epoxide (231%), cis-chlordane (322%), trans-nonachlor (412%), and 4,4'-DDT (186%) (Table 9-3). These high and variable recovery rates largely reflect the fact that these compounds were present in SRM 1941 at concentrations very close to the laboratory's detection limit, where a high degree of analytical uncertainty is expected. Nevertheless, all reported values for these pesticides are qualified with the "CH-C" code and should be used with discretion.

A major deficiency in the 1990 organics data set is related to the laboratory's failure to achieve the target detection limits originally specified in the QA Plan. These target detection limits were 10 ng/g (dry weight) for each PAH compound and 0.5 ng/g for each PCB congener and pesticide. In general, the detection limits achieved by the laboratory ranged from 1.5 to 30 times higher than the target value for PAH compounds and up to 15 times higher than the target value for PCB congeners and pesticides (Table 9-4). In addition, the detection limits varied widely because the laboratory analyzed a different amount (i.e., dry weight) of sediment from each sample. As a result, the analytes of interest were not detected in a large number of samples, and the "calculated" detection limit (i.e., the theoretical concentration of each analyte necessary for detection) differed significantly from sample to sample (Table 9-4).

Table 9-2. Results for SRM 1941 (Organics in Marine Sediment) used as the set control (Laboratory Control Material) for the 1990 sediment PAH analyses (n = 20 analysis sets or "batches").

Compound[1]	Average[2]	Stdv[3]	C.V.[4]	Min[5]	Max[6]
Phenanthrene	98.8	22.0	22.3	62	138
Anthracene	71.6	17.9	25.0	37	101
Fluoranthene	99.2	22.4	22.6	65	149
Pyrene	87.6	18.7	21.3	65	121
Benz[a]anthracene	93.9	20.8	22.1	57	141
Benzo[b+k]fluoranthene	104.6	18.9	18.1	67	142
Benzo[a]pyrene	64.9	15.4	23.7	40	90
Perylene	64.4	16.2	25.2	35	93
Benzo[ghi]perylene	86.2	23.3	27.0	48	145
Indeno[1,2,3-cd]pyrene	118.9	29.5	24.8	65	182

[1] SRM 1941 has certified concentrations for only a subset of the PAH compounds analyzed by the laboratory in 1990.
[2] Average percent recovery relative to the SRM certified value.
[3] Standard deviation of the percent recovery values.
[4] Coefficient of variation of the percent recovery values.
[5] Minimum percent recovery for 20 analysis sets
[6] Maximum percent recovery for 20 analysis sets

Table 9-3. Results for SRM 1941 (Organics in Marine Sediment) used as the set control (Laboratory Control Material) for the 1990 sediment PCB/pesticide analyses (n = 22 analysis sets or "batches").

Compound1	Average2	Stdv3	C.V.4	Min5	Max6
PCB 18	79.4	17.1	21.5	23	101
PCB 28	54.8	9.2	16.8	34	76
PCB 52	101.5	23.5	23.1	60	146
PCB 66	67.7	9.7	14.3	47	80
PCB 101	73.9	17.1	23.1	48	105
PCB 118	99.2	14.4	14.5	65	116
PCB 153	94.5	15.1	16.0	60	121
PCB 105	96.3	17.9	18.6	67	130
PCB 138	77.1	16.3	21.1	53	105
PCB 187	82.7	18.6	22.5	58	122
PCB 180	97.0	19.5	20.1	66	132
PCB 170	82.3	20.5	24.9	57	143
PCB 195*	147.0	39.0	26.5	80	213
PCB 206*	100.3	27.9	27.8	61	176
PCB 209	93.9	21.5	23.0	61	134
Heptachlor epoxide*	231.0	91.7	39.7	109	448
cis-Chlordane*	322.0	81.5	25.3	87	450
trans-Nonachlor*	411.9	710.7	172.5	86	2770
4,4'-DDE	104.8	32.0	30.5	65	212
4,4'-DDD	92.3	21.4	23.2	33	123
4,4'-DDT*	185.8	135.4	72.9	63	660

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

Table 9-4. Range in detection limits (in ng/g dry weight) reported for organic compounds in 1990 sediment samples. The target detection limits were 10 ng/g for each PAH compound and 0.5 ng/g for each PCB congener and pesticide.

Polycyclic Aromatic Hydrocarbons (PAHs)

	Minimum	Maximum	Median
Acenaphthene	21	207	34
Anthracene	17	121	28
Benz(a)anthracene	17	72	28
Benzo(a)pyrene	23	151	38
Benzo(e)pyrene	23	153	37
Biphenyl	23	150	36
Chrysene	22	72	35
Dibenz(a,h)anthracene	24	252	43
2,6-dimethylnaphthalene	24	156	38
Fluoranthene	16	114	24
Fluorene	25	176	43

Table 9-4, continued.

	Minimum	Maximum	Median
2-methylnaphthalene	25	162	39
1-methylnaphthalene	23	150	34
1-methylphenanthrene	13	86	21
Naphthalene	30	54	39
Perylene	27	189	46
Phenanthrene	16	44	26
Pyrene	15	39	22
Benzo(b+k)fluoranthene	22	145	33
Acenaphthlylene	22	212	38
Benzo(g,h,i)perylene	31	325	55
Ideno(1,2,3-c,d)pyrene	26	249	43
2,3,5-trimethylnaphthalene	23	219	38

DDT and its metabolites

	Minimum	Maximum	Median
2,4'-DDD	0.13	1.93	0.24
4,4'-DDD	0.12	6.10	0.20
2,4'-DDE	0.10	1.11	0.18
4,4'-DDE	0.04	0.45	0.07
2,4'-DDT	0.12	1.26	0.22
4,4'-DDT	0.18	3.22	0.58

Chlorinated pesticides other than DDT

	Minimum	Maximum	Median
Aldrin	0.10	1.78	0.27
Alpha-Chlordane	0.09	1.16	0.19
Trans-Nonachlor	0.04	0.87	0.07
Dieldrin	0.04	0.52	0.08
Heptachlor	0.10	1.47	0.19
Heptachlor epoxide	0.08	1.85	0.19
Hexachlorobenzene	0.03	7.23	0.09
Lindane (gamma-BHC)	0.16	27.5	0.64
Mirex	0.03	1.93	0.08

18 PCB Congeners:

	Minimum	Maximum	Median
PCB 08	0.08	4.46	0.63
PCB 18	0.37	5.89	0.94
PCB 28	0.08	1.03	0.17
PCB 44	0.06	1.50	0.17
PCB 52	0.11	2.70	0.38
PCB 66	0.09	1.01	0.18
PCB 101	0.12	1.39	0.20
PCB 105	0.07	0.60	0.14
PCB 118	0.06	0.65	0.12
PCB 128	0.12	1.62	0.23
PCB 138	0.11	1.31	0.18
PCB 153	0.11	1.03	0.19
PCB 170	0.09	2.15	0.32

Table 9-4, continued.

	Minimum	Maximum	Median
PCB 180	0.11	1.30	0.19
PCB 187	0.08	0.72	0.13
PCB 195	0.10	1.23	0.19
PCB 206	0.10	1.38	0.20
PCB 209	0.12	1.09	0.20

If the target detection limits had been achieved and consistent sample sizes had been used, the organic analytes of interest probably would have been detected and quantified in most of the 1990 Virginian Province samples. In reality, analytes of interest present in the samples at low concentrations were not detected and therefore not reported. This limits the comparability of the 1990 organics data with other data sets for which lower detection limits were achieved and limits data users' ability to make quantitative evaluations of sediment contamination for these organic compounds in the Virginian Province.

9.3.3 Mercury analyses

For the 1990 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 = 18 sample batches). The average percent recovery of 82% for mercury in this reference material fell just outside the accuracy control limit range of 85% to 115%, suggesting that mercury may have been slightly under-recovered in some sample batches. However, an average percent recovery of 96% 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 1990 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 1990 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). Since this certified concentration includes both organic and inorganic carbon, the laboratory established its own "true" value of 3.37% for total organic carbon in this reference material. Therefore, the percent recovery values reported in the 1990 data set for CRM PACS-1 are relative to this "internal" certified value of 3.37% TOC. The average percent recovery achieved by the laboratory for n = 18 batches of TOC samples (i.e., 18 separate analyses of CRM PACS-1) was 95%. Based on these results, the 1990 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 1990 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 method detection limit (DETLIMIT) established by the laboratory was 4 ng/g dry weight for both TBT and DBT and 10 ng/g dry weight for MBT. Assuming these Detection Limits 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 = 14 analysis sets were 73% for TBT, 57% for DBT and 394% for MBT. These recoveries fall outside the specified accuracy range of 85% to 115% and indicate that TBT and DBT were consistently under-recovered and MBT was grossly over-recovered in this reference material. However, average percent recoveries for matrix spike samples (97% for TBT, 87% for DBT and 80% for MBT) suggest the laboratory attained much better accuracy for these analyses than is indicated by the reference material results. 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.

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

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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. TABLE OF ACRONYMS

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