Technical Report 1552
September 1993

Acid Volatile Sulfides and Simultaneously Extracted Copper, Lead, and Zinc In Sediments of Sinclair Inlet, Washington

Robert K. Johnston

Approved for Public Release; Distribution is Unlimited

EXECUTIVE SUMMARY

INTRODUCTION

As part of an assessment of the availability and mobility of toxic metal contamination in the sediments of Sinclair Inlet, Puget Sound, Washington, acid volatile sulfide (AVS) and simultaneously extracted metal (SEM) concentrations of Cu, Pb, and Zn were measured in conjunction with deployments of a benthic flux chamber. The AVS and SEM measurements were made from sediment cores, collected at each of the benthic flux stations, to assess the geochemical availability and potential toxicity of the metal present. This report describes the procedures and methods used for sampling and analyzing AVS and SEM, presents the results obtained, and evaluates the significance of AVS and SEM concentrations measured in the sediments of Sinclair Inlet.

METHODS

Two sediment cores 10 to 30 cm in depth were collected from each of ten stations located in the Inlet. One core was sectioned into 2-cm intervals to determine the AVS profile. A composite sample was obtained from the other core by extruding and homogenizing the top 10 cm of the core.

The AVS in aliquots of homogenized sediment samples (2 to 10 grams) was released by reacting the sediments with 1 M HC1 and trapping the H_2S volatilized with a sulfide antioxidant buffer (SAOB) solution. The volume of the trap solutions was adjusted to 100 ml of 50% SAOB and 50% and 50% deaireated deionized water (DDIW). The concentrations of $S^{=}$ were determined with a sulfide ion–specific electrode previously calbrated with standards made in 1:1 SAOB:DDIW using a sulfide stock solution that was iodometrically titrated.

The SEM concentrations of Cu, Pb, and Zn were measured in extracts obtained from the 0–10-cm composite and 0–2-cm surface AVS samples. The SEM Cu concentration was also measured in extracts obtained from the AVS core profile samples. The extracts were prepared for metal analysis by decanting 45 or 35 ml of the elutriate from the storage vials into clean, unused centrifuge tubes and centrifuging at 8,000 rpm for 20 minutes. The metals were analyzed by graphite furnace atomic absorption spectrophotometry.

RESULTS

The AVS measured in composite samples ranged from 0.8 to 98.0 μmol/g. For nine of the ten stations, the composite AVS concentrations were 2.2 to 10.3 times higher than the SEM of Cu, Pb, and Zn, and 1.1 to 6.2 times higher than the divalent metal concentrations (Cd, Cu, Cr, Hg, Ni, Pb, Zn) reported from analysis of bulk sediment grabs collected from the same stations. One station had a composite AVS concentration lower than the composite SEM concentration resulting in a SEM to AVS ratio of 2.5. Seven of the ten stations had high AVS concentrations at the surface (> 20 μmol/g), which increased at intermediate depths and decreased toward the bottom of the core. Simultaneously extracted Cu profiles were relatively uniform with depth and ranged from 0.1 to 11.2 μmol/g.

CONCLUSIONS

The analytical method used to measure AVS in sediments from Sinclair Inlet was able to provide accurate measurements of the reactive sulfide in the sediment cores. The rapid turnaround between sample collection and sample analysis (less than a day for most of the samples) assured a minimum of change in the sediments before analysis.

High concentrations of AVS measured in the sediments for Sinclair Inlet suggest that most of the divalent metals were bound up as nonavailable and nonmobile sulfides.

The core profiles from Sinclair Inlet trace the time course of sulfide geochemistry. At the surface, AVS was relatively high, due to the rapid and sharp decline of oxygen measured in the first few millimeters of sediment, the high amount of organic matter present, and a readily available source of sulphate in the bottom water of the Inlet. The AVS maximum, measured at a 4–6-cm depth in most of the cores, reflects the optimal formation of reactive monosulfides. The decrease in AVS toward the bottom of the core suggests that more sulfide was tied up in less reactive polysulfide and mineral sulfide (pyrite) forms.

There was not a clear relationship between AVS and metal flux measured with the benthic chamber, although a trend of higher flux rates was observed for the metals with lower sulfide solubility (Ni and Zn).

The results reported here are only a snapshot in time, and do not take into consideration seasonal changes of AVS. Not enough information is yet known about the AVS dynamics in sediments. However, these results show that AVS production in the inlet is very high.

High concentrations of sulfide indicate the anoxic nature of the sediments, meaning that most of the metals will reside in a reduced state. As cleanup efforts in the Inlet proceed, it will be important to monitor the sediments. The reduction of pollution stress on the Inlet may increase water quality, attracting benthic organisms which may invade, colonize, and rework the sediments. The sediment reworking will in turn cause the sediments to become more aerobic, destroying AVS and oxidizing and mobilizing metals. The impact to the environment will depend on the rate sediment reworking occurs and on other mediating factors. Future exposure scenarios should be considered as part of any long-term monitoring for Sinclair Inlet.

CONTENTS

EXECUTIVE SUMMARY iii

INTRODUCTION 1

METHODS 4

RESULTS 12

DISCUSSION 35

CONCLUSIONS 40

REFERENCES 41

APPENDIXES:

A. Standard Operating Procedure for AVS Determination in Sediments Using Sulfide-Specific Electrode Detection A-1

B. Raw Data of AVS in Sediment Samples B-1

C. Raw Data for SEM Concentrations of Cu, Pb, and Zn C-2

D. Determinations of Organic Matter Content by Loss on Ignition for Sediment Samples From Sinclair Inlet D-1

FIGURES

1. Location of benthic flux stations in Sinclair Inlet, Puget Sound, Washington 1

2. Apparatus used for measuring acid volatile sulfides 5

3. Sulfide electrode calibration curves obtained from July 9 (Julian date 190) to July 19 (Julian date 200), 1991 17

4. Concentrations of AVS measured in the top 10 cm of cores collected from the stations in Sinclair Inlet 19

5. Vertical profiles of AVS measured in cores collected from Sinclair Inlet 20

6. Calibration curves obtained for copper analysis by GFAA 21

7. Calibration curves obtained for lead analysis by GFAA 21

8. Calibration curves obtained for zinc analysis by GFAA 22

9. SEM concentrations of Cu, Pb, and Zn measured in composite (0–10 cm) samples 24

10. SEM concentrations of Cu, Pb, and Zn measured in surface (0–2 cm) samples 25

11. Depth profiles of SEM copper concentrations 26

12. Ratio of SEM (Cu + Pb + Zn) to AVS surface (0–2 cm) and composite (0–10 cm) samples 27

13. Ratio of metal to composite (0–10 cm) AVS for SEM and bulk sediment metal concentrations measured during benthic chamber deployments (BFSD Metals, Chadwick et al., 1992) and the site investigation (SI Metals, URS Consultants, Inc., 1992) 27

14. Relationship between metal contamination and AVS measured at the stations in Sinclair Inlet 28

15. The fraction of organic matter (F_{om}) measured in composite (0–10 cm) and surface samples (0–2 cm) 29

16. Relationship between organic matter and AVS of sediment samples from Sinclair Inlet 31

17. Relationship obtained for organic matter and log-transformed AVS concentrations measured in surface (0–2 cm) sediment samples 31

18. The relationship between F_{om} measured in surface sediment samples (0–2 cm) and metal flux rates obtained from the benthic flux chamber 32

19. Relationship between AVS measured in surface sediment samples (0–2 cm) and metal flux rates obtained from the benthic chamber 32

20. The relationship between ratio of SEM to AVS measured in surface sediment samples (0–2 cm) and metal flux rates 33

21. The relationship between the ratio of SEM to AVS measured in composite sediment samples (0–10 cm) and metal flux rates 33

22. The relationship between the ratio of bulk divalent metal concentrations and AVS measured in composite (0–10 cm) sediment samples and metal flux rates 34

TABLES

1. The concentrations of divalent metals (μmol/g dry weight) measured in sediment grabs collected from the ten stations selected as locations for in-situ flux measurements (Chadwick and Lieberman, 1991) 2

2. The graphite furnace atomic absorption (GFAA) parameters and furnace programs used for the analysis of copper, lead, and zinc 8

3. Quality control criteria used for SEM analysis 9

4. Summary of samples collected for AVS and SEM analyses of sediments from Sinclair Inlet 12

5. The station location (Sta), core depth of sample (Depth), grams of wet sediment (G_w), the AVS concentration of the trap (μM), the dry-to-wet ratio of sediment (R) and the μmol/g dry weight (μmol/g) of AVS measured for each sample analyzed from sediment cores collected in Sinclair Inlet 13

6. Regression coefficients obtained for sulfide electrode calibration curves measured between July 8 (Julian Date 189) to July 22, 1991 (Julian Date 202) 16

7. Average concentrations of AVS and SEM in composite and surface sediment samples 18

8. Results of SEM analysis of field blanks (FBs) to determine possible contamination of copper, lead, and zinc 22

9. Ratios of SEM to bulk metal concentrations (BFSD) metals 24

10. Results of regression analysis 30

11. Summary of benthic flux measurements obtained for Ni, Zn, Cu, and Pb (from Chadwick et al., 1992), and composite (0–10 cm, Comp.) and surface (0–2 cm, Surf.) levels of F_{om}, AVS, bulk metals:AVS (BFSD/AVS), and SEM/AVS (SEM/AVS) 34

12. Values of AVS reported from other field studies 38

INTRODUCTION

As part of an assessment of the availability and mobility of toxic metals in the sediments of Sinclair Inlet, Puget sound, Washington, acid volatile sulfides (AVSs) and simultaneously extracted metal (SEM) concentrations of Cu, Pb and Zn were measured in conjunction with deployments of a benthic flux chamber (Chadwick and Lieberman, 1991). The benthic flux chamber was used to measure the in-situ metal flux between the sediments and the water column at ten stations in the Inlet (figure 1). The AVS and SEM measurements were made from sediment cores, collected at each of the benthic flux stations, to assess the geochemical availability and potential toxicity of the metal present. The stations were selected based on previous data (URS Consultants, Inc., 1990, 1992) to encompass the range of metal concentrations in the Inlet (table 1) and provide a representative analysis of the potential for the release of toxic metals from the sediments (Chadwick and Lieberman, 1991). Two replicate stations (a and b) were located in each of five areas of similar metal concentration levels. The areas were determined from the cluster analysis of data from the site inspection study (Chadwick et al., 1992). This report describes the procedures and methods used for sampling and analyzing AVS and SEM, presents the results obtained, and evaluates the significance of AVS and SEM concentrations measured in the sediments of Sinclair Inlet. The results obtained from the flux measurements are reported in Chadwick et al. (1992).

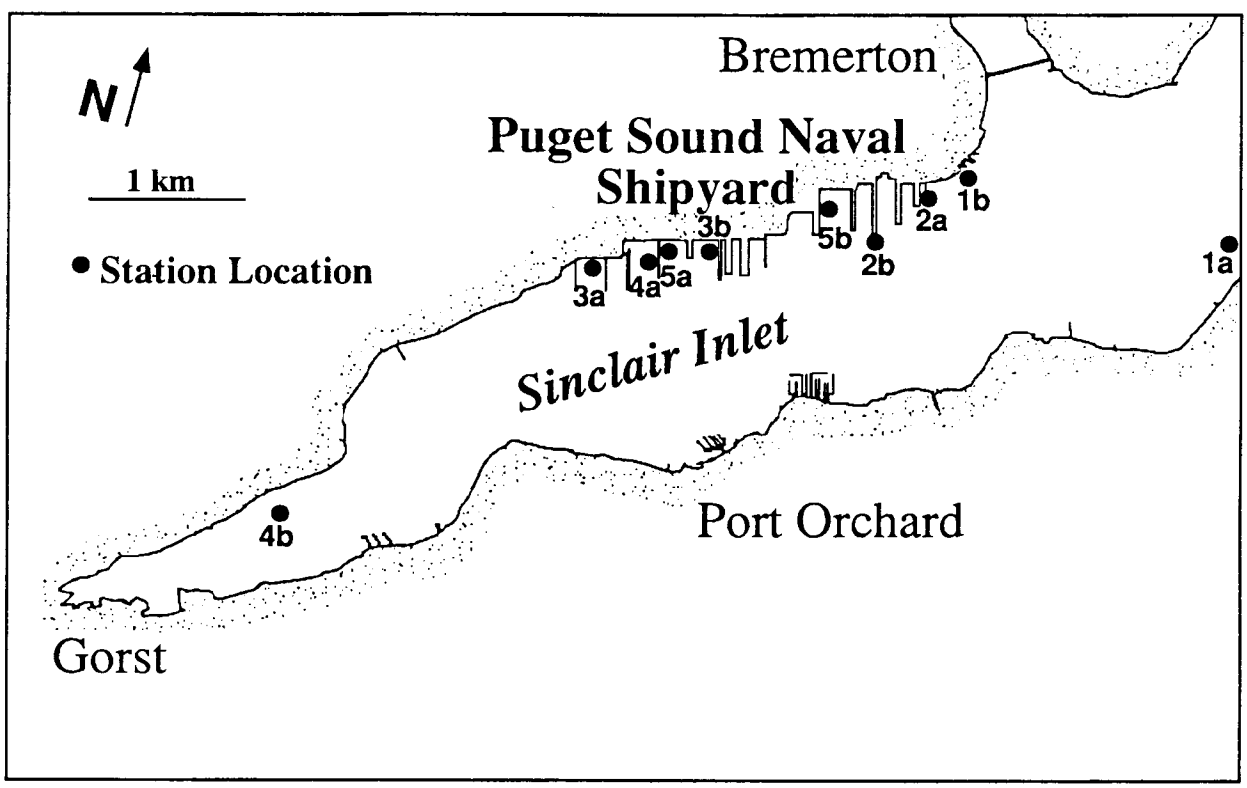


Figure 1. Location of benthic flux stations in Sinclair Inlet, Puget Sound, Washington. Two cores for AVS determination were collected from each station.

Table 1. The concentration of metals (μmol/g dry weight) measured in sediment grabs collected from the ten stations selected as locations for in-situ flux measurements (Chadwick and Lieberman, 1991).

(A) Data complied from measurements made during the Puget Sound Naval Shipyard Site Investigation (SI METALS) conducted fall 1989 (URS Consultants, Inc. 1992).

Station	Element (μmol/g)							Sum	Avg
	Cd	Cu	Pb	Hg	Ni	Ag	Zn		
1a	0.01	0.13	0.06	0.00	0.26	0.00	0.55	1.00	
1b	0.00	0.30	0.17	0.00	0.30	0.00	0.87	1.64	1.3
2a	0.01	2.20	0.68	0.00	0.58	0.01	3.49	6.97	
2b	0.03	2.03	0.46	0.00	0.65	0.01	3.57	6.76	6.9
3a	0.03	3.32	0.66	0.01	0.67	0.02	4.09	8.79	
3b	0.04	3.15	1.27	0.00	0.70	0.01	10.59	15.76	12.3
4a	0.02	4.31	0.51	0.01	0.67	0.01	4.56	10.09	
4b	0.04	2.17	0.46	0.00	0.76	0.03	3.07	6.52	8.3
5a	0.03	5.70	1.18	0.01	0.59	0.01	7.48	15.00	
5b	0.05	26.75	2.80	0.01	0.76	0.01	18.77	49.15	32.1

(B) Concentration of divalent metals measured in bulk sediments sampled during deployments of the benthic flux sampling device (BFSD METALS) July 1992 (Chadwick et al., 1992).

Station	Element (μmol/g)						Sum	Avg
	Cd	Cu	Pb	Hg	Ni	Zn		
1a	0.00	0.08	0.05	0.00	0.49	0.40	1.02	
1b	0.00	0.60	0.18	0.00	0.75	1.89	3.43	2.2
2a	0.01	3.02	1.60	0.00	1.38	42.63	48.64	
2b	0.04	2.12	0.28	0.00	0.94	0.66	4.05	26.3
3a	0.01	5.63	1.63	0.01	1.72	5.39	14.39	
3b	0.00	2.00	0.01	0.01	1.69	1.92	5.99	10.2
4a	0.01	3.70	1.35	0.00	1.45	10.19	16.70	
4b	0.01	2.00	0.40	0.00	1.43	1.69	5.54	11.1
5a	0.03	4.04	1.84	0.01	1.12	13.97	21.03	
5b	0.01	4.00.	0.80	0.00	1.58	4.18	10.57	15.8

The importance of AVS in controlling metal toxicity in sediments has been shown in a number of recent studies (Di Toro et al., 1990; Ankley et al., 1991; Carlson et al., 1991; Di Toro et al., 1992). Concentrations of AVS in sediments are operationally defined as the concentration of solid phase sulfide compounds that can be volatilized when treated with cold acid (Di Toro et al., 1990; Boothman and Helmstetter, 1992; Allen, Fu, and Deng 1993). The sulfides obtained from AVS measurements are generally considered to be derived from metal sulfides (MeS) of which iron sulfides (FeS) are the most abundant (Goldhaber and Kaplan, 1974; Cornwell and Morse, 1987). In marine and freshwater sediments, divalent metals form very insoluble compounds when they react with sulfide (Morse et al., 1987). It has been hypothesized that the quantity of AVS represents a "reactive pool" of sulfides (Di Toro et al., 1992) which are able to bind and reduce the availability and toxicity of the metals present (Di Toro et al., 1990).

In sediments, sulfides are produced through the digenesis (breakdown) of organic matter. Under anoxic conditions, sulphate ($SO_4^=$), which is abundant in marine waters (2700 mg/L) (Di Toro et al., 1990), is used as the electron donor to oxidize organic matter:

$$2CH_2O + SO_4^= \rightarrow 2CO_2 + S^= + 2H_2O$$

Since sulfide ($S^=$) is very reactive, it forms monosulfides with readily available iron (Fe), resulting in the formation of iron monosulfide solids:

$$Fe^{2+} + S^= \leftrightarrows FeS_{solid}$$

The geochemical processes occurring in the sediment will result in the partitioning of sulfides into three fractions: (1) AVS reactive sulfides made up of easily solubilizable iron- and other monosulfides; (2) more resistant and insoluble mineral phase sulfides such as iron pyrite; and (3) organic sulfides which are tightly associated with organic matter (Di Toro et al., 1990). The reactive pool of AVS will disassociate from the solid-phase amorphous iron and manganese sulfides to bind with toxic metals in the sediments, because the toxic metal sulfides are more insoluble (have a lower K_{sp}) than the iron sulfides. The iron sulfide in the sediments is in equilibrium with the dissolved phase; therefore, the presence of toxic metals will cause the iron sulfides to dissolve and the sulfides to bind with metals:

$$Cu^{2+} + FeS_{solid} \rightarrow CuS_{solid} + Fe^{2+}$$

Any metal sulfides formed by divalent metals (NiS, ZnS, CdS, PbS, CuS, HgS, etc.) that have lower metal sulfide solubility than FeS (or MnS) will form sulfides at the expense of iron and manganese sulfide (Di Toro et al., 1990; Cornwell and Morse, 1987; Morse, et al., 1987, Lide, 1990).

The form of the metal within the sediments will determine metal toxicity (Di Toro et al., 1990; Ankley et al., 1991; Carlson et al., 1991; Di Toro et al., 1992) as well as mobility (Goldhaber and Kaplan, 1974; Morse et al., 1987) and therefore risk to the ecosystem. A significant reduction in the toxicity of heavy metals has been observed when AVS concentrations (umol/g dry weight) are equal to or greater than the concentration of toxic metals (Di Toro et al. 1990, Ankley et al., 1991; Carlson et al., 1991). The explanation is that when the ratio of metals to AVS concentrations is less than one, the metals are not biologically available to organisms nor are they mobile, because they are bound up in the reactive pool of AVS (Di Toro et al. 1992). Under conditions where the ratio of toxic metals to AVS ([toxic metals]:[AVS]) is less than one (more AVS than metals), the potential flux of metals from the sediment into the water column

will be reduced or negligible. The actual metal flux will be a function of the form of the metal present, the concentration gradient between the sediment and water column, and the amount of bioturbation occurring in the sediment.

The analysis of AVS requires treating the sediments with a cold acid (HCl) to volatilize the reactive sulfide pool. When the sulfides are volatilized and driven off by the carrier gas (N_2), any metals that were bound up as metal sulfides are released and remain dissolved in the extract:

$$MeS + 2HCl \rightarrow H_2S + MeCl_{aqueous}$$

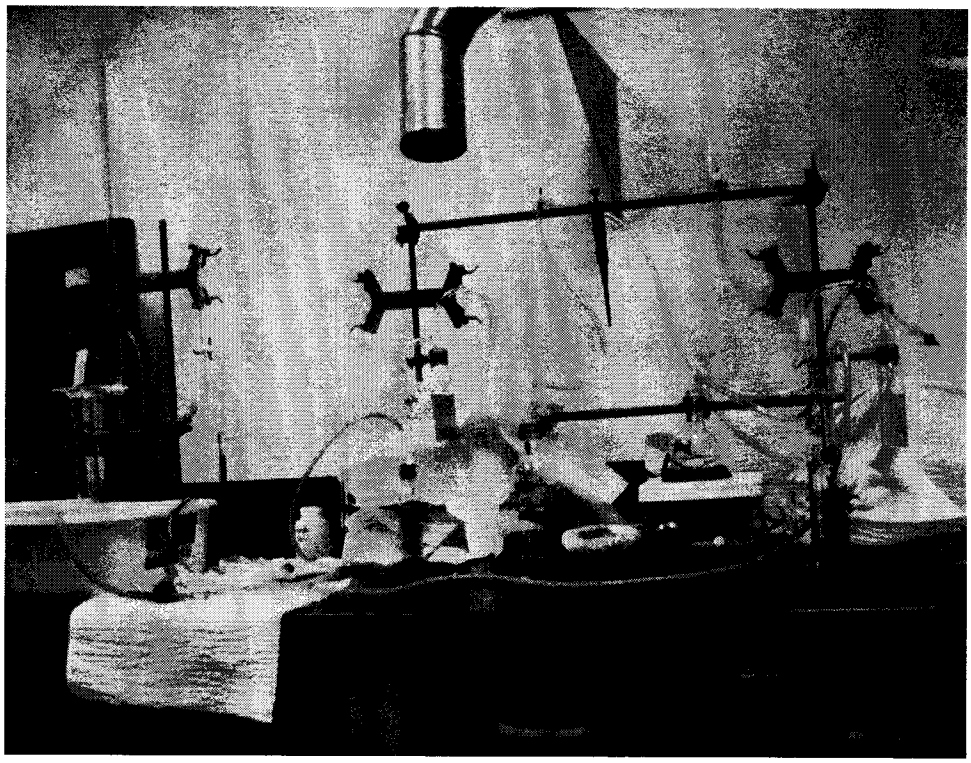
The concentration of the metals thus extracted is referred to as the simultaneously extracted metal (SEM), which represents the portion of metal activity associated with the reactive pool of AVS (Di Toro et al., 1992). The total extractable metal concentration, usually measured in bulk sediment analysis (see table 1), consists of the AVS-associated metals as well as other, more insoluble, mineral-bound and organic-bound forms of the metals.

METHODS

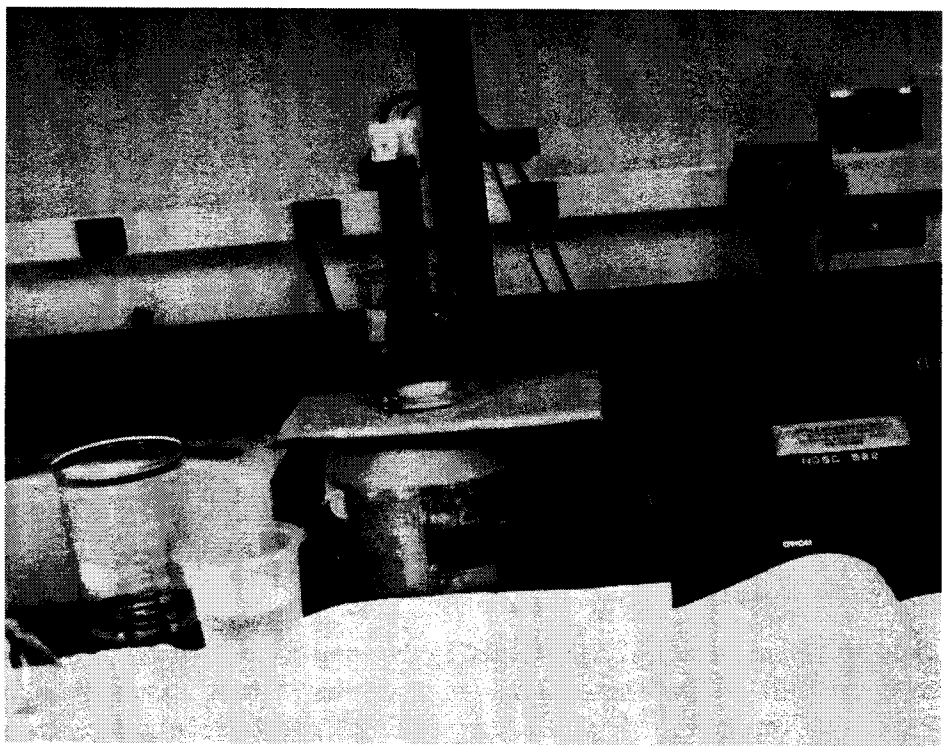
The AVS concentrations of sediments were determined by using the method described in Appendix A. Ultrapure N_2 gas, passed through an oxygen stripping solution of vanadous chloride, was used in a purge and trap system to evolve H_2S from sediment samples. Aliquots of sediment samples ranging from 2 to 10 grams of wet sediment were extracted by reacting the sediments with 1 M HCl and trapping the H_2S in a series of two traps (Trap1 and Trap2) containing a sulfide antioxidant buffer (SAOB) solution made from 2 M sodium hydroxide, 0.2 M ethylenediaminetetracetec acid (EDTA), and 0.2 M L-asorbic acid (Appendix A). The volume of the trap solutions was adjusted to 100 ml of 50% SAOB and 50% deareated deionized water (DDIW), and the concentration of $S^=$ was determined with a sulfide ion electrode previously calibrated with standards made in 1:1 SAOB:DDIW using a sulfide stock solution that was iodometrically titrated. A photograph showing the components of the setup is shown in figure 2.

An inverted graduated cylinder filled with water mounted on a ring stand was used to estimate the N_2 gas flow rate through the system. It was necessary to use the graduated cylinder because flowmeters were not available. The flow rate was measured by timing the displacement of water in the cylinder caused by bubbles exiting from tubing connected to the exit port of the second trap (Trap2). When two reaction vessels were used in parallel (System1 and System2), constant and equivalent flow was maintained by slightly constricting flow through System1 with a ring stand clamp attached to the tubing exiting from Trap2. When the system was configured in this manner, it was possible to maintain a constant flow rate for each analysis. The measured flow rate ranged between 120 and 200 ml/min and was found to be dependent on the ambient air temperature. The second sulfide trap (Trap2) was measured after each analysis to assure that no sulfide was blown past Trap1. No significant concentrations were detected in Trap2 during the analysis of Sinclair Inlet samples.

Sediment cores 10 to 30 cm in depth were collected with a 5-cm-diameter coring device from ten stations in Sinclair Inlet (figure 1). Cores were maintained intact on ice until they were extruded immediately before analysis. Two cores were collected from each station. One core was selected (usually the deepest core) to determine the AVS profile by extruding and homogenizing 2-cm sections sampled from 0–2, 4–6, 8–10, 20–22, and 30–32–cm depths (or until the



(a) Purge and trap system showing two parallel systems consisting of tubing, reaction vessel, and two SAOB traps.



(b) Measurement of SAOB solution with reference and sulfide electrodes.

Figure 2. Apparatus used for measuring acid volatile sulfides.

bottom of the core was reached). The remaining core for each station was used to obtain a composite sample by extruding the 0–10–cm section of the core. Each sample was thoroughly mixed with a rubber spatula and subsampled. About 2 to 6 grams of wet sediment were placed on a preweighed piece of parafilm, weighed on a Sarturius balance, and placed into the reaction vessel by washing with DDIW measured into a syringe. The volume of the reaction vessel was then adjusted to 50 ml with DDIW and placed on the stirring motor and connected to the system.

The dry-to-wet ratio (R) was determined by drying a sample of the sediment at 100° C for approximately 24 hours.

Ultrapure N_2 was purged through the system for a minimum of 10 minutes to remove all free oxygen. After the initial purge, the flow rate and stirring was stopped while 10 ml of 6 M HCl was slowly injected into the septum of the reaction vessel. After it was determined whether any gas was spontaneously formed within the reaction vessel, the gas flow and stirring were turned back on and maintained at a constant rate to trap any sulfide gas evolved by bubbling N_2 through the SAOB traps. After 30 minutes, the gas flow and stirring was stopped and the traps were removed from the system and adjusted to 100 ml volume (1:1 SAOB:DDIW) for measurement with the sulfide electrode. The material (sediment and elutriate) remaining in the reaction vessel was preserved in 80-ml centrifuge tubes for metals analysis to determine the SEM concentration of Cu, Pb and Zn.

The trap solutions were measured with the sulfide electrode for a period of 8–10 minutes. The mV response obtained from the pH meter connected to the sulfide electrodes was recorded at 2-minute intervals until a stable reading was obtained. It was observed that the mV reading would reach a peak and then diminish with time. Therefore, the average mV reading bracketing the peak was used to determine the sulfide concentration. Sulfide concentrations $[S^{=}]$ were determined by converting mV response to concentration by using a regression curve obtained from the electrode response to standards.

Standards, prepared fresh each week from the iodometrically titrated sulfide stock solution, were used to calibrate the sulfide electrode. On each analytical day a new standard curve was generated to calculate the sulfide concentrations for samples analyzed on that day. The concentration of AVS was determined by

$$\text{AVS} = \frac{[S^{=}] \cdot V_{\text{trap}}}{G_w \cdot R}$$

where

AVS	=	acid volatile sulfide concentration (μmol/g dry weight)
$[S^{=}]$	=	sulfide concentration determined from mV response
V_{trap}	=	trap volume (0.1 L)
G_w	=	grams wet weight of sediment sample
R	=	dry/wet ratio

Blanks and spike recoveries were analyzed in the same manner as the sediment samples. A blank consisting of only DDIW was analyzed to determine if there was any contamination in the system. System recoveries were determined by adding a known spike concentration of the sulfide stock solution, diluted with DDIW, to the reaction vessel before the initial purge. Spikes were added to blanks and to sediments. Recoveries were determined by comparing the $[S^{=}]$ of the blank spike to a bench spike created by adding the same sulfide spike directly to the 1:1 SAOB:DDIW matrix. Recoveries from sediment spike were determined by

$$\text{Recovery} = \frac{AVS_{spiked} - SAMPLE}{SPIKE}$$

where

AVS_{spiked}	=	the concentration of AVS in μmol/g dry weight determined for the sample+spike
SAMPLE	=	the AVS in μmol/g dry weight determined from replicates of the spiked sample
SPIKE	=	the concentration of H_2S (μM) in the spike added to the sample

An aliquot of sediment samples obtained from North Jamestown, Narragansett Bay, RI, was analyzed using this procedure as an intercalibration with a similar AVS procedure used at the EPA Environmental Research Laboratory, Narragansett, RI (ERLN). The values of 5.58 and 5.66 μmol/g were obtained for the two replicate measures of the aliquot. The concentration of AVS in the North Jamestown sample was independently determined to be approximately 8 μmol/g (W. Boothman, EPA ERLN).

The SEM concentrations of Cu, Pb, and Zn were measured by graphite furnace atomic absorption (GFAA) spectroscopy in extracts obtained from the 0–10–cm composite and 0–2–cm surface AVS samples. The SEM Cu concentration was also measured in extracts obtained from the AVS core profile samples. The extracts (which consisted of 50 ml DDIW, 10 ml 1 M HCl, and sediment samples) were preserved in tightly sealed and labeled 80-ml centrifuge tubes until SEM analysis was performed in January 1992. The extracts were prepared for metal analysis by decanting 35 or 45 ml of the elutriate from the storage vials in clean, unused centrifuge tubes. The extracts were not filtered; rather the suspended sediment was removed from the elutriate by centrifugation at 8,000 rpm for 20 minutes. Serial dilutions of the extracts were obtained by combining 200 μl of sample extract with 800 μl deionized water (DIW) (d_1) and combining 100 μl of d_1 with 900 μl of DIW (d_2):

d_1 = 200 μl sample extract + 800 μl DIW

d_2 = 100 μl d_1 + 900 μl DIW

The metal analyses were performed with a Perkin Elmer AA 5000 equipped with an HGA 500 furnace and an AS 40 autosampler. A standard uncoated graphite tube was used for the Cu analysis (Lindner and Caso, in preparation) and an platform graphite tube was used for the Pb and Zn analyses (John Andrews, Computer Sciences Corporation, personal communication). The parameters and programs used for the metal analyses are shown in table 2. No matrix modifiers were used.

Table 2. The graphite furnace atomic absorption (GFAA) parameters and furnace programs used for the analysis of copper, lead, and zinc. The AS 40 autosampler was set at a sample volume of 10 µl for all analyses.

(**A**) Copper parameters and program (Lindner and Caso, in preparation).

AA 5000 Parameters

Sample Time:	10.0 s
Lamp:	Hollow Cathode Lamp, 15-mA, 70-W output
Energy:	68 W
Wavelength	324.8 nm
Slit Length:	0.7 nm

HGA 500 Furnace Program

Step	Description	Temp, °C	Ramp Time, s	Hold Time, s	Gus Flow, ml/min	Read Time, s	Recorder on Time, s	Baseline Set Time, s
1	Dry	110	10	30	100			
2	Char	1150	10	45	100			
3	Cool Down	20	1	20	0			
4	Atomization	2100	0	10	0	0	–3	–11
5	Clean Up	2600	1	3	100			

(**B**) Lead parameters and program (John Andrews, Computer Sciences Corporation, personal communication).

AA 5000 Parameters

Sample Time:	5.0 s
Lamp:	Hollow Cathode Lamp, 10-mA
Energy:	68 W
Wavelength	283.3 nm
Slit Length:	0.7 nm

HGA 500 Furnace Program

Step	Description	Temp, °C	Ramp Time, s	Hold Time, s	Gus Flow, ml/min	Read Time, s	Recorder on Time, s	Baseline Set Time, s
1	Dry	120	10	50	150			
2	Char	850	10	30	150			
3	Cool Down	20	1	15	150			
4	Atomization	1800	0	10	0	0	–3	–11
5	Clean Up	2600	1	5	150			

(Contd)

Table 2. Continued.

(C) Zinc parameters and program (John Andrews, Computer Sciences Corporation, personal communication).

AA 5000 Parameters

Sample Time:	5.0 s
Lamp:	Hollow Cathode Lamp, 8-mA
Energy:	60 W
Wavelength	213.9 nm
Slit Length:	0.7 nm

HGA 500 Furnace Program

Step	Description	Temp, °C	Ramp Time, s	Hold Time, s	Gus Flow, ml/min	Read Time, s	Recorder on Time, s	Baseline Set Time, s
1	Dry	120	10	50	150			
2	Char	400	10	30	150			
3	Cool Down	20	1	15	150			
4	Atomization	1000	0	10	300	0	–3	–11
5	Clean Up	2600	1	5	150			

The sensitivity of the GFAA was determined by using elemental standards made in DIW. A calibration curve was generated with matrix standard additions. Quality assurance QA samples included in each batch consisted of DIW blanks, a sample duplicate, an internal reference sample (e.g., a matrix standard addition whose value was determined from repeated measurements), and a calibration check sample. The QA samples were used to check for laboratory contamination, precision of the method, and instrument drift. In addition, field blanks (FBs) were included as samples in the batch. The FBs were used to control for contamination during the AVS measurement. The control criteria for the QA samples are listed in table 3.

Table 3. Quality control criteria used for SEM analysis.

Quality Assurance Sample	Criteria
BLANK	No more than 2 times the value of a blank, determined by repeated measurements
DUPLICATE	No more than 10% difference between duplicate samples
INTERNAL REFERENCE	No more than 15% difference of the value of the reference material, determined by repeated measurements
CALIBRATION CHECK	No more than 15% difference of the value of the calibration material, determined by repeated measurements
FIELD BLANK	Used to identify possible contamination problems

The characteristic sensitivity (CS), which relates the instrument response to sensitivity per absorbance unit (ABS), was determined by the following relationship:

$$\text{Slope} = M\ (\text{ABS} \bullet \text{s})/\text{ppb}$$

$$\frac{1}{\text{Slope}} = \frac{\text{ppb}}{M\ \text{ABS} \bullet \text{s}} = \frac{(\mu\text{gl}^{-1}) \bullet (10^{-6}\ \text{l}\mu\text{l}^{-1}) \bullet (SV\mu\text{l}) \bullet (1\ \text{pg}\ 10^{6}\mu^{-1})}{M\ \text{ABS} \bullet \text{s}} \bullet \frac{(0.0044\ \text{ABS} \bullet \text{s})}{(0.0044\ \text{ABS} \bullet \text{s})}$$

$$= \frac{(SV\ \text{pg}) \bullet (0.0044)}{(M)\ \ (0.0044\ \text{ABS} \bullet \text{s})}$$

$$= \frac{(SV) \bullet (0.0044)}{M} \bullet \frac{\text{pg}}{0.0044\ \text{ABS} \bullet s}$$

where CS, in pg/(0.0044 ABS • s), is defined as

CS = $SV(0.0044)/M$

and

Slope = M	=	change in absorbance per unit increase in concentration obtained from the regression of DIW standards
SV	=	sample volume used in the GFAA
0.0044 ABS • s	=	measurement threshold of the AA 5000

The concentration (C_{extract}) of the sample extracts was determined by

C_{extract}	=	d_1/100 µl
d_1	=	(d_2 • 1000 µl)/200 µl
d_2	=	(CONC • 1000 µl)/100 µl
CONC	=	(ABS-BLANK)/M_{slope}

where

d_1, d_2	=	serial dilutions 1 and 2, respectively
CONC	=	concentration measured by GFAA
ABS	=	absorbance units measured on the AA 5000
M_{slope}	=	slope of the regression curve computed from matrix standard additions
BLANK	=	value of a blank determined from repeated measurements

The sediment concentration (C_{sed} µmol/g) was determined by

$$C_{\text{sed}} = \frac{(C_{extract} \bullet V_{ext})}{G_w \bullet R \bullet AW}$$

where

V_{ext}	=	total volume of extract
	=	$C_{\text{vol}} + (W_{\text{sto}} - G_w) \bullet (10\ \text{ml}/10.05\ \text{g})$

and

C_{vol}	=	volume of material centrifuged
W_{sto}	=	weight of material remaining in storage vial, determined by tarring the weight of the empty storage vial + label and then measuring the weight of the material (sediment + extract) remaining in the storage vial
G_w	=	amount of sediment extracted (measured weight of sample used to determine AVS)
AW	=	the atomic weight (μg/μmol) of the metal being analyzed
R	=	dry/wet ratio of sediment sample.

The surface (0–2 cm) and composite (0–10) AVS concentrations were compared to the SEM concentrations of Cu, Pb, and Zn measured from the same samples. The composite AVS was also compared to the bulk metal concentrations (BFSD METALs and SI METALs, table 1) to evaluate the availability and potential toxicity from metal contamination of the sediments of Sinclair Inlet. The relationships between metal fluxes and the concentrations of AVS and SEM were evaluated by regression analysis.

The fraction of organic matter in the sediment samples was determined by loss on ignition. Dried sediment samples were homogenized (5 to 12 grams weight) and combusted in a muffle furnace for 6 hours at 450°C. The combusted samples were desiccated for 24 hours and reweighed periodically until a constant weight was obtained. The fraction of organic matter present in the sample was determined as

$$F_{om} = (\text{Postburn} - \text{Dishwt})/(\text{Preburn} - \text{Dishwt})$$

where

F_{om}	=	fraction of organic matter
Dishwt	=	weight of dish used for combustion
Preburn	=	weight of sample before ignition
Postburn	=	weight of sample after ignition

The fraction of organic matter was compared to AVS concentrations and metal flux rates to determine the extent of correspondence.

RESULTS

The AVS samples were collected and analyzed from each station between July 8 and July 22, 1991 (see Appendix B for raw AVS data), and the SEM analyses were performed January 24–30 1992 (see Appendix C for raw SEM data). A surface composite sample (0–10 cm) and three to five profile samples were analyzed for each station, and a grab sample from station 5a was also analyzed (table 4). Replicates, blanks, and spiked samples were also analyzed periodically throughout the AVS and SEM analyses to provide quality assurance for the procedures. Dry to wet weight ratios showed that the water content of the sediment samples was variable, and it ranged from about 20% (station 1a) to 83% (station 3a) (table 5).

The electrode calibration curve showed very good repeatability throughout the study (figure 3, Appendix A). Titration of the sulfide primary standard stock solution on July 8 (189) and July 16 (197), 1991, yielded concentrations of 4843 and 4853 μM, respectively. There were only slight variations in the daily calibration curves used to compute sample AVS concentrations (table 6). The AVS data obtained from all the samples and replicates, spiked samples, and blanks are presented in table 5. Blank samples, consisting of only DDIW (sample numbers 1 and 56, Appendix B), showed only trace amounts of AVS. Spiked blank recoveries were all within ±5% of the spiked concentration (table 5). Recoveries for spiked sediment samples were more variable and ranged between a low of 37.9% and a high of 95.2% (table 5). Very good repeatability was obtained from duplicate samples (table 5).

Table 4. Summary of samples collected for AVS and SEM analyses of sediments from Sinclair Inlet.

Station	Composite	Profile	Grab
1a	1	3	
1b	1	4	
2a	1	4	
2b	1	5	
3a	1	5	
3b	1	4	
4a	1	4	
4b	1	4	
5a	1	4	1
5b	1	4	
Subtotal	10	41	1
Total Samples	52		

Table 5. The station location (Sta), core depth of sample (Depth), grams of wet sediment (G_w), the AVS concentration of the trap (μM), the dry to wet ratio of sediment (R) and the μmol/g dry weight (μmol/g) of AVS measured for each sample analyzed from sediment cores collected in Sinclair Inlet. The average AVS concentrations (Avg) for duplicate samples, AVS concentrations of spikes for blanks and spiked samples (Spike), the percent recovery (RECV), and the calculated AVS concentration (CALC) are also tabulated..

Sta	Depth	G_w, g	μM	R	AVS μmol/g	AVS Avg, μmol/g	Spike, μM	RECV, %	AVS CALC, μmol/g
1a	0–2a	7.18	5.25	0.7123	0.10				
1a	0–2b	7.88	7.39	0.7123	0.13	0.12			
1a	4–6	10.06	34.17	0.7829	0.43				
1a	4–6	10.06	34.17	0.7829	0.43				
1a	8–10	6.02	111.38	0.6102	3.03				
1a	0–10a	13.96	84.40	0.7688	0.79				
1a	0–10b	7.26	54.67	0.7688	0.98	0.88			
1a blksys1			495.49				511.00	97.0	
1a blksys2			499.32				511.00	97.7	
1b	0-2a	6.82	145.41	0.6376	3.34	3.05			
1b	0–2b	4.85	85.03	0.6376	2.75				
1b	4–6a	4.48	138.84	0.7065	4.39				
1b	4–6b	8.10	282.70	0.7065	4.94	4.66			
1b	8–10a	3.08	209.90	0.5998	11.36				
1b	8–10b	4.66	246.74	0.5998	8.83	10.09			
1b	20–22	5.95	176.73	0.7566	3.93				
1b	0–10a	4.76	293.45	0.5895	10.46				
1b blank1			1265.88				1236.98	102.3	
2a	0–2a	6.81	1546.51	0.3209	70.77				
2a*	0–2b	2.98	1552.48	0.3209	162.35		1190.25	73.6	37.88
2a	4–6a	2.04	1130.69	0.3551	156.09				
2a	4–6b	2.43	1282.24	0.3551	148.60	152.34			
2a	8–10	1.99	976.78	0.3664	133.96				
2a	18–20	3.73	1993.98	0.3838	139.29				
2a	0–10a	3.48	967.32	0.3779	73.56				
2a	0–10b	2.90	756.97	0.3779	69.07	71.31			
2a* 0–10c		0.86	1130.00	0.3779	347.70		1027.16	87.4	31.64
2a blank1			0.47						
2a blank2			1104.72				1139.11	97.0	

* Spiked sediment sample

(Contd)

Table 5. Continued.

Sta	Depth	G_w, g	µM	R	AVS µmol/g	AVS Avg, µmol/g	AVS Spike, µM	RECV, %	AVS CALC, µmol/g
2b#	0–2a	2.62	155.64	0.2947	20.16				
2b#	0–2b	2.46	699.04	0.2947	96.43				
2b	0–2c	8.17	1259.02	0.2947	52.30	56.30			
2b#	4–6a	1.33	385.08	0.3480	83.19				
2b#	4–6b	1.20	437.64	0.3480	104.79				
2b	4–6c	4.15	838.98	0.3480	58.09	82.02			
2b	8–10a	5.44	1860.44	0.3786	90.34				
2b	20–22	4.31	2083.08	0.4112	117.54				
2b	0–10a	4.15	335.31	0.3679	21.96				
2b	0–10b	5.83	477.99	0.3679	22.29	22.13			
2b blksys1			467.06				469.47	99.5	
2b blksys2			482.92				469.47	102.9	
3a	0–2a	2.84	383.92	0.1957	69.06				
3a	0–2b	5.96	811.60	0.1957	69.57	69.32			
3a	4–6a	4.01	986.32	0.2336	105.29				
3a*	4–6b	3.75	1751.89	0.2336	199.99		128.85	73.5%	71.12
3a	8–10a	4.24	596.59	0.2574	54.66				
3a	8–10b	2.16	310.80	0.2574	55.90	55.28			
3a	20–22	4.59	3.10	0.1727	0.39				
3a	30–32	5.25	4.12	0.1727	0.45				
3a	0–9	5.82	67.98	0.3377	3.46				
3a blank1		1	20.92				119.33	101.3%	
3a blank2			1155.66				1183.11	97.7%	
3b	0–2a	2.75	60.97	0.3639	6.09				
3b	0–2b	2.85	65.13	0.3639	6.28	6.19			
3b	4–6a	2.27	141.31	0.5123	12.15				
3b	4–6b	2.48	164.73	0.5123	12.97	12.56			
3b	8–10	3.81	34.08	0.5225	1.71				
3b	20–22	3.94	270.05	0.6860	9.99				
3b	0–10a	2.61	67.06	0.5801	4.43				
3b	0–10b	5.18	125.13	0.5801	4.16	4.30			
3b blksys1			396.20				449.80	88.1	
3b blksys2			378.79				449.80	84.2	

* Spiked sediment sample

Problem with balance; sample weight may be inaccurate

(Contd)

Table 5. Continued.

Sta	Depth	G_w, g	µM	R	AVS µmol/g	AVS Avg, µmol/g	AVS Spike, µM	RECV, %	AVS CALC, µmol/g
4a	0–2a	5.40	533.86	0.2402	41.16				
4a	0–2b	4.14	369.04	0.2402	37.11	39.13			
4a	4–6a	3.49	902.35	0.3071	84.19				
4a	4–6b	4.14	1094.41	0.3071	86.08	85.14			
4a*	4–6c	2.60	1668.91	0.3071	209.02		1097.03	90.2	71.62
4a	8–10a	5.63	699.44	0.3633	34.20				
4a	20–22	6.45	339.00	0.4912	10.70				
4a	0–10	10.90	954.90	0.4349	20.14				
4a blank1			1095.81				1158.14	94.6	
4a blank2			1097.03				1111.43	98.7	
4b	0–2	2.29	125.46	0.2307	23.75				
4b	0–2b	1.51	80.26	0.2307	23.04	23.39			
4b	4–6a	1.21	127.98	0.2828	37.40				
4b	4–6b	2.32	287.36	0.2828	43.80	40.60			
4b	8–10	3.45	329.27	0.3344	28.54				
4b	20–22	3.80	228.63	0.4145	14.52				
4b	0–10a	5.47	693.91	0.3044	41.67				
4b	0–10b	4.94	686.61	0.3044	45.66	43.67			
4b blksys1			449.80				449.80	100.0	
4b blksys2			448.62				449.80	99.7	
5a	0–2a	6.97	1698.81	0.3686	66.12				
5a	0–2b	7.87	1646.83	0.3686	56.77	61.44			
5a	4–6a	5.96	2111.63	0.3899	90.86				
5a*	4–6b	4.47	1992.11	0.3899	114.29		968.00	95.2	58.75
5a	8–10a	6.33	7234.24	0.4072	280.66				
5a	8–10b	8.23	8582.64	0.4072	256.10	268.38			
5a	0–10a	7.27	3023.78	0.4245	97.98				
5a blank1			16.96				19.35	87.6	
5a blank2			177.14				181.32		97.7
5a (grab)a		5.84	1395.31	0.3879	61.60				
5a (grab)b		3.30	966.47	0.3879	75.51	68.55			
5a*(grab)c		2.09	763.38	0.3879	94.17		242.00	85.8	64.32
5a*(grab)d		3.29	966.47	0.3879	75.74		242.00	37.9	56.77
5a blksys1			501.21				510.44	98.2	
5a blksys2			506.73				510.44	99.3	

* Spiked sediment sample

(Contd)

Table 5. Continued.

Sta	Depth	G_w, g	µM	R	AVS µmol/g	AVS Avg, µmol/g	AVS Spike, µM	RECV, %	AVS CALC, µmol/g
5b	0–2a	1.15	171.10	0.2821	52.74				
5b	0–2b	2.87	535.70	0.2821	66.17	59.45			
5b	4–6a	2.75	1788.01	0.4032	161.26				
5b	4–6b	2.54	1733.94	0.4032	169.31	165.28			
5b	8–10	2.13	1862.74	0.4455	196.30				
5b	20–22	3.17	1818.93	0.5095	112.62				
5b	0–10a	3.32	857.33	0.3958	65.24				
5b	0–10b	3.64	991.49	0.3958	68.82	67.03			
5b blksys1			367.75				360.29	102.1	
5b blksys2			366.80				360.29	101.8	

Table 6. Regression coefficients obtained for sulfide electrode calibration curves measured between July 8 (Julian Date 189) to July 22, 1991 (Julian Date 202). New standards were prepared on July 8 and July 17, 1991.

Day	X Coefficient	Constant	r^2
New Standards Prepared			
July 8 (189)	–29.6	–723.1	0.9999
July 10 (191)	–29.4	–722.8	0.9999
July 11 (192)	–29.8	–721.0	0.9997
July 12 (193)	–29.9	–720.5	0.9998
July 13 (194)	–30.1	–719.0	0.9999
New Standards Prepared			
July 17 (198)	–29.7	–722.7	0.9997
July 18 (199)	–30.0	–722.0	0.9998
July 19 (200)	–29.9	–721.8	0.9999
July 22 (202)	–31.6	–718.7	0.9997

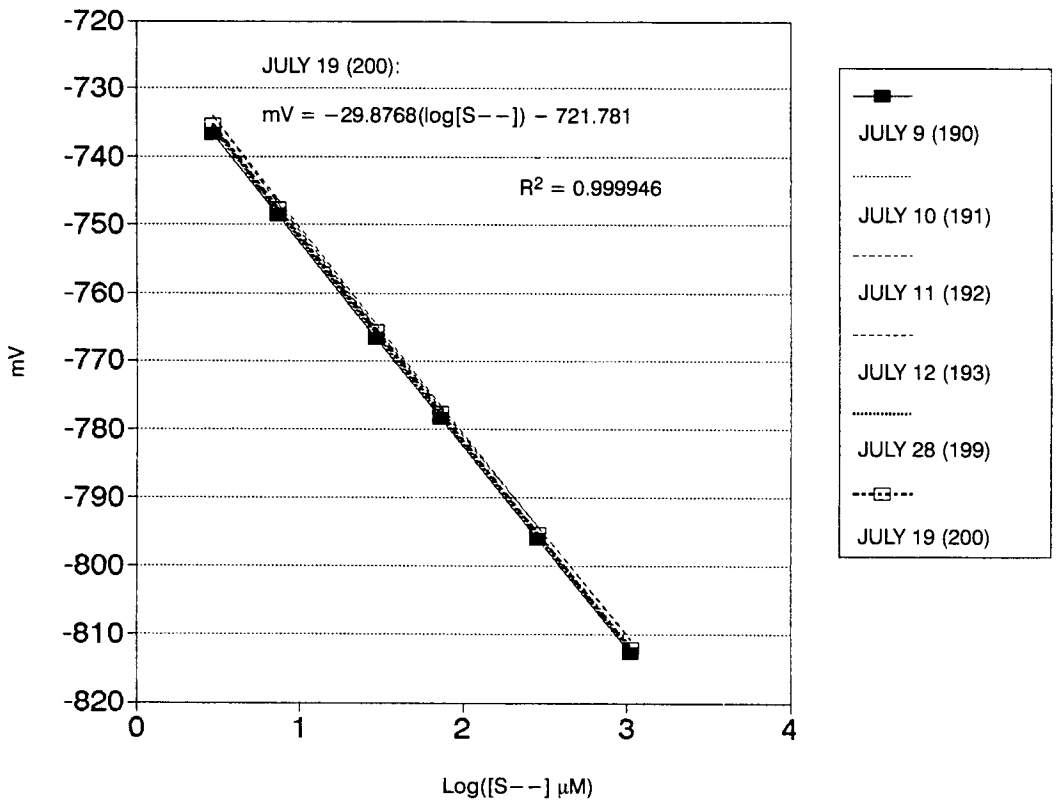


Figure 3. Sulfide electrode calibration curves obtained from July 9 (Julian date 190) to July 19 (Julian date 200), 1991. New standards were prepared on July 8 and July 16, 1991.

The average AVS concentrations measured in the composite samples ranged from 0.88 (station 1a) to 97.98 μmol/g (station 5a) (table 7a). The highest composite sulfide measurements were obtained from stations 5a, 2a, and 5b, while the lowest composites measurements were made from samples for stations 1a, 3a, and 3b (figure 4). The highest mean concentrations from the three profile AVS samples, collected from the top 10 cm of the profile core, were obtained from stations 5a, 5b, and 2a, while the lowest were measured for stations 1a, 1b, and 3b. The composite AVS concentrations were generally lower than the mean core profile samples. Station 3a had the largest difference between the mean profile and composite samples (table 5, figure 4). The average surface (0–2 cm) AVS concentrations ranged from 0.12 (station 1a) to 70.77 μmol/g (station 2a) (table 7b).

The AVS core profiles showed that the highest concentrations (> 160 μmol/g) were measured for the 8–10-cm section of cores 5a and 5b and the lowest AVS concentrations were measured in cores 1a, 1b, and 3b (figure 5). In general, most cores had high AVS concentrations at the surface (> 20 μmol/g), increased AVS at intermediate depth (4–6 cm), and decreased AVS toward the bottom of the core.

The calibration curves used to measure SEM concentrations of Cu, Pb, and Zn are shown in figures 6, 7, and 8, respectively. The DIW characteristic sensitivity (CS) for the copper analysis (15.92 pg/0.0044 ABS•s) was very close to the optimal CS (16.00 pg/0.0044 ABS•s) recommended for the instrument (Perkin Elmer AA 5000 operation manual). The sample matrix

slightly reduced the instrument's sensitivity, but a linear calibration curve was obtained for the range of sample concentration analyzed (figure 6). Although there was a much-reduced sensitivity for GFAA analysis of Pb, good linearity was achieved (figure 7). The GFAA analysis of Zn was more problematic. Although the sensitivity was fairly close to the optimal instrument sensitivity, it was very difficult to obtain a linear response for the sample matrix. For this reason, the DIW standard curve, which was linear from 0–300 ppb, was used as the calibration curve for Zn (figure 8). This was done because most of the sample extract concentrations were below 250 ppb (table B-2 (C)). The lack of sensitivity, matrix interference, and possible Zn contamination problems could mean that there is about a 36% error in the Zn concentrations presented here.

The quality assurance criteria were achieved for each batch for the blank, duplicate, and internal reference samples. Two of the calibration check samples exceeded the QA criteria (copper batches RUN3 and RUN4, Appendix B). An analysis of field blanks (table 8) showed an indication of Zn contamination in samples analyzed for AVS on July 11, 1993 (Julian Date 192). However, the contamination appeared to be isolated and was not present throughout the analysis. Only trace levels of Cu and Pb were detected in the field blanks.

Table 7. Average concentrations of AVS and SEM in composite and surface sediment samples.

(A) Composite 0–10 cm depth.

Station	AVS µmol/g	SEM (µmol/g)			Sum SEM	SEM/AVS
		Cu	Pb	Zn		
1a	0.88	0.13	0.08	0.44	0.65	0.74
1b	10.46	0.43	0.24	1.48	2.15	0.21
2a	71.31	2.97	0.90	6.98	10.85	0.15
2b	22.13	3.02	1.26	5.68	9.96	0.45
3a	3.46	3.35	0.83	4.47	8.65	2.50
3b	4.30	1.16	0.29	2.32	3.77	0.88
4a	20.14	2.00	0.74	2.53	5.27	0.26
4b	43.67	1.64	0.50	3.13	5.27	0.12
5a	97.98	2.67	1.36	5.50	9.53	0.10
5b	67.03	6.99	1.65	8.08	16.72	0.25

(Contd)

Table 7. Continued.

(B) Surface 0–2 cm depth.

Station	AVS µmol/g	SEM (µmol/g)			Sum SEM	SEM/AVS
		Cu	Pb	Zn		
1a	0.12	0.10	0.08	0.50	0.68	5.67
1b	3.05	0.29	0.40	1.17	1.86	0.61
2a	70.77	3.10	0.72	4.26	8.08	0.11
2b	56.30	3.32	0.64	3.32	7.28	0.13
3a	69.32	5.66	1.19	7.66	14.51	0.21
3b	6.19					
4a	39.13	4.17	1.01	6.23	11.41	0.29
4b	23.39	1.58	0.43	4.26	6.27	0.27
5a	61.44	2.87	0.93	6.07	9.87	0.16
5b	59.45	5.83	1.02	9.54	16.39	0.28

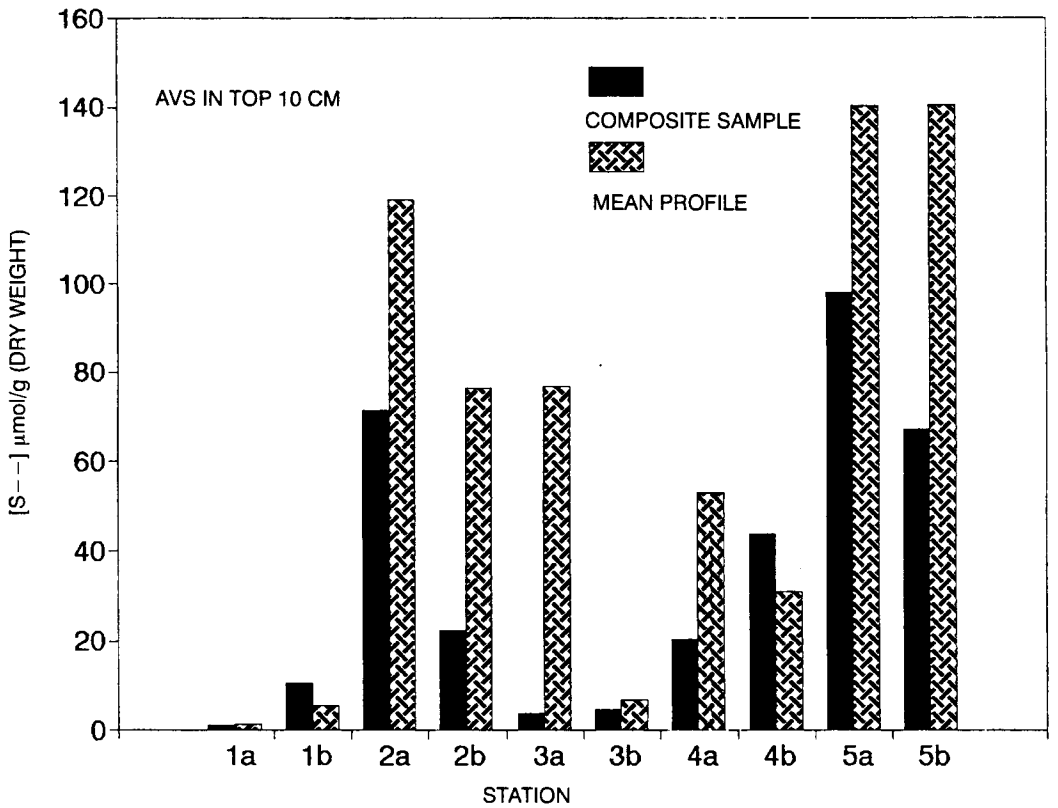


Figure 4. Concentrations of AVS measured in the top 10 cm of cores collected from the stations in Sinclair Inlet. Data are presented for the 0–10-cm composite samples and the mean of the 0–2, 4–6, and 8–10-cm profile samples.

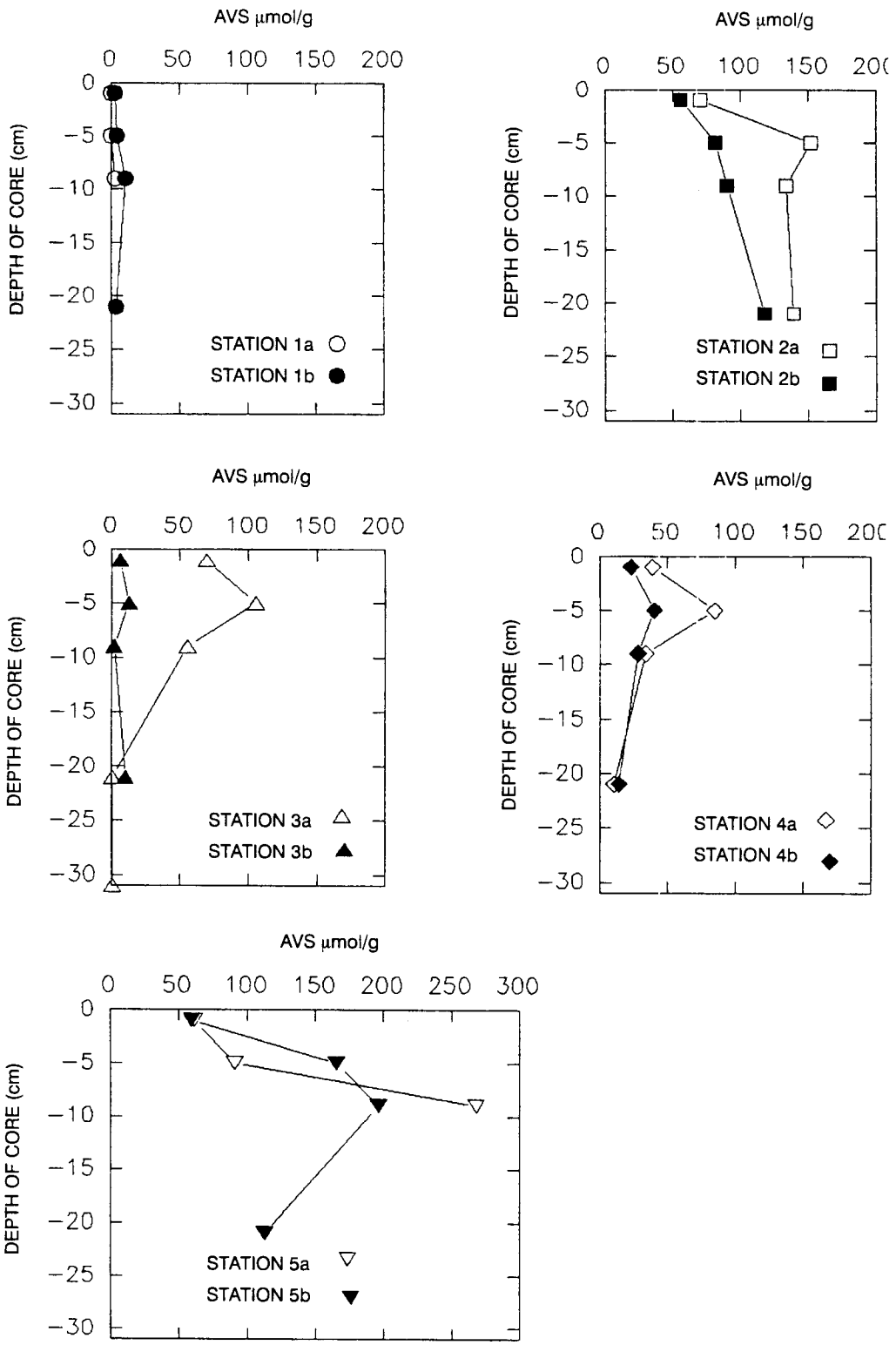


Figure 5. Vertical profiles of AVS measured in cores collected from Sinclair Inlet.

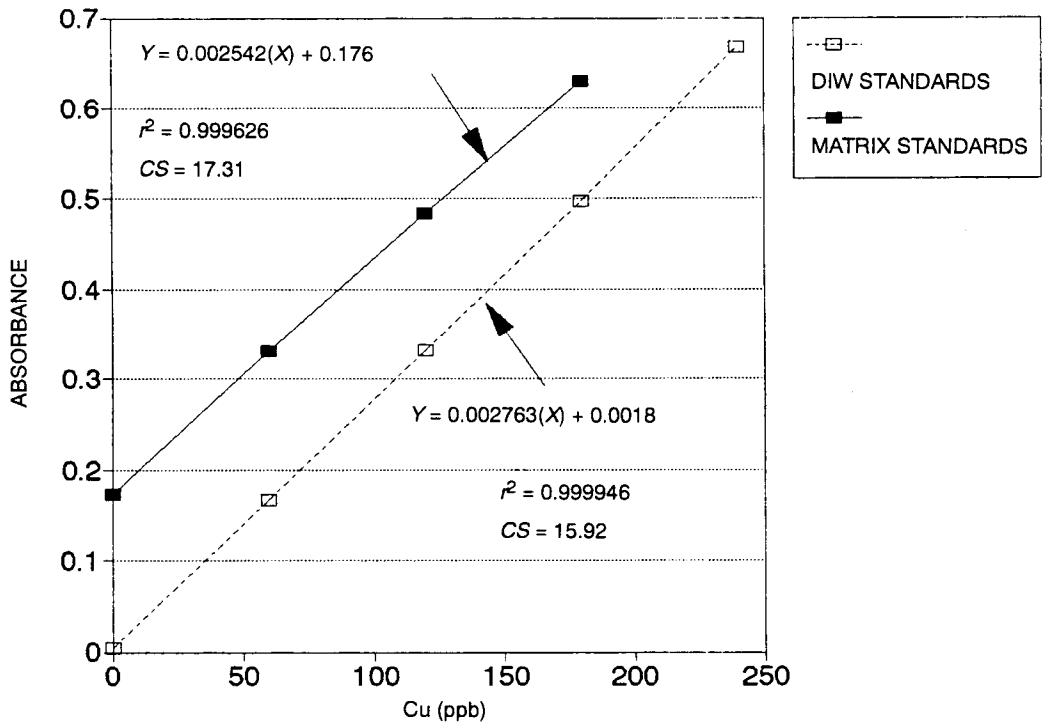


Figure 6. Calibration curves obtained for copper analysis by GFAA.

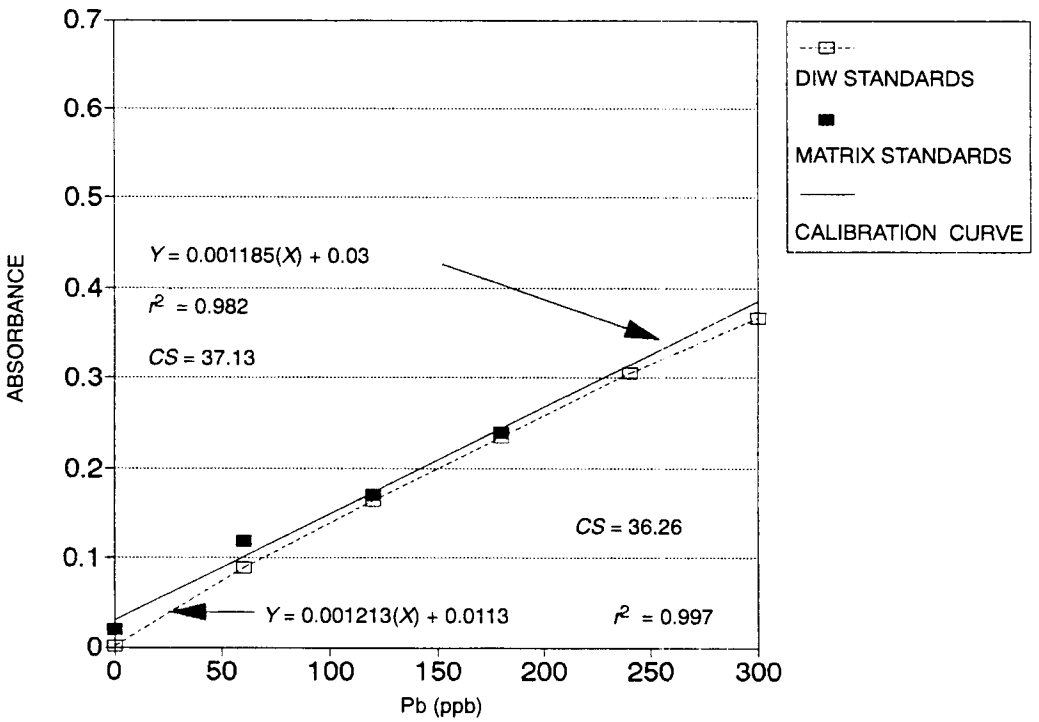


Figure 7. Calibration curves obtained for lead analysis by GFAA.

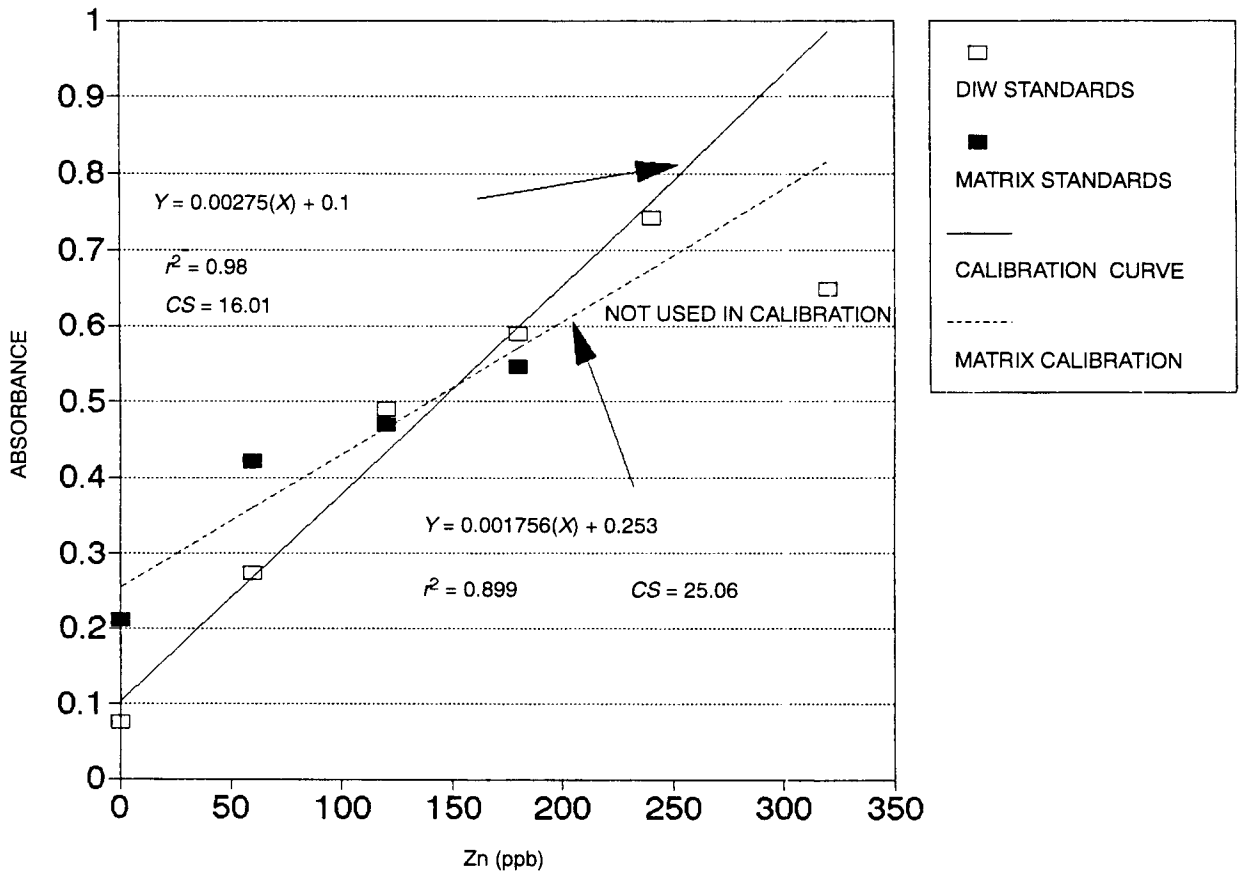


Figure 8. Calibration curves obtained for zinc analysis by GFAA.

Table 8. Results of SEM analysis of field blanks (FBs) to determine possible contamination of copper, lead, and zinc. The sample identification number (ID#), the Julian date and time (Date) the sample was taken, the absorbance reading for the AA 5000 (ABS), and the extract concentration (CONC) in μg/L are given for each FB sample analyzed.

(A) Copper FB (ABS 0.004 is indistinguishable from a DIW blank)

ID#	Date	ABS	CONC, μg/L
7	190 2300	0.026	0.43
26	192 1210	0.002	0.04
16	192 2000	0.027	0.53
10	193 1800	0.007	0.06
42	194 1100	0.003	0.06
24	198 0015	0.005	0.02
34	200 1700A	0.003	0.06
18	200 1700B	0.001	0.02

(Contd)

Table 8. Continued.

(**B**) Lead FB (ABS 0.001 is indistinguishable from a DIW blank)

ID#	Date	ABS	CONC, µg/L
26	192 1210	0.001	0.04
16	192 2000	0.003	0.13
10	193 1800	0.001	0.04
24	198 0015	0.000	0.00
18	200 1700B	0.000	0.00

(**C**) Zinc FB (ABS 0.059 is indistinguishable from a DIW blank)

ID#	Date	ABS	CONC, µg/L
26	192 1210	0.435	6.83*
16	192 2000	0.177	2.14*
10	193 1800	0.085	0.46
24	198 0015	0.085	0.46
18	200 1700B	0.086	0.48

* Indicates possible contamination

Average SEM concentrations in the composite samples ranged from 0.13 to 6.99 µmol/g for Cu, 0.08 to 1.65 µmol/g for Pb, and 0.44 to 8.08 µmol/g for Zn (table 7). The levels of composite SEM concentrations were in the order of 5b > 2a > 2b > 5a > 3a (figure 9). Only station 3a had higher SEM than AVS (figure 9, table 7). The concentrations of SEM were higher than those of bulk sediment metals at stations 1a, 2b, and 5b for Cu, Pb, and Zn, at stations 4b for Pb and Zn, at station 1b for Pb, and at station 3b for Zn (table 9).

The concentrations of SEM measured in composite (0–10 cm) and surface (0–2 cm) samples were predominantly Zn and Cn (figures 9 and 10). Surface SEM concentrations were higher than composite SEM concentrations at stations 1a, 3a, 4a, 4b, and 5a (table 7). Except for some variations detected at stations 5a and 5b, the SEM Cu concentrations determined for the core profiles showed that copper was uniformly distributed to a depth of about 20 cm (figure 11).

The ratio between SEM concentrations of Cu, Pb, and Zn and the AVS showed that AVS was in excess of metals at all the stations, except for the surface sample at station 1a, and the composite sample from station 3a (figure 12). When the bulk metal concentrations were compared to the average AVS from composite samples, only stations 1a, 3a, and 3b were found to have higher metal than AVS concentrations (figure 13).

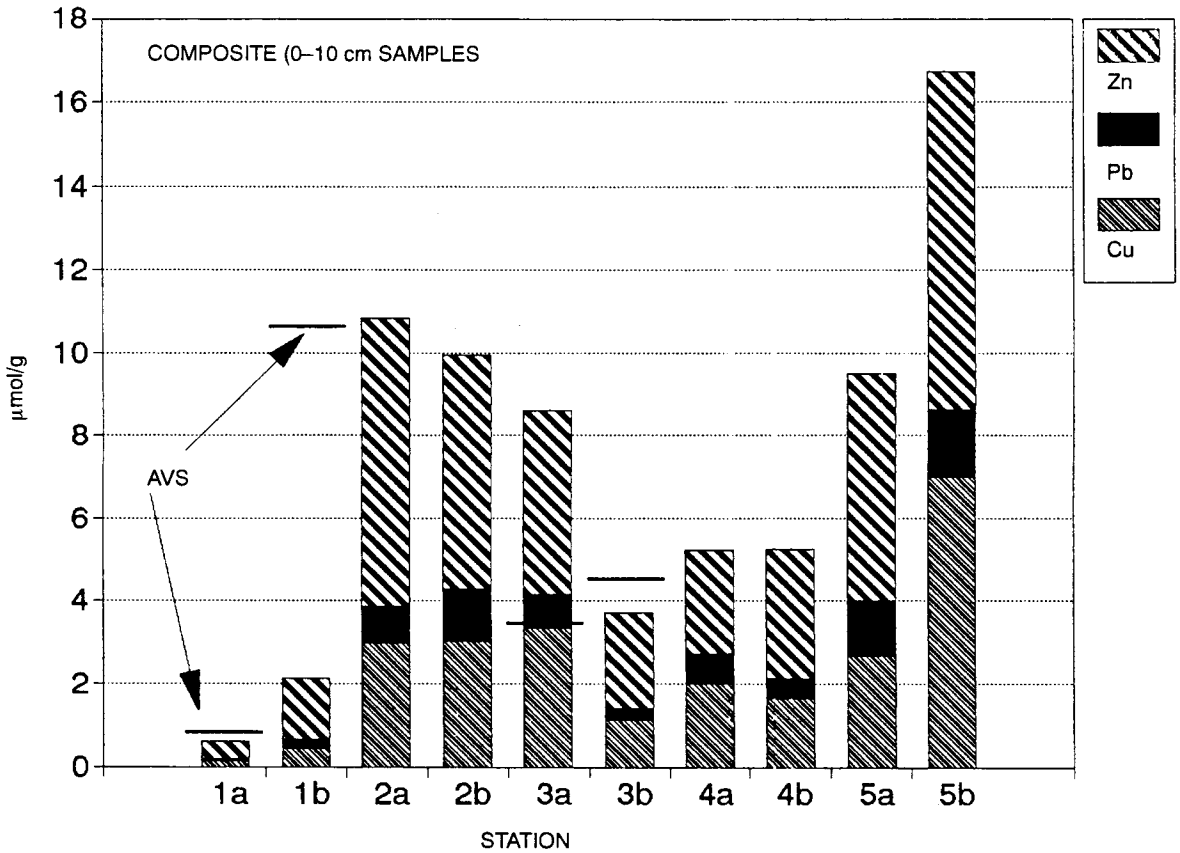


Figure 9. SEM concentrations of Cu, Pb, and Zn measured in composite (0–10 cm) samples. Levels of AVS for stations with AVS less than 18 µmol/g are also indicated.

Table 9. Ratios of SEM to bulk metal concentrations (BFSD metals). The ratio of SEM measured in 0–10-cm composite samples to bulk metal concentrations measured at the same stations ([SEM]/[BFSD metal]) are calculated for Cu, Pb, and Zn.

Station	Cu	Pb	Zn
1a	1.62	1.60	1.10
1b	0.71	1.33	0.73
2a	0.98	0.56	0.16
2b	1.42	4.50	8.61
3a	0.59	0.51	0.83
3b	0.58	0.78	1.21
4a	0.54	0.55	0.07
4b	0.82	1.25	1.85
5a	0.66	0.74	0.39
5b	1.73	2.06	1.93

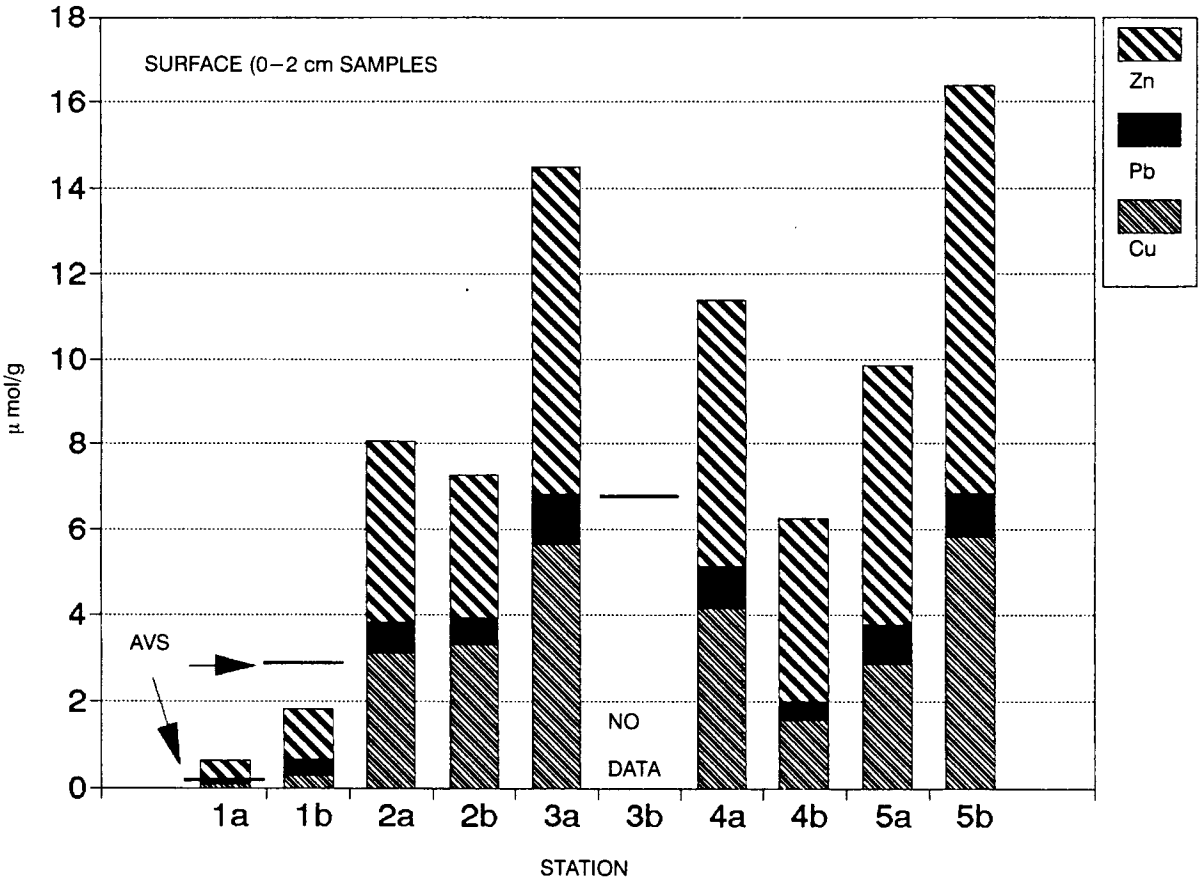


Figure 10. SEM concentrations of Cu, Pb, and Zn measured in surface (0–2 cm) samples. Level of AVS for those stations with AVS less than 18 μmol/g are indicated.

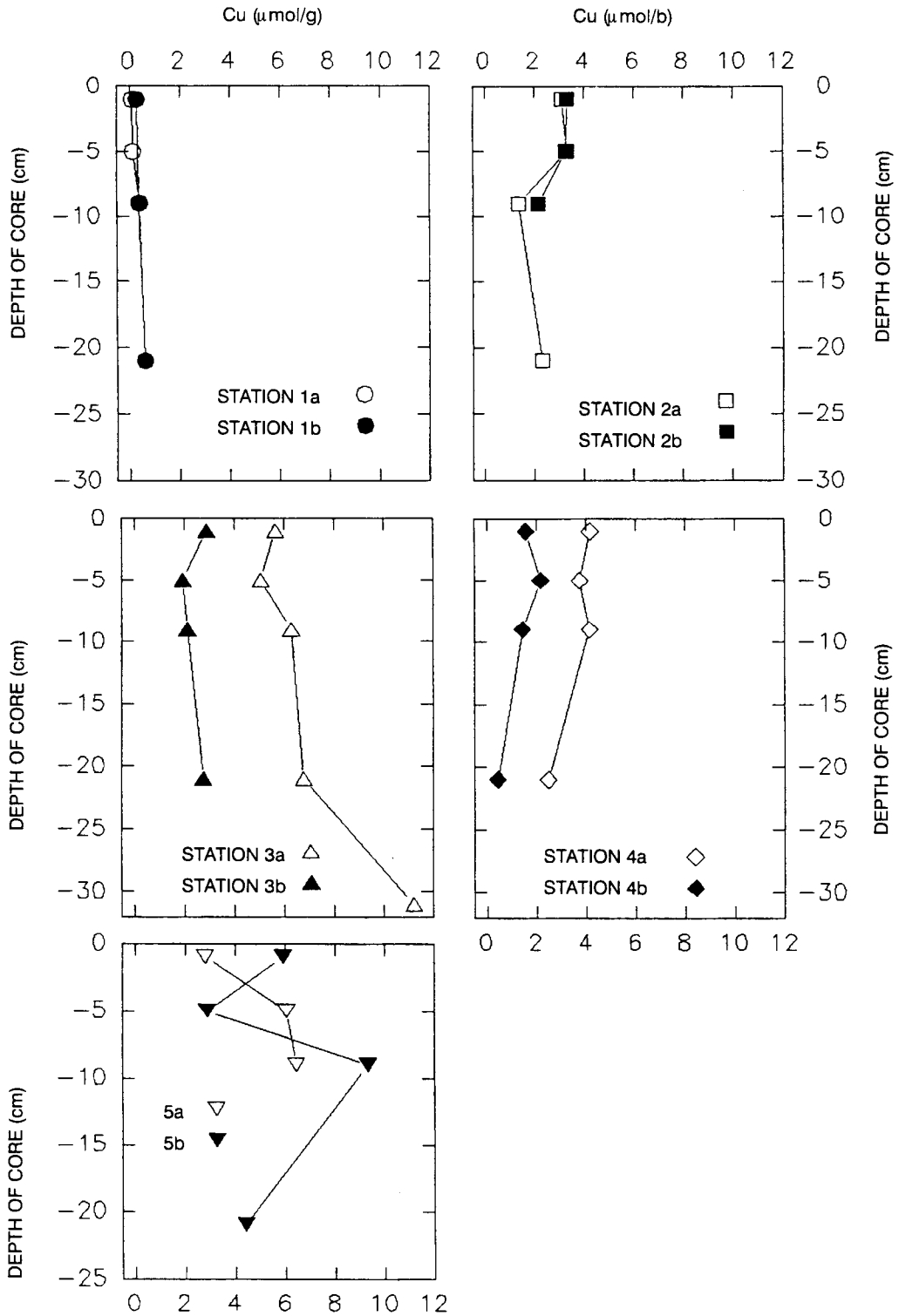


Figure 11. Depth profiles of SEM copper concentrations.

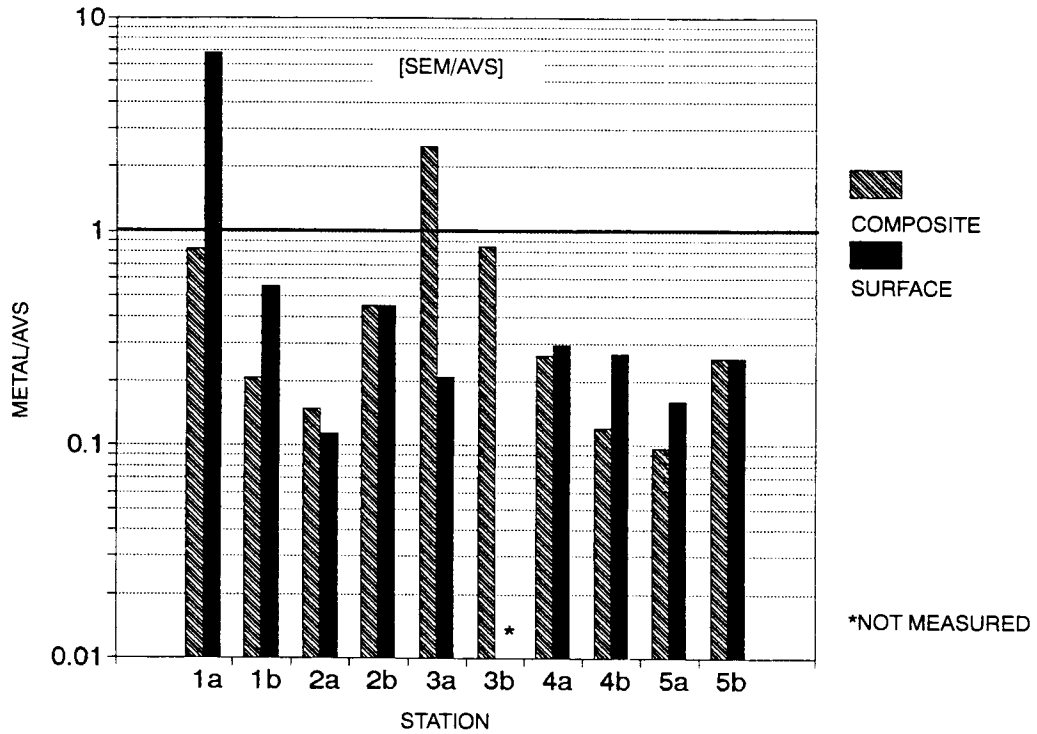


Figure 12. Ratio of SEM (Cu + Pb + Zn) to AVS for surface (0–2 cm) and composite (0–10 cm) samples.

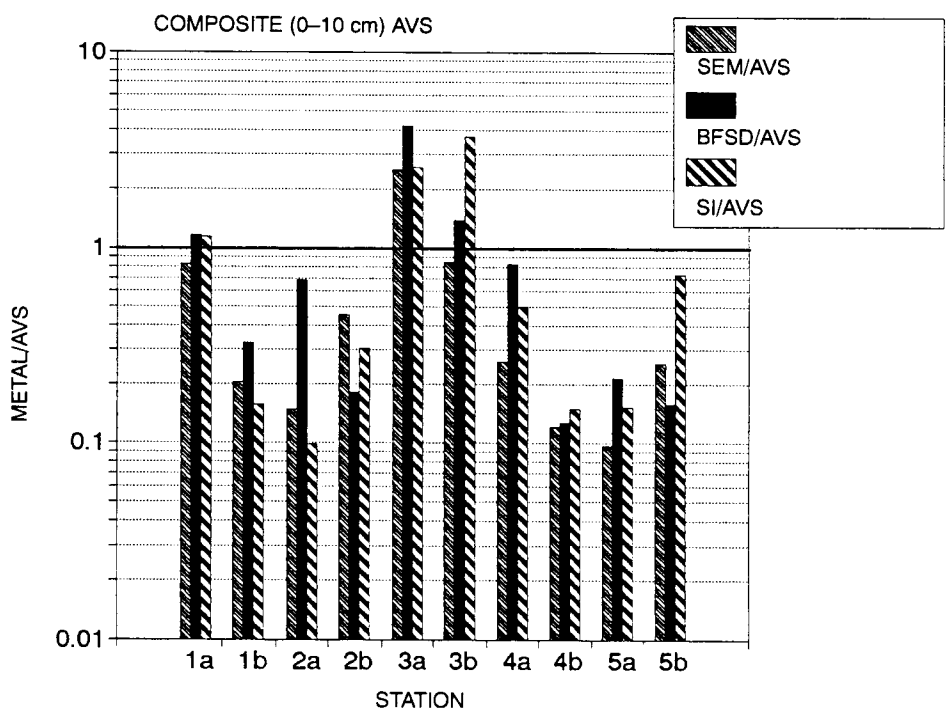


Figure 13. Ratio of metal to composite (0–10 cm) AVS for SEM and bulk sediment metal concentrations measured during benthic chamber deployments (BFSD Metals, Chadwick et al., 1992) and the site investigation (SI Metals, URS Consultants, Inc., 1992).

The relationship between AVS and metal contamination in the inlet is shown by figure 14. The majority of stations, especially those with metal contamination levels greater than 10 µmol/g, had AVS concentrations in excess of metal concentrations. Stations 1a, 3a, and 3b had metal concentrations in excess of AVS concentrations. Of these stations, only station 3a had SEM concentrations high enough to place it in the range of increasing toxicity (METAL/AVS) > 1.5. Borderline stations such as 1a and 1b, which were near the range of metals in excess, had relatively low metal concentrations.

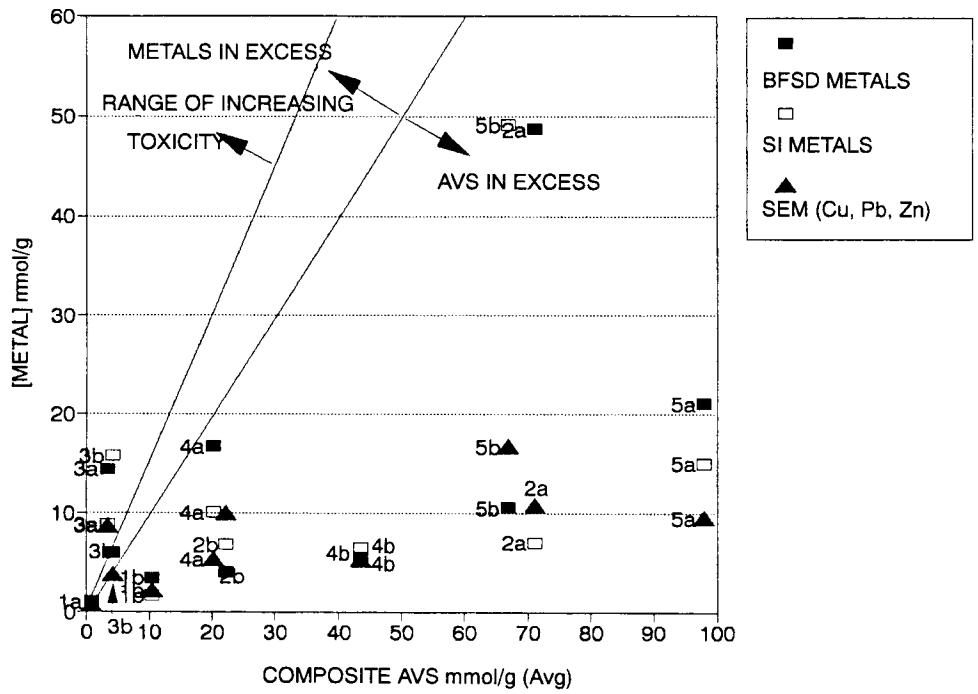


Figure 14. Relationship between metal contamination and AVS measured at the stations in Sinclair Inlet. The distribution is shown for the average AVS measured in composites samples versus the SEM and bulk sediment metal concentrations. The ratio [metal]:[AVS] = 1.5 is shown to denote the range of increasing toxicity.

The fraction of organic matter determined for the sediment samples ranged from 0.01 (station 1a) to 0.17 (station 2a) (see Appendix D for determinations of organic matter content). Organic matter levels greater than 10% were measured in surface samples from stations 2a, 2b, 4a, 4b, 5a, and 5b (figure 15). The regression between the fraction of organic matter (F_{om}) and AVS was significant (probability $p < 0.05$) for all data (table 10, figure 16). Additionally, AVS concentrations were best predicted using the transformed (logarithm base 10) surface F_{om} data (table 10, figure 17).

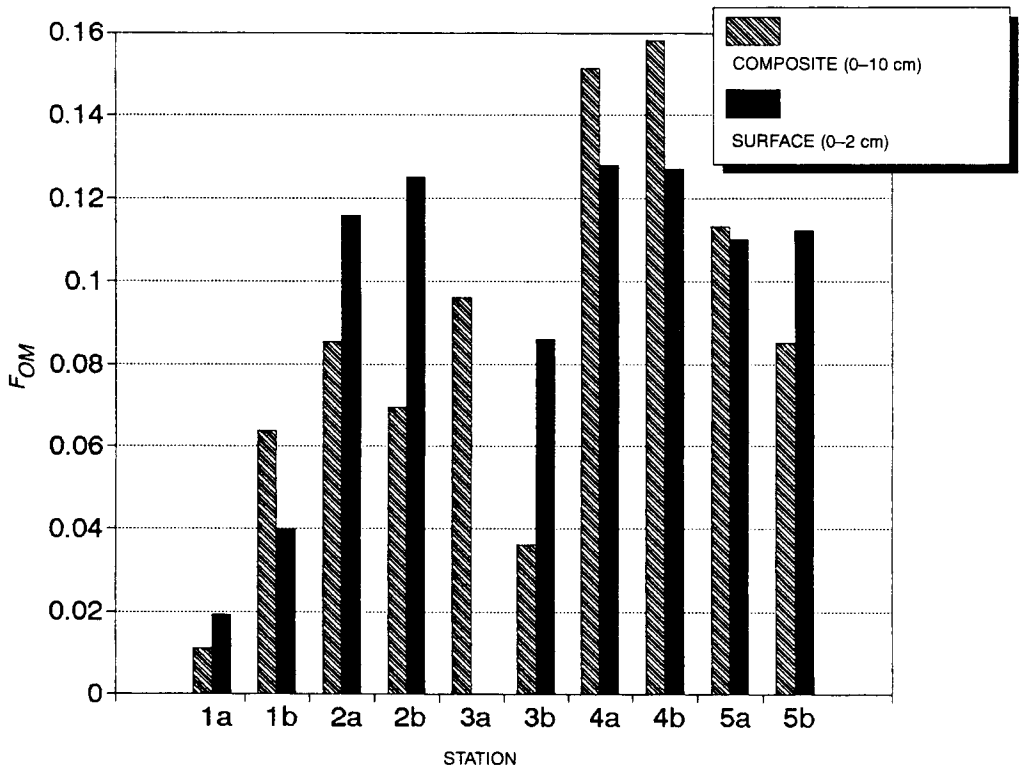


Figure 15. The fraction of organic matter (F_{om}) measured in composite (0–10 cm) and surface samples (0–2 cm).

The F_{om}, AVS, and SEM/AVS data were not capable of predicting the flux rates obtained from the benthic chamber (table 10B). The flux rates of Ni, Cu, Pb, and Zn seemed to be independent of F_{om} (figure 18), AVS (figure 19), SEM/AVS (figures 20 and 21), and BFSD/AVS (figure 22). The regressions between SEM Cu concentrations and Cu flux rates were significant ($p \leq 0.05$) for both the surface and composite data (table 10). A summary of the divalent metal flux rates (Chadwick et al., 1992), organic matter content, AVS concentrations, and ratios of bulk metals and SEM to AVS measured in the Inlet is presented in table 11.

Table 10. Results of regression analysis.

(**A**) Regression between F_{om} and AVS

Independent Variable	Dependent Variable	p	Equation	r^2
All Data:				
F_{om}	AVS	0.0007	AVS = 628.7 (F_{om}) − 6.9	0.23
F_{om}	Log (AVS)	<0.0001	Log (AVS) 14.7 (F_{om}) − 0.07	0.51
Surface (0–2cm):				
F_{om}	AVS	0.03	AVS = 523.4 (F_{om}) − 13.9	0.53
F_{om}	Log (AVS)	0.0004	Log (AVS) = 21.2 (F_{om}) − 0.9	0.85

(**B**) Regression between F_{om}, AVS, SEM/AVS, Cu_{SEM}, Zn_{SEM} and flux rates

Independent Variable	Dependent Variable	p	Equation	r^2
Surface (0–2 cm)				
F_{om}	Sum Flux	0.47		0.07
AVS	Sum Flux	0.20		0.22
SEM/AVS	Sum Flux	0.11		0.35
SEM/AVS	Zn Flux	0.16		0.30
SEM/AVS	Cu Flux	0.34		0.15
Cu_{SEM}	Cu Flux	0.05	Cu Flux = 1.1 (Cu_{SEM}) − 2.2	0.44
Zn_{SEM}	Zn Flux	0.25		0.16
Composite (0–10 cm)				
F_{om}	Sum Flux	0.24		0.16
AVS	Sum Flux	0.08		0.32
SEM/AVS	Sum Flux	0.97		<.01
BFSD/AVS	Sum Flux	0.99		<.01
Cu_{SEM}	Cu Flux	0.03	Cu Flux = 1.4 (Cu_{SEM}) − 3.0	0.47
Zn_{SEM}	Zn Flux	0.25		0.16

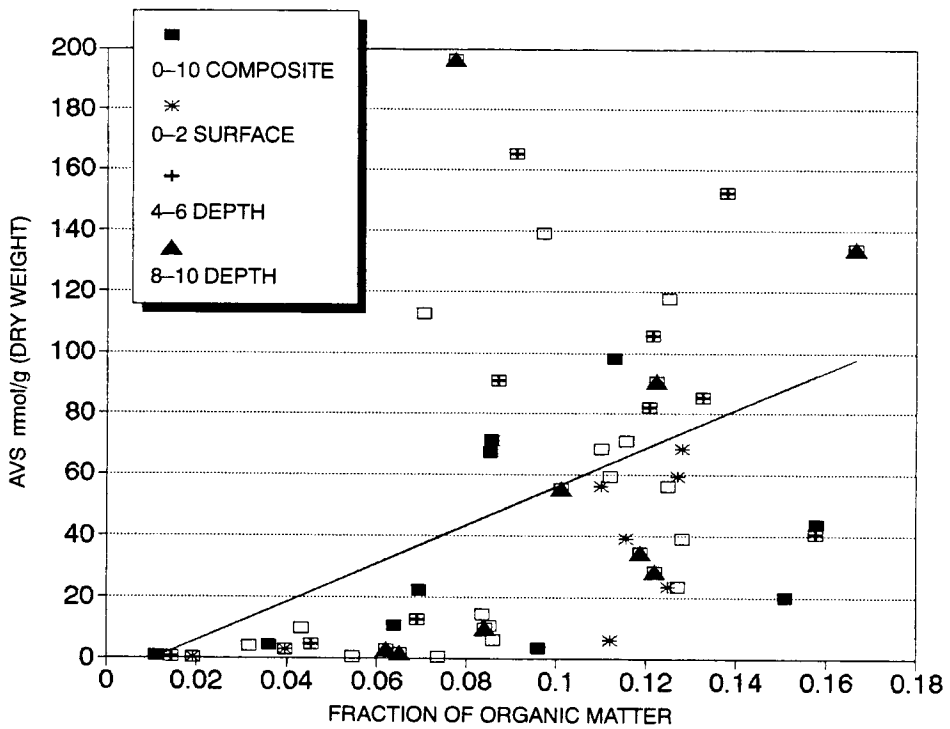


Figure 16. Relationship between organic matter and AVS of sediment samples from Sinclair Inlet. AVS = 628.7 (F_{om}) – 6.9, r^2 = 0.23.

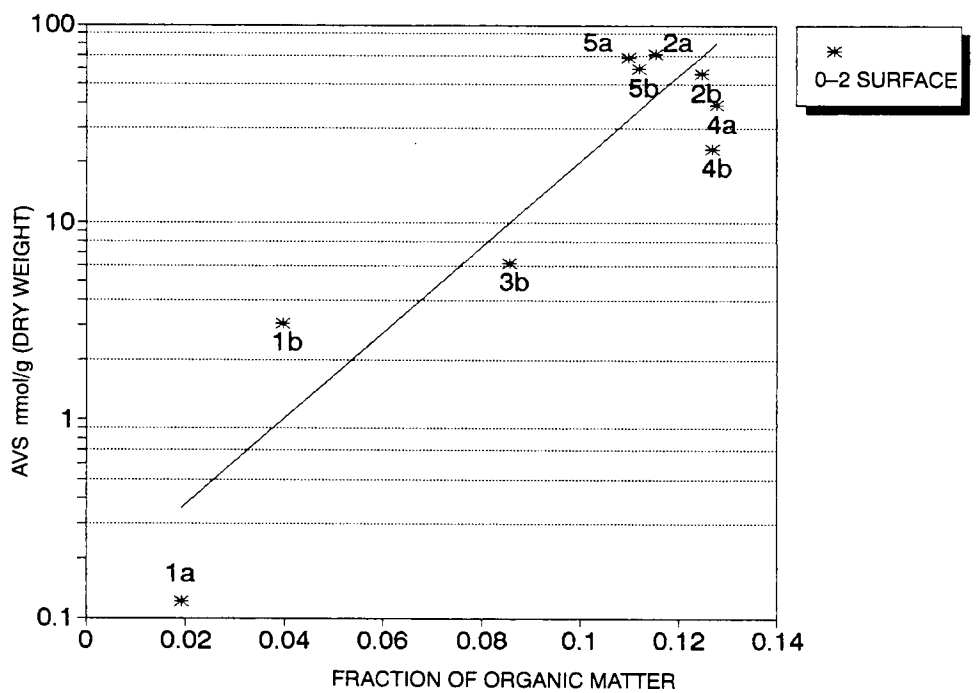


Figure 17. Relationship obtained for organic matter and log-transformed AVS concentrations measured in surface (0–2 cm) sediment samples. Log (AVS) = 21.2 (F_{om}) – 0.9, r^2 = 0.85.

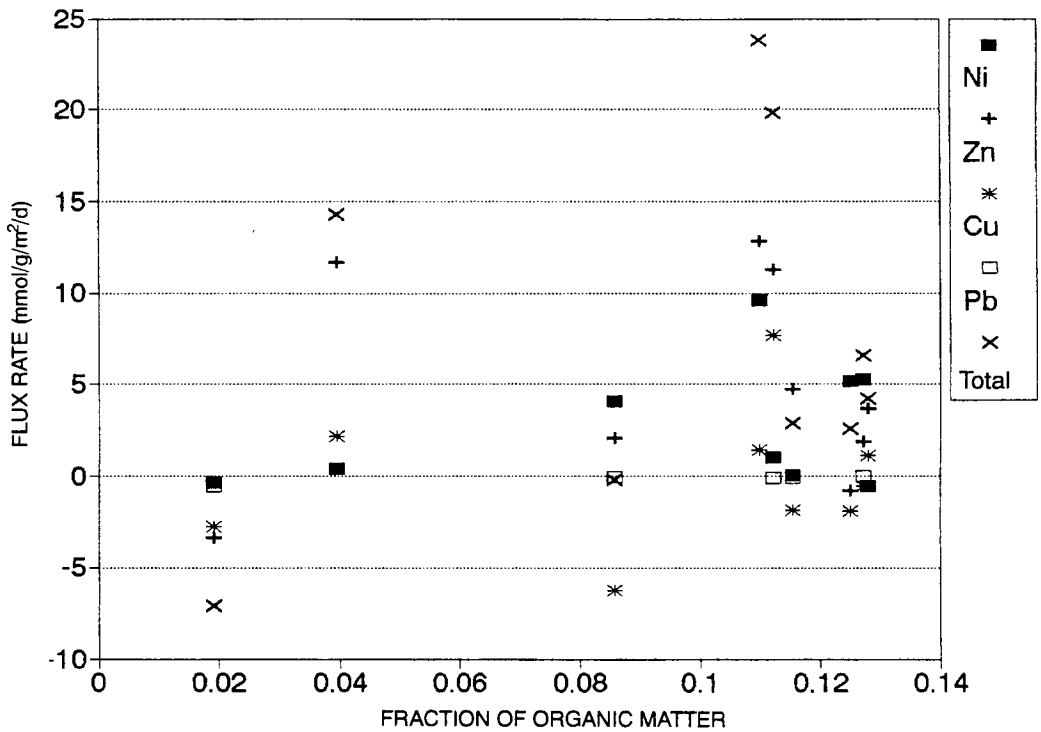


Figure 18. The relationship between F_{om} measured in surface sediment samples (0–2 cm) and metal flux rates obtained from the benthic flux chamber.

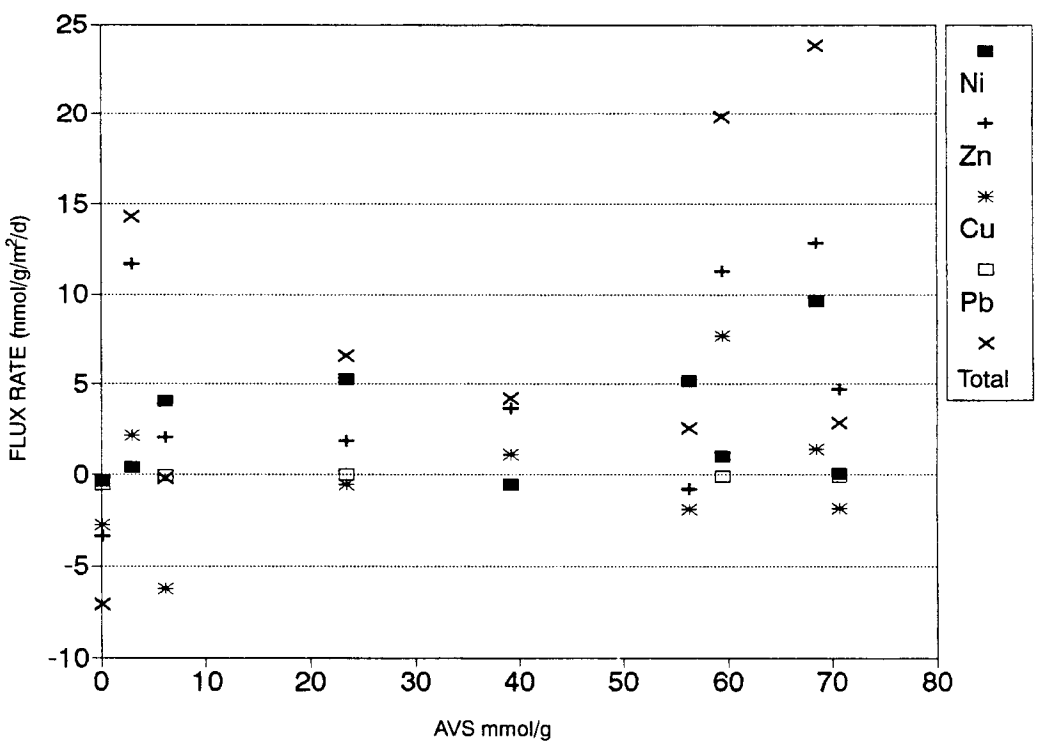


Figure 19. Relationship between AVS measured in surface sediment samples (0–2 cm) and metal flux rates obtained from the benthic chamber.

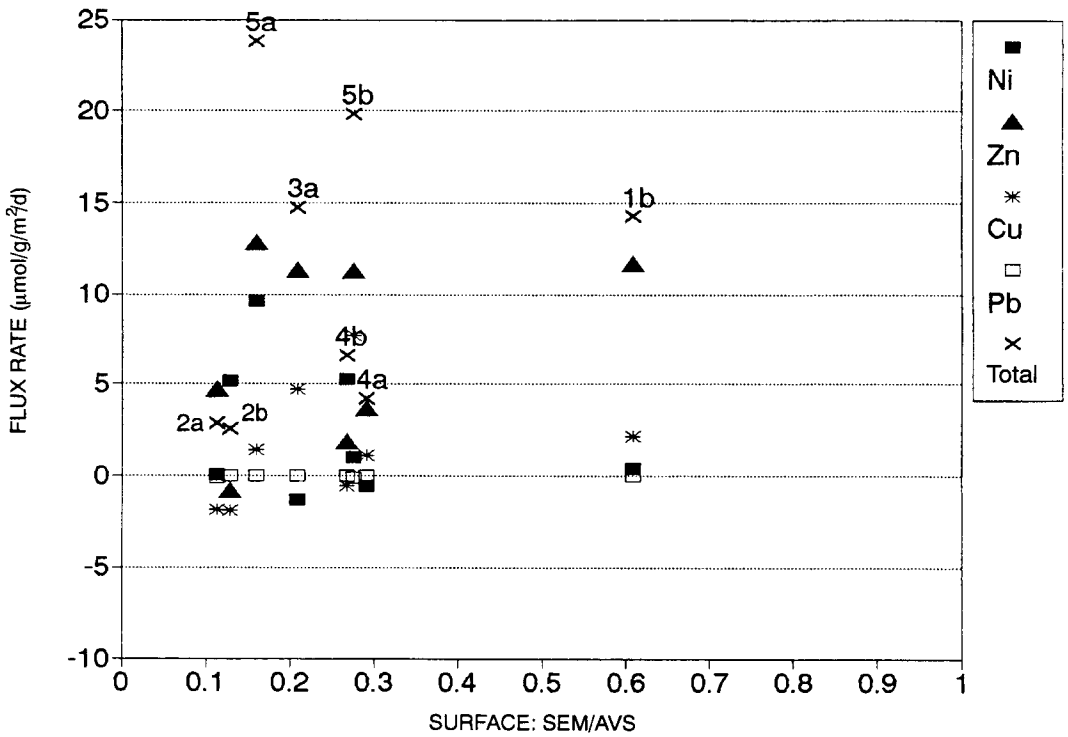


Figure 20. The relationship between ratio of SEM to AVS measured in surface sediment samples (0–2 cm) and metal flux rates.

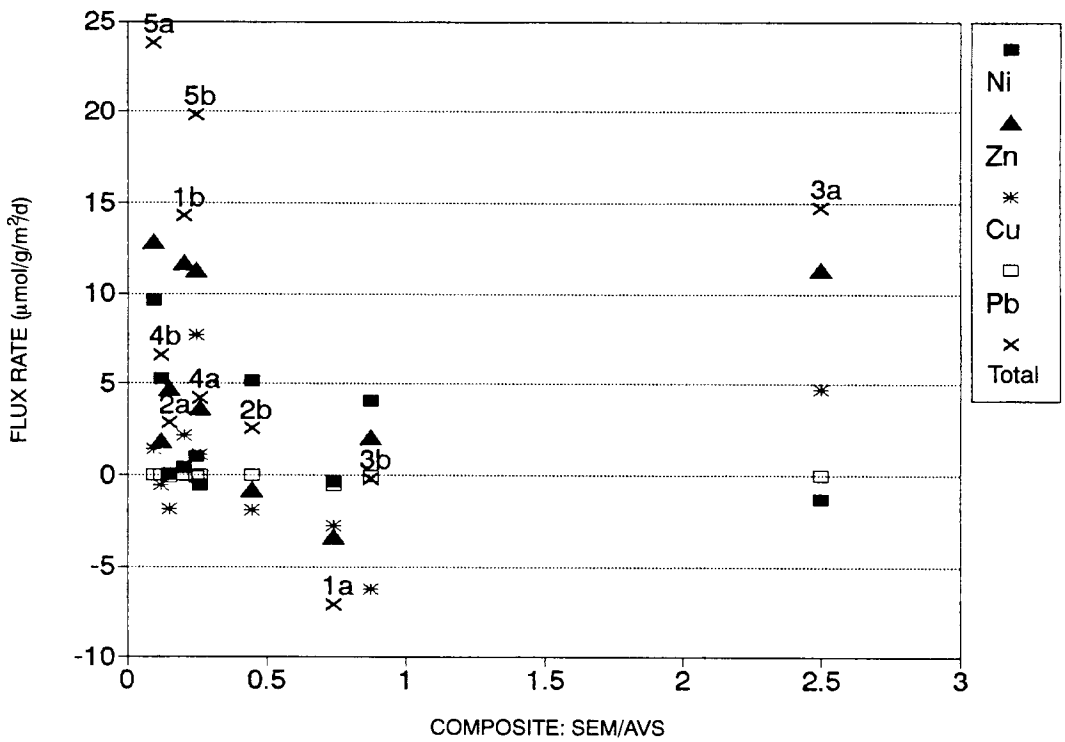


Figure 21. The relationship between the ratio of SEM to AVS measured in composite sediment samples (0–10 cm) and metal flux rates.

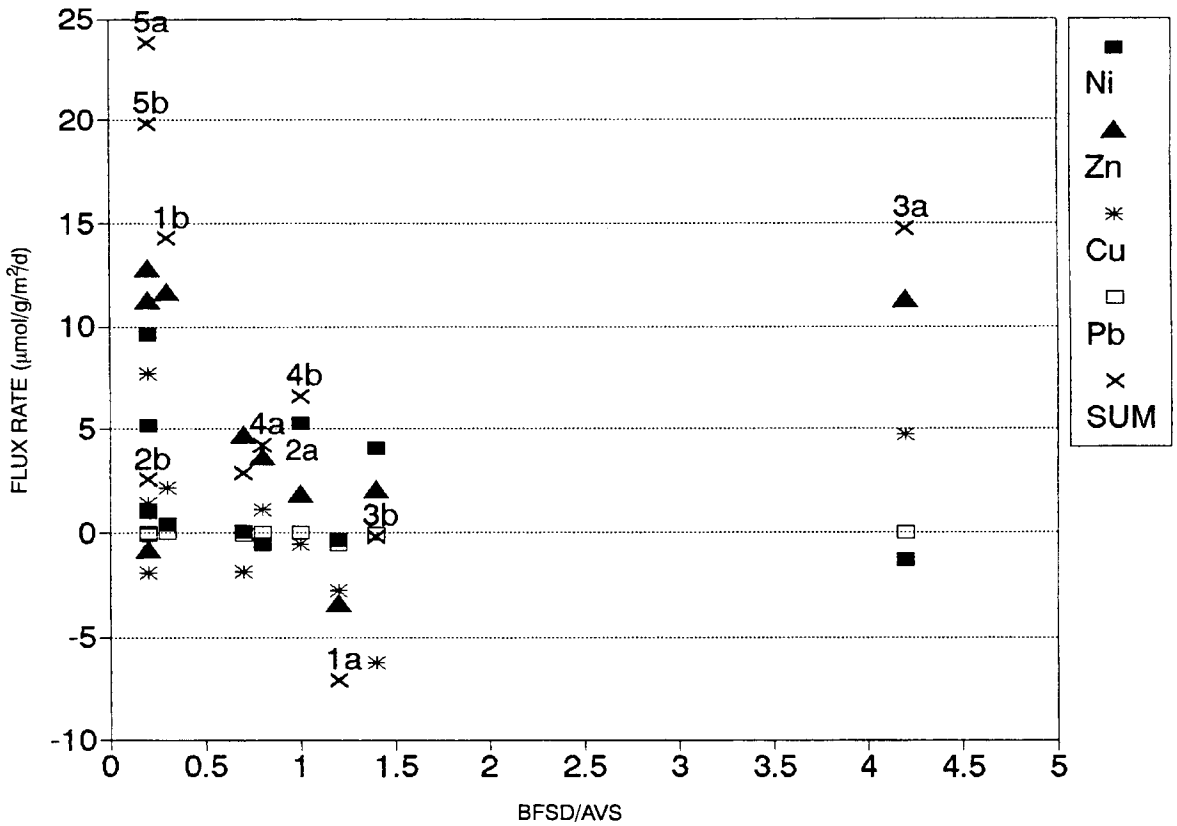


Figure 22. The relationship between the ratio of bulk divalent metal concentrations and AVS measured in composite (0–10 cm) sediment samples and metal flux rates.

Table 11. Summary of benthic flux measurements obtained for Ni, Zn, Cu, and Pb (from Chadwick et al., 1992), and composite (0–10 cm, Comp.) and surface (0–2 cm, Surf.) levels of F_{om}, AVS, bulk metals to AVS (BFSD/AVS), and SEM to AVS (SEM/AVS).

	Fluxes µmol m^{-2} d^{-1}				F_{om}		AVS (µmol/g)		BFSD/AVS	SEM/AVS	
Station	Ni	Zn	Cu	Pb	Comp.	Surf.	Comp.	Surf.	Comp.	Comp.	Surf.
1a	-0.4	-3.4	-2.8	-0.6	0.01	0.02	0.9	0.1	1.2	0.7	5.7
1b	0.4	11.7	2.2		0.06	0.04	10.5	3.1	0.3	0.2	0.6
2a	0.1	4.7*	-1.8	-0.1	0.09	0.12	71.3	70.8	0.7	0.2	0.1
2b	5.2*	-0.8	-1.9		0.70	0.13	22.1	56.3	0.2	0.5	0.1
3a	-1.3	11.3*	4.7*		0.10		3.5	69.3	4.2	2.5	0.2
3b	4.1*	2.0	-6.2	-0.1	0.04	0.09	4.3	6.2	1.4	0.9	
4a	-0.5	3.7	1.1		0.15	0.13	20.1	39.1	0.8	0.3	0.3
4b	5.2*	1.9	-0.6	0.0	0.16	0.13	43.7	23.4	0.1	0.1	0.3
5a	9.6*	12.8*	1.4		0.11	0.11	98.0	61.4	0.2	0.1	0.1
5b	1.0	11.2*	7.7	-0.1	0.09	0.11	67.0	59.5	0.2	0.3	0.3
Average for Inlet	2.3	5.5	0.4	-0.2	0.09	0.10	34.1	38.9	0.9	0.6	0.9

* Indicates statistically significant release (Chadwick et al., 1992).

DISCUSSION

The benthic flux stations were selected to provide a representative sample of contamination levels in Sinclair Inlet (Chadwick and Lieberman, 1991). The station groups were selected based on the weight of metal contamination levels (μg/g). A somewhat different distribution is obtained when the contamination levels are displayed on a molar concentration basis (μmol/g) (table 1). The molar concentration has more relevance when assessing the importance of AVS interaction to the availability and flux of metals.

The proximity of the stations (figure 1) and the wide variation in contamination levels and AVS concentrations (table 1, figure 4) indicate that the Inlet sediments are highly variable and heterogeneous. Another example of the spatial variability of the Inlet sediments is seen in the dry:wet ratio measured for the sediments (table 6). Differences in water content of the sediment cores are indicative of different depositional environments. The presence of numerous bulkheads, piers, and pilings in and around the shipyard and their interaction with tidal currents and eddy patterns can create vastly different sedimentation regimes at stations only 20 to 30 meters apart (Håkanson, 1992). The sampling regime used to evaluate the AVS distribution (two cores per station, one for a composite sample, one for profile samples) was used to obtain representative measures of AVS relative to the range of contamination levels present. The AVS data provided background information to evaluate the flux measurements.

The quality control data used to evaluate the accuracy and precision of the AVS measurements showed that the sampling method provided acceptable data. The sulfide electrode response was very stable and showed good linearity and repeatability for standard concentrations ranging from 2.9 to 1050 μM $S^{=}$. Very good precision was obtained for duplicate samples which spanned a wide range of AVS concentrations. The accuracy of the sampling method was also tested with spiked samples. Blank spike recoveries were within ± 5% of the spiked concentration. However, spiked sediment samples rarely resulted in better than ± 10% recovery of the spiked concentration. A problem with spiking sediments is that one is not always sure what the sediment AVS concentration was to which the spike was added. Since there is not much possibility of sulfide contamination during the AVS analysis, the biggest quality assurance concern is to assure that AVS is not lost during the analysis. It is possible that the free sulfide spike (made in DDIW) added to the sediment reacts with sediment monosulfides present, converting a portion of the sulfide into non-AVS forms (Morse et al., 1987; Berner, 1970). Underestimates of AVS due to interferences caused by elemental sulphur, produced by reactions between ferric iron and sulfide, have been reported in the literature (Morse et al., 1987). This interference would not occur in the spiked blanks because no sediment is present. The reaction between the sulfide in the spike and the monosulfides in the sediments would have to occur during the initial purge step (nominally 10 minutes) before the sample is acidified to release the AVS. Similar problems with spiked sediment recoveries have been encountered by other workers (W. Boothman, EPA ERLN, personal communication; Boothman and Helmstetter, 1992).

A wide range of AVS was measured from the different stations. Clearly stations 5a and 5b had the highest AVS (figures 4 and 5) and stations 1a, 1b, and 3a had the lowest. The low AVS at stations 1a and 1b may be explained by the sandy and what appeared to be well-oxygenated sediments sampled at those locations. Stations 1a and 1b were closer to the Sound and subject to more mixing (figure 1). The high AVS measured at the other stations around the shipyard indicates that the anoxic sediments favored the formation of sulfides. Station 3b was an anomaly.

Oxygen microprofiles obtained from station 3b showed that the aerobic sediments extended down to about 0.5 cm, which was the deepest aerobic layer obtained from the four oxygen microprofiles measured (stations 2b, 3b, 4a, and 5b) (Chadwick et al., 1992). Oxygenated sediments at depth could account for the low AVS measured from the cores collected at station 3b.

The differences between the composite AVS and the mean profile AVS (figure 4) may be due to the variability in the sediment samples. Dry to wet ratios (R) obtained for composites were similar to the average R of the profile samples, suggesting that the composite samples were well homogenized. It appears that homogenizing the core has the effect of reducing AVS, because the higher AVS material at the intermediate core depth (4–6 cm) is diluted by the lower AVS material at the surface and deeper in the core (figure 5).

The core profiles, which showed higher AVS at intermediate depths, are indicative of the sulphur chemistry in sediments. The major processes which control the form and abundance of sulphur in anoxic sediments include (1) the reduction of sulfate to sulfide, (2) the reaction of sulfides with iron (and other metals) to form monosulfides, and (3) the reaction between the monosulfides and elemental sulphur to form pyrite (Morse et al., 1987). The rate of these reactions will be controlled by the amount of organic matter and bacteria available to reduce sulphate, the rate of diffusion of sulphate from the overlying water into the sediment, the concentration and activity of metals (mainly iron), and the evolution of elemental sulphur (Morse et al., 1987). The core profiles from Sinclair Inlet trace the time course of the above reactions. At the surface, AVS is relatively high, because of the rapid and sharp decline of oxygen measured in the first few millemeters of sediment, the high amount of organic matter present, and a readily available source of sulphate in the bottom water of the inlet (Chadwick et al., 1992). The high water content of the surface sediment suggests that the diffusion of sulphate into the sediment is not impeded. The AVS maximum, measured at a 4–6–cm depth in most of the cores, reflects the optimal formation of reactive monosulfides. The decrease in AVS toward the bottom of the core suggests that more sulfide is tied up in less reactive polysulfide and mineral sulfide (pyrite) forms (Morse et al., 1987; Cornwell and Morse, 1987). These profiles are comparable to AVS core profiles commonly measured from a variety of marine environments (Di Toro et al., 1990; Boothman and Helmstetter, 1992).

The relationship of toxic metal contamination to AVS was provided by the analysis of SEM concentrations of Cu, Pb, and Zn. These three metals accounted for about 70–90% of the total toxic metals present at stations in the Inlet (table 1). Since the monosulfides formed by CuS, PbS, and ZnS have lower solubility products (K_{sp}) than FeS (Di Toro et al., 1990), they are associated with the reactive pool of AVS. After Fe, Ni and Zn would be metals most likely to be released (Di Toro et al., 1992), because the K_{sp} of these sulfides are higher than those for the other compounds (e.g., the K_{sp} of MnS > FeS > NiS > ZnS > CdS > PbS > CuS > HgS (Di Toro et al., 1990)).

Copper, which was one of the more abundant contaminants, was also measured in the core profile samples to provide information on the relative distribution of the metal in the top 30 cm of the sediments sampled. If Cu can be considered as a tracer of metal contamination (i.e., Cu has the same source and is involved in the same depositional processes as the other metals), then it appears that the metal concentrations are fairly uniform in the top 20 to 30 cm of the sediment. This could be an indication of constant loading over time, or evidence that the sediments have been reworked by bioturbation, prop wash, diffusion, etc.

The method used for GFAA Cu analysis provided very good sensitivity for the range of Cu concentrations measured during this study. The method used was developed as part of an extensive program to evaluate the leaching rates of copper from bottom paints and was optimally suited for measuring relatively high Cu concentrations in a seawater-like matrix (Lindner and Caso, in preparation). The sensitivity obtained for the GFAA Pb analysis was much reduced, although the response was linear over the range of samples analyzed. The GFAA analysis of Zn was hampered by contamination problems (table 8) and a nonlinear response. The DIW standard curve, rather than the matrix standard addition curve, was used to calibrate Zn response because the DIW standard curve was linear over a greater concentration range (0 to 250 ppb). It was thought that this would provide a better method of comparing the relative Zn levels observed at the stations. The methodology used requires further development to improve the accuracy of the Pb and Zn analysis.

Since it was not possible to obtain an accurate and comprehensive analysis of all the SEM concentrations, bulk sediment metal concentrations, determined from grab samples collected from the same stations (Chadwick et al., 1992; URS Consultants, Inc., 1990), were used as surrogates for SEM. This provides a much more conservative analysis of metal to AVS ratios because bulk sediment metal analysis uses a strong acid digestion step and therefore releases more tightly bound, and not biologically available, solid phase metals (Di Toro et al., 1990; Ankley et al., 1991; Di Toro et al., 1992). By normalizing the bulk sediment metals with the composite AVS, it is possible to evaluate the potential availability of toxic metal contamination in the Inlet.

The data presented here show that AVSs were very abundant and are available to react and bind with the toxic metals. Recent studies have shown that when the metal:AVS ratio is less than or equal to one, organisms are not sensitive to toxic metal exposure. Di Toro et al., (1990) showed that AVS normalization explained the observed metal toxicity to amphipods (*Ampelisca* sp., and *Rhepoxynius hudsoni*) exposed to sediment contaminated with Cd. The theoretical and technical basis of AVS-mediated toxicity, presented by Di Toro et al. (1990), has been supported by other studies. Ankley et al. (1991) reported that toxicity and bioaccumulation of Ni and Cd to the amphipod *Hyalella azteca* and oligochaete *Lumbriculus variegatus* were greatly reduced when the SEM:AVS ratio was less than one. Similarly, Carlson et al. (1991) showed that AVS reduces the toxicity and bioavailablity of metals in freshwater systems. Further work indicates that the SEM:AVS ratio may be used to predict the acute toxicity of metals in sediments (Di Toro et al. 1992) and can therefore be used to develop sediment quality criteria (Di Toro et al., 1991; Burton, 1992; Power and Chapman, 1992).

The levels of AVS measured in the sediments of Sinclair Inlet are very high and compare to the high end of values reported in the literature from field studies (table 12). The high AVS means that the sediments have a high buffering capacity, enabling toxic metals to be assimilated and detoxified (Di Toro et al., 1992; Burton, 1992). The AVS neutralizes the toxic metal activity in the aqueous and solid phases of the sediment (Di Toro et al., 1990), and therefore can be used determine the absolute metal toxicity to aquatic organisms when AVSs are present in sufficient quantities (e.g., SEM/AVS < 1) (Di Toro et al., 1992). However, AVS has been shown to vary seasonally, with the lowest concentrations measured during winter (Di Toro et al., 1990; Boothman and Helmstetter, 1992). As such, the July 1991 AVS measurements made for Sinclair Inlet should be viewed as probably being higher than the average yearly concentration. If the levels of AVS can be viewed as determining the boundary between low and high metal activity (Di Toro et al., 1992), the high level of AVS (many times higher than metal concentrations)

indicates that during this sampling period a very high metal assimilation capacity existed in the sediments of the Inlet.

There appeared to be no direct correlation between the flux rates measured for Ni, Zn, Cu, and Pb and the AVS measured in composite and surface samples, nor for the bulk sediment metal concentrations normalized by AVS (table 11). Chadwick et al. (1992) reported significant positive correlations between the bulk sediment concentrations of Cu and Zn and flux of Cu and Zn.

Table 12. Values of AVS reported from other field studies.

Location	Depth (cm)	AVS Range (μmol/g)	Source
Long Island Sound, NY	0–10	8.4 – 17.4	Di Toro et al., 1990
Sapelo Island	0–10	14.6 – 43.2	Di Toro et al., 1990
Lake Mendota, WI	0–10	8.7 – 112.0	Nriagu & Coker, 1976
Freshwater marsh, NY	grab	0.1 – 75.5	Ankley et al., 1992
Narragansett Bay, RI	grab	1.9 – 53.6	Johnston, unpublished
Black Rock Harbor, CT	—	175.0 ± 41.0	Di Toro et al., 1990
Hudson River, MU	—	12.6 ± 2.8	Di Toro et al., 1990
Pequaywan lake, MN	—	42.8 ± 8.0	Carlson et al., 1990
East River, WI	—	8.8 ± 1.4	Carlson et al., 1990
W. Bearskin Lake, MN	—	3.6 ± 1.6	Carlson et al., 1990
Lake Ontario, Canada	0–10	27.1	Nriagu, 1968
Pettaquamscutt Cove, RI	0–1	<5.0	Boothman & Helmstetter, 1992
Pettaquamscutt Cove, RI	2–5	15.0 – 35.0	Boothman & Helmstetter, 1992
Pettaquamscutt Cove, RI	6–15	10.0 – 15.0	Boothman & Helmstetter, 1992

The AVS data alone do not explain the observed flux rates; however, the AVS analysis does provide some indications of the metal availability in the sediment. The flux chamber measured the in situ interaction between the sediment surface and bottom water. Independent measurements of dissolved oxygen and $S^{=}$ showed steep gradients in the top 0.5 cm of sediment (Chadwick et al., 1992). Therefore, it would be necessary to measure AVS in the top 0 to 0.5 cm, or at most 0 to 1.0 cm, in order to compare AVS more directly to the flux measured by the benthic chamber. In this sense, the AVS measured in the deeper sediment and in composite samples may relate more to the long-term availability and in-place toxicity of the sediments than to the instantaneous metal flux measured at a particular point in time by the benthic chamber. Another factor could be that the flux rates are governed by the redox potential at the sediment interface, which is controlled by the dissolved O_2 concentration (Riley and Chester, 1971), rather than AVS reactions. The sharp dissolved O_2 gradient in the very surface of the sediment suggests that O_2 diffusion rates are high and are probably independent of AVS processes. In addition, the variability factor (discussed above) could result in vastly different sediment conditions (e.g., AVS and metal flux) over relatively short distances at the same sampling sites.

The AVS and flux rate measurements do indicate certain trends in the metal availability and toxicity in the sediments. The very low AVS measured at station 1a suggests that other processes are controlling the metal distribution. The excess metal concentrations measured at stations 3a and 3b (figure 14) are consistent with statistically significant release rates at stations 3a (Zn, and Cu) and 3b (Ni) (table 11). Station 4a, which was on the borderline of excess metals, also showed a statistically significant release of Ni (table 11). Stations 5a and 5b clearly had excessive levels of AVS present (table 5), yet significant release rates were measured (table 11). These were the most contaminated stations, and the increased flux signal may be more related to diffusion in pore water and other non-AVS metal species.

A wide variety of factors will influence metal mobility and availability. Chemical reactions, including cation exchange, oxidation reduction, acid-base reactions, and interaction with organic complexing agents; biological transformations mediated by benthic micro- and macroorganisms; and physical advection, diffusion, and convection mechanisms will affect the availability and flux of metals from the sediment (Burgess and Scott, 1992). If the ten Sinclair Inlet stations are taken as replicate measures of sediment conditions in the Inlet, the average release rates and AVS concentrations can be evaluated (table 11). On average, Ni and Zn had the highest flux rates, which is consistent with the predicted release based on sulfide solubility (Di Toro et al., 1990; Di Toro et al., 1992; Chadwick et al., 1992). The average AVSs measured for composite and surface samples are comparable to the high range of AVS reported in the literature (table 12). The conservative estimate of bulk/AVS results in the ratio of 0.9 and SEM/AVS (without the Ni contribution to SEM) results in a ratio of about 0.5 to 0.9. While the conservative estimate indcates that the metal/AVS ratio is nearing the toxic threshold (figure 14), it assumes that all the metals are available. A more reasonable conclusion is that the "real" metal/AVS ratio lies somewhere between the two and that, on average, the AVS pool is sufficient to reduce the mobility and toxicity of the metals present (table 11).

It should also be noted that the results reported here are only a snapshot in time. Other workers have reported large seasonal variations in sediment AVS concentrations (Di Toro et al., 1990; Schubauer-Berigan, 1992; Boothman and Helmstetter, 1992). Not enough information is yet known about the AVS dynamics in sediments. However, these results show that AVS production in the Inlet is very high and that AVSs are abundant in most of the cores analyzed.

Finally, because the high concentrations of sulfides indicate the anoxic nature of the sediments, the metals will most likely reside in a reduced state. As cleanup efforts in the Inlet proceed, the sediments should be monitored. As water quality increases and high loads of organic matter (biological oxygen demand) are reduced, benthic organisms may invade the bottom of the Inlet and begin to colonize and rework the sediments. This will cause the sediments to become aerobic, destroying the AVS and allowing the metals to oxidize and become more mobile. In any case, there will be a large pool of anoxic sediments and AVS in the Inlet for some time. Even as the upper sediments are reworked and oxidized, the large concentration of AVS at depth will act as a sink (or source) for dissolved metals as they diffuse through the sediment, possibly resulting in a reduction of metal availability in the aerobic layer (Di Toro et al., 1992). The impact to the environment will depend on the rate this occurs and on other mediating factors. Future exposure scenarios should be considered as part of any long-term management plan for Sinclair Inlet.

CONCLUSIONS

The analytical method used to measure AVS in sediments from Sinclair Inlet was able to provide accurate measurements of the reactive sulfide in the sediment cores. The rapid turnaround between sample collection and sample analysis (less than a day for most of the samples) assured a minimum of change in the sediments before they were analyzed.

High concentrations of AVS measured in the sediments for Sinclair Inlet suggest that most of the divalent metals are bound up as nonavailable and nonmobile sulfides.

The core profiles from Sinclair Inlet trace the time course of sulfide geochemistry. At the surface, AVS is relatively high, due to the rapid and sharp decline of oxygen measured in the first few millimeters of sediment, the high amount of organic matter present, and a readily available source of sulphate in the bottom water of the Inlet. The AVS maximum, measured at a 4–6–cm depth in most of the cores, reflects the optimal formation of reactive monosulfides. The decrease in AVS toward the bottom of the core suggests that more sulfide is tied up in less reactive polysulfide and mineral sulfide (pyrite) forms.

There was not a clear relationship between AVS and metal flux measured with the benthic chamber, although a trend of higher flux rates was observed for metals with lower sulfide solubility (Ni and Zn).

The results reported here are only a snapshot in time and do not take into consideration seasonal changes of AVS. Not enough information is yet known about the AVS dynamics in sediments. However, these results show that AVS production in the Inlet is very high.

High concentrations of sulfide indicate the anoxic nature of the sediments, meaning that most metals will reside in a reduced state. As cleanup efforts in the Inlet proceed, the sediments should be monitored. As water quality increases and high loads of organic matter (biological oxygen demand) are reduced, benthic organisms may invade the bottom of the Inlet and begin to colonize and rework the sediments. This will cause the sediments to become aerobic, destroying AVS and oxidizing metals, making them more mobile. The impact to the environment will depend on the rate this occurs and on other mediating factors. Future exposure scenarios should be considered as part of any long-term management plan for Sinclair Inlet.

REFERENCES

Allen, H. E., G. Fu, and B. Deng, 1993. "Analysis of acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediments" *Environmental Toxicology and Chemistry*, 12: pp 1441–1453.

Ankley, G. T., G. L. Phipps, E. N. Leonard, D. A. Benoit, V. R. Mattson, P. A. Kosian, A. M. Cotter, J. R. Dierkes, D. J. Hansen, and J. D. Mahoney, 1991. Acid volatile sulfide as a factor in mediating cadmium and nickel bioavailability in contaminated sediments," *Environmental Toxicology and Chemistry*, **10**: pp 1299–1307.

Berner, R. A., 1970. "Sedimentary pyrite formation," *Am. J. Sci.,* **268**: pp 1–23.

Boothman, W. S., and A. Helmstetter, 1992. "Vertical and seasonal variability of acid volatile sulfides in marine sediments", Environmental Monitoring and Assessment Program Research Project, Final Report. USEPA Environmental Research Laboratory Narragansett, Narragansett, RI, 33 pp.

Burgess, R.M., and K.J. Scott, 1992. "The significance of in-place contaminated marine sediments on the water column: processes and effects," in *Sediment Toxicity Assessment*, G. Allen Burton, Jr., ed, pp 129–165, Lewis Publishers, Chelsea, MI.

Burton, G. A., Jr., 1992. "Sediment collection and processing: Factors affecting realism, in *Sediment Toxicity Assessment*, G. Allen Burton, Jr., ed, pp 19–35, Lewis Publishers, Chelsea, MI.

Carlson, A. R., G. L. Phipps, V. R. Mattson, P. A. Kosian, and A. M. Cotter. 1991. "The role of acid volatile sulfide in determining cadmium bioavailability and toxicity in freshwater sediments," E*nvironmental Toxicology and Chemistry*, **10**: pp 1309–1319.

Chadwick, D. B., and S. H. Lieberman. 1991. "Sampling and analysis plan: Evaluation of release of toxicant from contaminated sediments in Sinclair Inlet using the Benthic Flux Chamber," Naval Ocean Systems Center internal report, San Diego, CA.

Chadwick, D. B., S. H. Lieberman, C. E. Reimers, and D. Young, 1992. "An evaluation of contaminant flux rates from sediments of Sinclair Inlet, WA, using a benthic flux sampling device," Naval Command, Control and Ocean Surveillance Center, RDT&E Division Technical Document 2434, San Diego, CA. 186 pp .

Cornwell, J.C. and J.W. Morse. 1987. "The characterization of iron sulfide minerals in anoxic marine sediments," *Marine Chemistry,* **22**: pp 193–206.

Di Toro, D.M., C. Zarba, D. Hansen, W. Berry, R. Swartz, C. Cowan, S. Pavlou, H. Allen, N. Thomas, and P. Paquin. 1991. "Technical basis for establishing sediment quality criteria for nonionic organic chemicals by using equilibrium partitioning," *Environ. Toxicol. Chem.* **10**: pp 1541–1586.

Di Toro, D. M., J. D. Mahony, D. J. Hansen, K. J. Scott, A. R. Carlson, and G. T. Ankley. 1992. "Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments," *Environ. Sci. Technol*, **26**: pp 96–101.

Di Toro, D. M., J. D. Mahony, D. J. Hansen, K. J. Scott, M. B. Hicks, S. M. Mayr, and M. S. Redmond, 1990. "The toxicity of cadmium in sediments: The role of acid volatile sulfide," *Environmental Toxicology and Chemistry*, **9**: pp 1487–1502.

Goldhaber, M. B., and I.R. Kaplan. 1974. "The sulfur cycle," in *The Sea*, E.D. Goldberg, ed, Vol 5, pp 569–655, John Wiley and Sons, New York, NY.

Håkanson, L., 1992, "Sediment variability," in *Sediment Toxicity Assessment,* G. Allen Burton, Jr., ed, pp 19–35, Lewis Publishers, Chelsia, MI.

Johnston, R. K., unpublished. "An evaluation of acid volatile sulfides in sediments of embayments in Narragansett Bay, RI and Sinclair Inlet, WA: Preliminary Data Report, August 3, 1991." Internal Naval Command, Control and Ocean Surveillance Center, RDT&E Division report, San Diego, CA.

Lide, D.R., ed, 1990. *Handbook of Chemistry and Physics, 71st Edition 1990–1991,* CRC Press, BOCA Raton, LA.

Lindner, E., and J. S. Caso, in preparation. "Analysis of copper in leaching rate determinations for antifoulant coatings," Naval Command, Control and Ocean Surveillance Center, RDT&E Division Technical Report, San Diego, CA.

Morse, J. W., F. J. Millero, J. C. Cornwell, and D. Rickard, 1987. "The chemistry of the hydrogen sulfide and iron sulfide systems in natural waters," *Earth–Science Reviews,* **24**: pp 1–42.

Nriagu, J. O. 1968. "Sulfur metabolism and sedimentary environment: Lake Mendota, Wisconsin," *Limnol. Oceanogr,* **13**: 430–439.

Nriagu, J.O., and R.D. Coker. 1976. "Emission of sulfur from Lake Ontario sediments. *Limnol. Oceanogr.*," **21**: pp 485–489.

Power, E.A., and P.M. Chapman, 1992. "Assessing sediment quality," in *Sediment Toxicity Assessment,* G. Allen Burton, Jr., ed, pp 19–35, Lewis Publishersm, Chelsia MI.

Riley, J. P., and R. Chester. 1971. *Introduction to Marine Chemistry.* Academic Press, New York, 465 pp.

Schubauer-Berigan, J.P. 1992. "Acid volatile sulphide: What is it, where does it come from, and how useful is it in predicting the toxicity of metals in sediments?" Paper presented at 12th annual meeting of the Society of Environmental Toxicology and Chemistry, Seattle, WA.

URS Consultants, Inc., 1990. *Site Inspection Study Puget Naval Shipyard, Bremerton, WA: Draft Sampling and Analysis Plan.* URS Consultants, Inc, Seattle, WA. CTO-0017, US Navy CLEAN, Northwest Area.

URS Consultants, Inc., 1992. *Site Inspection Study, Puget Sound Naval Shipyard, Bremerton, Washington.* Vol 1–4. Site Inspection Report, CTO #0017, US Navy CLEAN, Northwest Area.

Appendix A

STANDARD OPERATING PROCEDURE FOR AVS DETERMINATION IN SEDIMENTS USING SULFIDE-SPECIFIC ELECTRODE DETECTION

Warren S. Boothman
U.S. Environmental Protection Agency
Environmental Research Laboratory
Narragansett, R.I.

I. Introduction

Acid volatile sulfides (AVS) are amorphous or moderately crystalline metal monosulfides, primarily FeS. They have been hypothesized as the single most important factor controlling the availability of heavy metals to benthic organisms in anoxic sediments (1). The molar ratio of extractable metal to AVS is postulated as an indicator of metal availability. However, methods used to determine AVS have been quite varied in both reagents and conditions. In order to insure that data used by different investigators to test the AVS hypothesis be comparable, a common protocol for the sampling and analysis of AVS needs to be established. The method described follows the findings of Cornwell and Morse (2). Comparisons of this method with a gravimetric method used at Manhattan College have reportedly given equivalent results (D. Hansen, personal communication).

II. Sample collection and storage

The accurate determination of acid volatile sulfides in sediments places a number of rather stringent requirements on the handling of samples after collection. Sulfide ion is thermodynamically unstable in the presence of dissolved oxygen, and so sediments from anoxic environments must be preserved in such a way as to protect any sulfides present from reaction with air. Storage containers must exclude or minimize air space above the sediments; if possible, purging of container headspace with dry, oxygen-free nitrogen gas would be helpful. Sediments should be kept cold or frozen during storage and transportation. Wet sediments may be stored at 4°C for short time, but anoxic sediments stored at 4°C for 20 days show significant changes in metals' partitioning, suggestive of oxidation of the sediment (3). Freezing of sediments seems to cause the least change in the speciation of metals (and by implication sulfides) in anoxic sediments; comparison of metals' extractability in fresh sediments and sediments stored for 20 days at -30°C showed essentially no significant differences. Drying of sediments, either in air or by freeze-drying, has been shown to reduce the concentration of AVS measured in anoxic sediments and should be avoided. The loss of AVS may be due to oxidation or formation of more crystalline (and non-acid volatile) sulfides

III. Determination of Acid Volatile Sulfides

The classification of sulfides as "acid volatile" is an operational definition, that is, the extent to which mineral sulfide phases are volatilized by the analysis will depend on the analytical conditions employed, e.g. acid concentration, time, etc. For AVS data obtained by different investigators to be comparable, the reaction conditions utilized to volatilize sediment sulfides must be similar; the methods used to isolate and quantify the volatilized sulfides, on the other hand, may vary according to instrumental or laboratory availability. In the method presented here, acid volatile sulfides are determined by reaction of sediment sulfides with 1M HCl to form gaseous H_2S and purging the evolved H_2S with nitrogen. The purged H_2S is then trapped in sulfide anti-oxidant buffer (SAOB)(4), diluted to volume and the $S^=$ concentration measured with a sulfide ion-specific electrode (Orion 94-16A). Overall sulfide recovery is determined by analysis of aliquots of a working sulfide standard solution and sediments which have been previously well characterized.

A. Volatilization and trapping of sediment sulfides

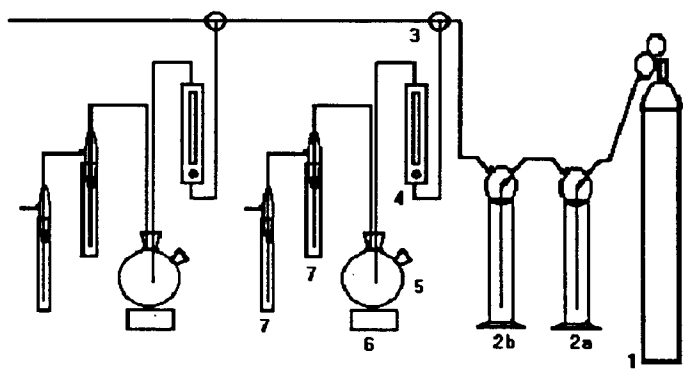


Figure 1. Apparatus for AVS determination: 1.N_2 cylinder; 2.Gas washing bottles: (a) oxygen scrubbing solution, (b) deionized water; 3.Three-way stopcock; 4.Purge flow controller; 5.Reaction flask; 6.Magnetic stirrer; 7.Sulfide traps.

The apparatus used for the volatilization and trapping of acid volatile sulfides in sediments, illustrated in Figure 1, is an adaptation of the system developed by Allen and co-workers at the University of Deleware (5) and DiToro et al.(1). This configuration of the glassware allows the acidification of the sediment while minimizing the entrainment of laboratory air into reaction vessel. It also allows the use of more than one analytical setup at a time while providing purge gas control for each individual analysis.

To prevent oxidation of sulfides due to oxygen in the analytical train, the apparatus should be purged with oxygen-

free nitrogen for at least 30 minutes prior to initiating analyses.

1. Wet sediment (ca. 10 g) is weighed into a 250-ml standard taper round bottom flask.
2. Fifty milliliters (50 ml) of deaerated deionized water (DDIW) is added to cover the sediment, a magnetic stir bar placed in the flask and the flask is placed into the sampling apparatus. Impinger (trap) bottles should be filled with 50 ml of SAOB and 30 ml of DDIW.
3. Initiate purge gas flow at 100 ml min^{-1} to remove any entrained air from the headspace and purge for 10 minutes. Reduce flow to 40 ml min^{-1}.
4. Halt purge gas flow and slowly inject 10 ml of 6M HCl (over approximately 15 sec.) through the septum sidearm, resulting in a concentration of 1.0 M HCl (neglecting the water content of the sediment).
5. Resume purge gas flow of 40 ml min^{-1} and stir sediments vigorously. Purge and trap generated H_2S for desired time (usually 30 minutes).
6. Stop purge flow, rinse impingers with DDIW into bottles and remove bottles from apparatus.

B. Measurement of sulfides by ion-specific electrode

Note: Sulfide electrode and meter should be calibrated prior to performing sediment analyses using sulfide standards prepared in SAOB diluted 1:1 with DDIW.

1. Pour bottle contents into 100-ml volumetric flask. Rinse bottle with DDIW, adding rinse to the vol. flask. Dilute to volume with DDIW.
2. Pour contents of volumetric flask into 150-ml beaker, add magnetic stirring bar and place on stirrer. Begin stirring with minimum agitation to avoid entrainment of air into solution and minimize oxidation of sample during the measurement.
3. Rinse sulfide and reference electrodes into waste container and blot dry with absorbent tissue. Immerse electrodes in sample solution.
4. Allow electrode response to stabilize (8-10 minutes), then take measurement of sulfide concentration ($C_{S}2-$). Reading may be directly in concentration units, if the meter is in **concentration** mode and a 2-point calibration has been performed, or in millivolts. If the millivolt reading is used, convert millivolts to concentration using the calibration curve obtained from standard solutions.

C. Calculation of AVS concentration in sediments

1. The sediment dry weight/wet weight ratio (R) must be determined separately. Acid volatile sulfides can be oxidized or altered to non-acid volatile forms during various drying processes.

2. AVS concentration in a sample is calculated using the formula:

$$\text{AVS}(\mu\text{mol/g dry sediment}) = \frac{(C_S2-) \times V_{trap}}{\text{g wet sediment} \times R}$$

$$= \frac{0.1 \times C_S2-}{\text{g wet sediment} \times R}$$

when C_S2- = μmole liter^{-1} (μM) and V_{trap} = 100 ml.

D. <u>Calibration of sulfide-specific electrode</u>

1. Direct concentration (2-point calibration)
   a. select **CONC** mode on meter.
   b. press the **CAL** button on the meter. The **CAL1** light should come on.
   c. immerse electrodes in first calibration standard as for sample (III.B.3-4) and allow response to stabilize. Adjust the concentration displayed to match the standard concentration, using the ↑ and ↓ keys. Press the **ENTER** key.
   d. After a few seconds, the **CAL1** light should go off and the **CAL2** light should come on. Repeat step c for the second calibration standard. After pressing **ENTER**, the **SAMPLE** light should come back on, indicating calibration is complete and providing direct readout of concentration.
   e. Press **SLOPE** and verify that a value near the theoretical slope (-29.6 mV/decade) is displayed. If the value is far off, repeat the calibration or prepare new standards.
2. multipoint calibration
   a. select **MV** mode on meter.
   b. immerse electrodes in first calibration standard as for sample (III.B.3-4) and allow response to stabilize. Record the electrode response. Repeat for other standards.
   c. The calibration curve is obtained by linear regression of millivolts against log concentration.
3. Sulfide calibration standards
   Calibration standards are prepared from the primary sulfide stock solution (IV.D.). The primary stock concentration <u>must</u> standardized by iodometric titration (IV.D.2) before preparing standards.
   a. Prepare 700 ml of diluent by mixing 350 ml of SAOB (IV.B) with an equal volume of deaerated deionized water (IV.A).
   b. Prepare a working stock solution (approx. 1500 μM). Pour 50 ml of the 1:1 SAOB diluent in a 100-ml volumetric flask. Pipette an appropriate volume of the primary stock and an equal volume of SAOB into

the flask. Dilute to volume with the diluent.

c. Prepare calibration standard solutions by dilution of the working stock solution. An example of the calculation of standard concentrations is illustrated below.

Primary Stock Concentration 55.07 umol/ml
1766 ug/ml

Working stock preparation
Primary stock aliquot 2.750 ml
Working stock volume 100
Working stock concentration 1514 uM
48.6 ug/ml

Working Stock Volume ml	Calibration Standard Volume ml	Concentration uM	Concentration ug/ml
0.200	100	3.03	0.097
0.500	100	7.57	0.243
2.00	100	30.3	0.97
5.00	100	75.7	2.43
20.00	100	303	9.7
50.00	100	757	24.3

IV. Preparation of reagents and stock solutions

A. **Deaerated Deionized Water (DDIW)**
Dissolved oxygen-free water for preparation of standards, reagents, etc. should be prepared daily by bubbling nitrogen gas (N2) vigorously through 2.5 l of deionized water for a minimum of 1 hour. The nitrogen gas should be stripped of traces of oxygen by passing through a gas washing bottle filled with vanadous chloride solution (IV.C.).

B. **Sulfide Anti-oxidant Buffer Reagent (SAOB)**
(2M NaOH, 0.2M EDTA, 0.2M ascorbic acid)
1. Dissolve 80.00 g NaOH slowly in 700 ml DDIW.
2. When cool, add 74.45 g EDTA (disodium form) and stir until dissolved.
3. Add 35.23 g ascorbic acid and stir until dissolved.
4. Pour solution into a 1.00-l volumetric flask and dilute to volume with DDIW.

C. **Vanadous Chloride Oxygen-stripping Solution**
1. Weigh 4 g of ammonium metavanadate (NH_4VO_3) in a 100-ml beaker. Add 50 ml concentrated HCl and heat to near boiling. Cool and dilute to 500 ml with deionized water. Pour the solution into a 500-ml gas washing bottle.
2. Prepare amalgamated zinc by covering 15 g of zinc metal with deionized water, adding 3 drops (150 μl) of concentrated HCL, and adding a small amount of mercury. Stir slightly to mix in the mercury.
3. Add the amalgamated zinc to the vanadous chloride solution in the gas washing bottle. The solution should

be green or blue. Bubble nitrogen through the solution until the color becomes purple. When the solution returns to a blue or green color, the oxygen stripping capacity has been exhausted; it may be replenished by the addition of more amalgamated zinc or a slight amount of conc. HCl.

D. **Sulfide stock solution**

A sulfide stock solution should be prepared and maintained for use in quality assurance and calibration. An aqueous solution of $Na_2S \cdot 9H_2O$ of sufficient concentration may be used aa a stock for secondary stocks for spiking sediments, calibrating, etc. The concentration of this stock should be determined before each use by iodometric titration or other standardization techniques.

1. Preparation
   a. Wash crystals of $Na_2S \cdot 9H_2O$ with deionized water and blot dry.
   b. Weigh approximately 12 g of $Na_2S \cdot 9H_2O$ and dissolve in 900 ml DDIW.
   c. Pour into a 1.00-l volumetric flask and dilute to volume with DDIW.
2. Standardization
   a. Pipette 10.00 ml of standard iodine solution into each of two 125-ml Erlenmeyer flasks.
   b. Pipette 2.000 ml of sulfide stock into one flask. Pipette 2.000 ml of DDIW as a blank into the other flask.
   c. Add 5.00 ml of 6M HCl into each flask, swirl slightly, then cover and place in the dark for 5 minutes.
   d. Titrate each with 0.025N thiosulfate solution, adding soluble starch indicator when the yellow iodine color fades. The end point is reached when the blue color disappears.
   e. The sulfide concentration may be calculated from:

$$\text{Sulfide } (\mu\text{mol/ml}) = \frac{(T_{blank} - T_{sample}) \times N_{S2O3}2-}{V_{sample}} \times \frac{1 \text{ mole } S^{2-}}{2 \text{ equiv } S^{2-}} \times \frac{1000\ \mu\text{moles}}{1 \text{ mmole}}$$

where T = volume of titrant used for the blank and sample (ml)

N = concentration of S_2O_32- titrant
V = volume of sample used (2.00 ml)

E. **Standard Iodine solution (0.025N)**: Dissolve 20-25 g KI in 100 ml deionized water. Weigh 3.2 g I_2 and dissolve in KI solution. Dilute to 1.00-l with deionized water. This solution may be standardized against the thiosulfate solution.

F. **Thiosulfate titrant (0.025N)** may be purchased commercially or prepared in the laboratory. If prepared in the lab, it should be standardized against potassium dichromate.

1. Preparation: Weigh approx. 6.2 g of $Na_2S_2O_3 \cdot 5H_2O$ into 500-ml beaker. Add 0.1 g Na_2CO_3 and dissolve in 400 ml DDIW. Pour into 1.00-l vol. flask and dilute to volume with DDIW.
2. Standardization
   a. Weigh 0.2 g dry K_2CrO_7 into a 500-ml Erlenmeyer flask and dissolve in 50 ml deionized water.
   b. Dissolve 3 g of KI in 50 ml of deionized water, add 5 ml of 6M HCl, and add to KI solution. Swirl, cover and store in dark for 5 minutes. Add 200 ml deionized water and titrate with the thiosulfate solution, adding starch indicator when the yellow iodine color fades, until the blue color fades to pale green.
3. Calculate the thiosulfate concentration as follows:

$$N(S_2O_3^{2-}) = \frac{g\ K_2CrO_7}{ml\ S_2O_3^{2-}} \times \frac{1\ mole\ K_2CrO_7}{294.19\ g\ K_2CrO_7} \times \frac{6\ equiv\ K_2CrO_7}{1\ mole\ K_2CrO_7} \times \frac{1000\ ml}{1\ l}$$

G. **Soluble starch** indicator is prepared by dissolving 1.0 g starch in 100 ml boiling deionized water.

V. Preparation of sulfide electrode and meter

The sulfide and reference electrodes and meter should be used and maintained as per the manufacturer's specifications. The instructions below give the brief description; see the meter or electrode operating manuals for detailed instructions.

1. Clean the inner sleeve of the double junction reference electrode with deionized water and fill the inner sleeve with the appropriate filling solution (saturated AgCl).
2. Clean and dry the outer sleeve walls with deionized water. Moisten the gasket of the outer sleeve with the outer sleeve filling solution (10% KNO_3), slide the sleeve on over the inner sleeve and screw on the end cap. Fill the outer sleeve with filling solution.
3. Inspect the surface of the sulfide electrode and polish if necessary (see electrode operating instructions for details).
4. Connect the electrodes to the meter.

VI. References

(1) DiToro, D.M., J.D. Mahoney, D.J. Hansen, K.J. Scott, M.B. Hicks, S.M. Mayr and M.S. Redmond, Toxicity of Cadmium in Sediments: the Role of Acid Volatile Sulfide, Environmental Toxicology and Chemistry, **1990**, 9, 1487-1502.

(2) Cornwell, J.C. and Morse, J.W., The characteristics of iron sulfide minerals in anoxic marine sediments, Marine Chemistry, **1987**, 22, 193-206.

(3) Rapin, F., A. Tessier, P.G.C. Campbell and R. Carignan, Environ. Sci. Technol., **1986**, 20, 836-840.

(4) Baumann, E.W., Analytical Chemistry, **1974**, 46, 1345-1347.

(5) Allen, H.E., G. Fu, B. Deng, Determination of Acid Volatile Sulfide (AVS) in Sediment, Final Report to EPA (CSD?), 1990.

Appendix B

RAW DATA OF AVS IN SEDIMENT SAMPLES

Standard curves were generated daily using the log base 10 (log[S--]) of the standardized SAOB concentrations ([S--]uM), versus the electrode response (mV). Regression were calculated using QUATROPRO spreadsheet software.

July 8, 1991 STANDARD CURVE

[S--]uM	log[S--]	mV
2.900	0.462398	-736.8
7.265	0.861236	-748.6
29.058	1.463266	-766.7
72.645	1.861206	-778.5
290.580	2.463266	-796.0
1050.450	3.021375	-812.7

Regression Output:

Constant	-723.16
Std Err of Y Est	0.15816
R Squared	0.99998
No. of Observations	6
Degrees of Freedom	4
X Coefficient(s)	-29.6386
Std Err of Coef.	0.0734

Y = -29.6386(logX) - 723.163
logX = (Y+723.163)/-29.6386

Sample Log: For each entry the sample identifier is given. If the entry is a sediment sample the wet weight (g) of sediment is also given. Results obtained from measurements of the trap solutions are tabulated for sulfide electrode response (mV) and the sulfide concentration in uM ([S--]) calculated using the current day standard curve. If the sample was spiked the spike concentration in uM is given (SpkAdd) and the recovery ratio is determined for the measured versus added concentrations (Meas/Add) and the system spike versus the bench spike (Sys/Ben) of the same spike concentration. The AVS per unit gram wet sediment is also calculated (uM/g).

No.	Sample ID wet wt (g)	g or mV	[S--]	SpkAdd	Recovery Meas/Add	uM/g or Recovery Sys/Ben
1	SysBlank			0		
	Trap2	-588.5	0.00			
	Trap1	-545.9	0.00			
2	SysSpk1			19.37		
	Trap2	-540.0	0.00			
	Trap1	-759.6	16.96		0.88	0.88
3	BenSpk1	-761.3	19.35	19.37	1.00	
4	BenSpk2	-790.1	181.32	193.70	0.94	
5	SysSpk2			193.70		
	Trap2	-554.6	0.00			
	Trap1	-789.8	177.14		0.91	0.98
6	sin190-5a4-avs-0-2a	7.0		1723.41	[Total recv. after 1hr]	
	trap2	-715.2	0.54			
	trap1-30min	-818.9	1698.81		0.99	[Meas. of 30min recovery, after
	trap2+15min	-718.5	0.70			
	trap1+15min	-760.2	17.77		0.01	another 15min,+
	trap2+15min(again)	-717.0	0.62			another 15min
	trap1+15min(again)	-747.9	6.83		0.00	of extraction]
7	sin190-5a4-avs0-2b	7.9				
	trap2	-725.4	1.19			
	trap1	-818.5	1646.83			
		-814.1	1170.02			
						uM/g
8	sin190-5a4-avs4-6a	6.0				354.30
	trap2	-728.4	1.50			
	trap1	-821.7	2111.63			
9	sin190-5a4-avs4-6b +spike	4.5		968.0		
	trap2	-729.7	1.66			408.38

	trap1.2114	-821.3	2047.02			
	trap1.2122	-820.6	1938.67			
	avg	-821.0	1992.11			
10	sin190-5a4-avs8-10a	6.3				1142.85
	trap2	-735.7	2.65			
	trap1.2213	-838.3	7668.27			
	trap1.2221	-836.8	6824.77			
	avg	-837.6	7234.24			
			0.00			
11	sin190-5a4-avs8-10b	8.2				1042.85
	trap2	-740.2	3.76			
	trap1.2309	-840.4	9027.16			
	trap1.2317	-839.1	8159.99			
	avg	-839.8	8582.63			
12	sin190-5a4-2300sysspk					
	spike			1937.2		
	trap2	-740.2	3.76			
	trap1.0003	-816.0	1356.13			
	trap1.0012	-815.5	1304.46		0.67	
	trap1.jul10.0930	-815.3	1284.35			

July 10, 1020 Standard Curve

[S--]uM	log[S--]	mV
2.900	0.462	-736.10
7.265	0.861	-748.30
29.058	1.463	-766.00
72.645	1.861	-778.00
290.580	2.463	-795.10
1050.450	3.021	-811.60

Regression Output:

Constant	-722.82
Std Err of Y Est	0.30329
R Squared	0.99991
No. of Observations	6.00
Degrees of Freedom	4.00
X Coefficient(s)	-29.43
Std Err of Coef.	0.14

Y = -29.4267(logX) - 722.821
logX = (Y + 722.821)/-29.4267

No.	Sample ID wet wt (g)	g or mV	[S--]	SpkAdd	Recovery Meas/Add	uM/g or Recovery Sys/Ben
13	benchspike(121.1uM)			121.1		
	1220	-784.3	122.81			
	1217	-783.4	114.46			
	1246	-784.1	120.90			
	avg	-783.9	119.33		0.99	
14	sin190-3a4-avs1210syspike					
	trap2	-693.5	0.10	121.1		
	trap1.1259	-784.3	122.81			
	trap1.1327	-783.9	119.02			
	avg	-784.1	120.90		1.00	1.01
			120.92			
15	sin190-3a4-avs0-2a	2.8				135.18
	trap2~	-671.5	0.02			
	trap1.1414	-798.7	378.95			
	trap1.1424	-799.0	387.95			
	trap1.1447	-798.9	384.92			
	avg	-798.9	383.92			
			0.00			
16	sin190-3a4-avs0-2b	6.0				136.17
	trap2	-688.2	0.07			
	trap1.1503	-808.4	809.49			
	trap1.1508	-808.6	822.25			
	trap1.1514	-808.3	803.18			
	avg	-808.4	811.60			
17	sin190-3a4-avs0-6a	4.0				245.96
	trap2	-690.3	0.08			
	trap1.1553	-811.0	992.12			
	trap1.1557	-811.2	1007.77			
	trap1.1603	-810.8	976.71			
	trap1.1611	-810.7	969.10			
	avg	-810.9	986.32			
18	Bench spike			1211.0		
	1613	-813.0	1160.19			
	1626	-812.3	1098.35			
	avg	-812.7	1128.85		0.93	
19	sin190-3a4-avs4-6b(s	3.8			0.74	
	trap2	-695.5	0.12		0.86	
	trap1.1707	-819.1	1869.93			
	trap1.1710	-818.4	1770.26			
	trap1.1716	-817.3	1624.26			
	avg	-818.3	1751.89			

20	sin190-3a4-avs8-10a	4.2				140.71
	trap2	-702.0	0.20			
	trap1.1738	-804.7	606.00			
	trap1.1748	-804.3	587.33			
	avg	-804.5	596.59			
21	sin190-3a4-avs8-10b	2.2				143.89
	trap2	-700.6	0.18			
	trap1.1828	-796.5	319.02			
	trap1.1834	-796.1	309.19			
	trap1.1839	-795.9	304.39			
	avg	-796.2	310.80			
22	sin190-3a4-avs20-22a	4.6				0.67
	trap2	-695.2	0.12			
	trap1.1917	-737.1	3.06			
	trap1.1923	-737.8	3.23			
	trap1.1928	-736.9	3.01			
	avg	-737.3	3.10			
23	sin190-3a4-avs30-32a	5.3				0.78
	trap2	-697.8	0.14			
	trap1.2002	-740.9	4.12			
	trap1.2007	-741.1	4.18			
	trap1.2012	-740.7	4.05			
	avg	-740.9	4.12			
24	benchspike			1211.0		
	2027	-813.3	1187.75			
	2032	-813.2	1178.49			
	2043	-812.3	1098.35			
	avg	-813.3	1183.11		0.98	
25	sin190-3a4-avs2000syspike			1211.0		
	trap2	-699.8	0.17			
	trap1.2049	-812.9	1151.15			
	trap1.2034	-813.0	1160.19			
	trap1.2104	-812.0	1072.87			
	avg	-812.6	1127.38		0.95	0.93
	avg'	-813.0	1155.66		0.98	0.95
			0.00			

JULY 11, 1991 STANDARD CURVE

[S--]uM	log[S--]	mV
2.900	0.462	-734.10
7.265	0.861	-746.90
29.058	1.463	-765.10
72.645	1.861	-777.00
290.580	2.463	-794.20
1050.450	3.021	-810.80

Regression Output:

Constant	-720.97
Std Err of Y Est	0.53371
R Squared	0.99972
No. of Observations	6.00
Degrees of Freedom	4.00
X Coefficient(s)	-29.83
Std Err of Coef.	0.25

Y = -29.8312(logX) - 720.971
logX = (Y + 720.971)/-29.8312

No.	Sample ID wet wt (g)	g or mV	[S--]	SpkAdd	Recovery Meas/Add	uM/g or Recovery Sys/Ben
26	benchspike0930			1211.0		
	0932	-812.4	1161.12			
	0934	-812.6	1179.19			
	0958	-812.1	1134.55			
	avg	-812.4	1158.14		0.96	
27	sin190-4a1-avs0900syspike			1211.0		
	trap2	-684.9	0.06			
	trap1.1007	-811.6	1091.59			
	trap1.1013	-811.7	1100.05			
	avg	-811.7	1095.81		0.95	0.90
			0.00			
28	sin190-4a1-avs0-2a	5.4				98.86
	trap2	-593.2	0.00			
	trap1.1057	-802.5	540.77			
	trap1.1106	-802.3	532.48			
	trap1.1122	-802.2	528.39			
	avg	-802.3	533.86			
29	sin190-4a1-avs0-2b	4.1				89.14
	trap2	-691.8	0.11			
	trap1.1143	-797.6	370.47			
	trap1.1143	-797.5	367.62			
	avg	-797.6	369.04			
30	sin190-4a1-avs4-6a	3.5				258.55
	mtrap2	-694.0	0.12			
	trap1.1227	-809.1	900.03			
	trap1.1236	-809.2	907.00			
	trap1.1246	-809.1	900.03			
	avg	-809.1	902.35			
31	sin190-4a1-avs4-6b	4.1				264.35
	trap2	-701.4	0.22			
	trap1.1314	-811.7	1100.05			
	trap1.1317	-811.8	1108.58			
	trap1.1324	-811.4	1074.87			
	avg	-811.6	1094.41			
32	sin190-4a1-avs4-6cspk	2.6		1211.00 uM spike		0.85
	trap2	-703.8	0.27			
	trap1.1400	-816.9	1643.34			
	trap1.1402	-817.2	1681.84			
	trap1.1409	-817.2	1681.84			
	avg	-817.1	1668.90			

33	sin190-4a1-avs8-10a	5.6				124.23
	trap2	-704.7	0.28			
	trap1.1448	-805.8	697.64			
	trap1.1450	-806.0	708.50			
	trap1.1455	-805.7	692.28			
	avg	-805.8	699.44			
34	sin190-4a1-avs20-22	6.5				52.56
	trap2	-704.7	0.28			
	trap1.1540	-796.6	342.95			
	trap1.1551	-796.3	335.10			
	avg	-796.5	339.00			
35	sin190-4a2-avs0-10a	10.9				87.61
	trap2	-707.8	0.36			
	trap1.1630	-810.0	964.77			
	trap1.1632	-810.1	972.25			
	trap1.1640	-809.5	928.25			
	avg	-809.9	954.90			
36	sin190-3a3-avs0-9	5.8				11.68
	trap2	-707.7	0.36			
	trap1.1729	-775.7	68.33			
	trap1.1733	-775.9	69.39			
	trap1.1741	-775.3	66.25			
	avg	-775.6	67.98			
37	sin190-5a5-avs0-10a	7.3				415.93
	trap2	-720.4	0.96			
	trap1.1818	-824.9	3047.21			
	trap1.1820	-824.7	3000.53			
			0.00			
	avg	-824.8	3023.78			
38	benchspike			1211.0 uM spike		
	1750	-811.8	1108.58			
	1752	-812.0	1125.82			
	1753	-811.7	1100.05			
	avg	-811.8	1111.43		0.92	
39	sin190-5af-avs1800syspike			1211.0 uM spike		
	trap2	-719.0	0.86			
	trap1.1903	-811.4	1074.87			
		-811.5	1083.20			
		-811.6	1091.59			
		-811.3	1066.61			
		-811.5	1079.03		0.97	0.89
		-812.9	1206.81			

July 12, 1991 sunny, hot and warm

[S--]uM	log[S--]	mV
2.900	0.462	-734.00
7.265	0.861	-746.30
29.058	1.463	-764.60
72.645	1.861	-776.60
290.580	2.463	-794.10
1050.450	3.021	-810.60

Regression Output:

Constant	-720.54
Std Err of Y Est	0.34758
R Squared	0.99988
No. of Observations	6.00
Degrees of Freedom	4.00
X Coefficient(s)	-29.90
Std Err of Coef.	0.16

Y = -29.8998(logX) - 720.539
logX = (Y + 720.539)/-29.8998

No.	Sample ID wet wt (g)	g or mV	[S--]	SpkAdd	Recovery Meas/Add	uM/g or Recovery Sys/Ben
40	benchspike			1210.8 uM spike		
		-812.9	1227.49			
		-813.1	1246.54			
	avg	-813.0	1236.98		1.02	
41	syspike			1210.8		
	1335	-813.4	1275.67			
	1346	-813.3	1265.89			
	1348	-813.2	1256.18			
	avg	-813.3	1265.89		1.02	1.05
42	sin1b193-a2(0-2)a	6.8				21.32
	trap2	-703.3	0.27			
	trap1.1527	-785.0	143.19			
	trap1.1532	-785.4	147.67			
	trap1.1534	-785.2	145.41			
	avg	-785.2	145.41			
43	sin1b193-a2(0-2b)	4.9				17.53
	trap2	-707.3	0.36			
	trap1.1622	-778.4	86.13			
	trap1.1624	-778.2	84.82			
	trap1.1631	-778.1	84.16			
	avg	-778.2	85.03			
44	sin1b193-a2(4-6a)	4.5				30.99
	trap2	-706.0	0.33			
	trap1.1707	-784.6	138.84			
	trap1.1709	-784.8	141.00			
	trap1.1716	-784.4	136.72			
	avg	-784.6	138.84			
			0.00			
45	sin1b193-a2(4-6b)	8.1				34.90
	trap2	-705.6	0.32			
	trap1.1751	-793.8	281.98			
	trap1.1755	-793.9	284.16			
	trap1.1756	-793.8	281.98			
	avg	-793.8	282.70			
46	sin1b193-a2(8-10a)	3.1				68.15
	trap2	-704.8	0.30			
	trap1.1841	-790.4	217.02			
	trap1.1851	-789.9	208.82			
	trap1.1858	-789.6	204.06			
	avg	-790.0	209.90			

47	sin1b193-a2(8-10b)	4.7				52.95
	trap2	-707.1	0.36			
	trap1.1928	-792.0	245.48			
	trap1.1933	-792.2	249.29			
	trap1.1935	-792.0	245.48			
	avg	-792.1	246.74			
48	sin1b193-a2(20-22a)	6.0				29.70
	trap2	-706.9	0.35			
	trap1.2012	-787.8	177.64			
	trap1.2014	-787.8	177.64			
	trap1.2019	-787.6	174.93			
	avg	-787.7	176.73			
49	sin2a193-a2(0-2a)	6.8				227.09
	trap2	-712.6	0.54			
	trap1.2053	-816.2	1582.65			
	trap1.2100	-816.1	1570.51			
	trap1.2109	-815.4	1488.09			
	avg	-815.9	1546.51			
50	sin2a193-a2(0-2b)spk	3.0		1210.75	0.72	114.67
	trap2	-711.0			0.48	sys/ben 0.73
	trap1.2140	-816.1	1570.51			
	trap1.2148	-815.8	1534.65			
			0.00			
	avg	-816.0	1552.48			
	2253	-815.8	1534.65			sys/ben 0.72
51	benchspike			1210.8		
	2137	-812.6	1199.45			
	2137	-812.7	1208.73			
	2139	-812.6	1199.45			
	avg	-812.6	1202.54			
	2255	-812.5	1190.25			
52	sin2a193-a2(4-6a)	2.0				554.26
	trap2	-712.7	0.55			
	trap1.2231	-811.8	1127.79			
	trap1.2232	-811.9	1136.51			
	trap1.2232	-811.8	1127.79			
	avg	-811.8	1130.69			
53	sin2a1193-a2(4-6b)	2.4				527.67
	trap2	-722.9	1.20			
	trap1.2321	-813.6	1295.47			
	trap1.2324	-813.5	1285.54			
	trap1.2327	-813.3	1265.89			
	avg	-813.5	1282.24			
54	sin2a193-a2(8-10a)	2.0				490.84
	trap2	-723.1	1.22			
	trap1.0007	-810.2	997.05			
	trap1.0011	-810.0	981.81			
	trap1.0019	-809.6	952.03			
	avg	-809.9	976.78			
55	sin2a193-2a-(18-10)	3.7				534.58
	trap2	-722.8	1.19			
		-819.1	1978.68			
		-819.3	2009.40			
		-819.2	1993.98			
		-819.2	1993.98			
			0.00			

July 13, 1991 STANDARDS
cool, cloudy ... showers

[S--]uM	log[S--]	mV
2.900	0.462	-732.80
7.265	0.861	-744.80
29.058	1.463	-763.20
72.645	1.861	-775.40
290.580	2.463	-792.90
1050.450	3.021	-809.70

Regression Output:

Constant	-719.05
Std Err of Y Est	0.27228
R Squared	0.99993
No. of Observations	6.00
Degrees of Freedom	4.00
X Coefficient(s)	-30.05
Std Err of Coef.	0.13

Y = -30.0491(logX) - 719.053
logX = (Y + 719.053)/-30.0491

JULY 13 1991

No.	Sample ID wet wt (g)	g or mV	[S--]	SpkAdd	Recovery Meas/Add	uM/g or Recovery Sys/Ben
56	sin194-a100 (blank)					
	trap1	-709.2	0.47			
57	benchspike			1211.0 uM spike		
	1147	-810.9	1139.11			
	1148	-811.2	1165.60			
	1149	-811.1	1156.70			
	avg	-811.1	1153.75		0.95	
	1240	-810.9	1139.11			
58	systemspike1100	1211.0	uM Spike			
	trap2	-707.2	0.40			
	trap1.1151	-811.2	1165.60			
	trap1.1153	-811.1	1156.70			
	trap1.1159	-810.9	1139.11			
	avg	-811.1	1153.75		1.00	0.95
	1240	-810.5	1104.72		0.97	
59	sin2a193-a1(0-10)a	3.5				277.96
	trap2	-709.7	0.49			
	trap1.1258	-808.7	962.39			
	1300	-808.9	977.25			
	1302	-808.7	962.39			
	avg	-808.8	967.32			
60	sin2a193-a1(0-10)b	2.9				261.02
	trap2	-711.9	0.58			
	trap1.1346	-805.5	753.11			
	1348	-805.7	764.74			
	1351	-805.5	753.11			
	avg	-805.6	756.97			
61	sin2a193-a(0-10)cspk	0.9		1211.0	0.84 using sys	
	trap2	-710.3	0.51			
	trap1.1430	-810.5	1104.72			
		-810.8	1130.41			
			0.00			
62	sin1b193-a3(0-10)a	4.8				61.65
	trap2	-710.2	0.51			
	trap1	-793.3	295.70			
	trap1.1521	-793.1	291.21			
		-793.2	293.45			
			0.00			

63	systemspike1500			1211.0 uM	spike
	trap2=trap1	-810.0	1063.20		
	1604	-809.7	1039.03		
	1606	-809.5	1023.23		
	1610	-809.0	984.77		
		-809.6	1027.16		
			0.00		

JULY 16 1991, STANDARD CURVE 1919; cloudy with clearing, cool temp

[S--]uM	log[S--]	mV
2.900	0.462	-736.80
7.265	0.861	-748.60
29.058	1.463	-766.70
72.645	1.861	-778.50
290.580	2.463	-796.00
1050.450	3.021	-812.70

Regression Output:

Constant	-723.16
Std Err of Y Est	0.15816
R Squared	0.99998
No. of Observations	6.00
Degrees of Freedom	4.00
X Coefficient(s)	-29.64
Std Err of Coef.	0.07

Y = -29.6386(logX) - 723.1
logX = (Y + 723.163)/-29.6386

No.	Sample ID wet wt (g)	g or mV	[S--]	SpkAdd	Recovery Meas/Add	uM/g or Recovery Sys/Ben
64	bench spike:1915			1211.0 uM spike		
	1917	-812.0	993.90			
	1920	-812.3	1017.33			
	1928	-812.1	1001.65			
	avg	-812.2	1009.46			
65	sys-spike			1211.0 uM spike		
	sys1-trap2	-468.3	0.00			
	sys1-trap1	-812.1	1001.65			0.99
66	sys2-trap2	-712.5	0.44			
	sys2-trap1	-811.9	986.21			
		-812.0	993.90			
		-812.1	1001.65			
	avg	-812.0	993.90		0.98	0.99

JULY 17, 1991: partly cloudy, temp still cool

[S--]uM	log[S--]	mV
2.911	0.464	-735.90
7.280	0.862	-748.70
29.118	1.464	-766.60
72.795	1.862	-778.40
291.180	2.464	-795.60
1052.616	3.022	-812.40

Regression Output:

Constant	-722.73
Std Err of Y Est	0.47312
R Squared	0.99978
No. of Observations	6.00
Degrees of Freedom	4.00
X Coefficient(s)	-29.71
Std Err of Coef.	0.22

Y = -29.0348(logX) - 724
logX = (Y + 724.17)/-29.034

No.	Sample ID wet wt (g)	g or mV	[S--]	SpkAdd	Recovery Meas/Add	uM/g or Recovery Sys/Ben
67	benchspike 1054	-801.4	457.00	485.30 uM spike		
		-801.2	449.80			
		-801.0	442.73			
	avg	-801.2	449.80		0.93	
	1253	-801.5	460.63		0.95	
68	sys1spike			485.3 uM spike		
	trap2	-587.0	0.00			
		-801.4	457.00			
		-801.2	449.80			
		-801.0	442.73			
	avg	-801.2	449.80			1.00
	1253	-801.2	449.80			0.98
69	sys2spike			485.3 uM spike		
	trap2	-711.7	0.37			
	trap1	-801.2	449.80			
		-801.3	453.39			
		-801.0	442.73			
	avg	-801.2	448.62		0.97	1.00
	1253	-800.5	425.51		0.92	0.95
70	sin4b197-a2(0-2)a	2.3				54.79
	trap2	-515.8	0.00			54.79
	trap1	-785.0	124.47			
		-785.2	126.46			
			0.00			
	avg	-785.1	125.46			
	1354	-785.1	125.46			
71	sin4b197-a2(0-2)b	1.5				53.15
	trap2	-710.9	0.35			52.87
	trap1	-779.3	79.21			
		-779.6	81.11			
		-779.5	80.47			
	avg	-779.5	80.26			
	1354	-779.4	79.84			
72	sin4b197-a2(4-6)a	1.2				105.76
	trap2	-585.1	0.00			107.03
	trap1	-785.4	128.48			
		-785.3	127.47			
	avg	-785.4	127.98			
	1520	-785.5	129.51			

73	sin4b197-a2(4-6)b	2.3		123.86
	trap2	-710.2	0.33	123.37
	trap1	-795.4	283.96	
		-795.7	290.80	
	avg	-795.6	287.36	
	1520	-795.5	286.22	
74	sin4b197-a2(8-10)	3.5		95.44
	trap2	-548.2	0.00	
	trap1	-797.1	324.95	
		-797.3	330.14	
		-797.4	332.77	
	avg	-797.3	329.27	
75	sin4b197-a2(20-22)	3.8		60.16
	trap2	-711.5	0.37	
	trap1	-792.8	231.05	
		-792.6	227.42	
		-792.6	227.42	
	avg	-792.7	228.62	
76	sin4b197-a1(0-10)a	5.5		126.86
	trap2	-674.0	0.02	
	trap1	-806.6	690.25	
		-806.7	695.75	
		-806.7	695.75	
	avg	-806.7	693.91	
77	sin4b197-a1(0-10)b	4.9		138.99
	trap2	-711.4	0.36	
	trap1	-806.4	679.39	
		-806.7	695.75	
		-806.5	684.80	
	avg	-806.5	686.61	
78	sin3b197-a1(0-2)a	2.8		22.17
	trap2	-594.1	0.00	
	trap1	-775.9	60.49	
		-776.1	61.45	
		-776.0	60.97	
	avg	-776.0	60.97	
79	sin3b197-a1(0-2)b	2.9		22.85
	trap2	-711.6	0.37	
	trap1	-776.7	64.45	
		-777.0	66.00	
		-776.8	64.96	
		-776.8	65.13	
80	sin3b197-a1(4-6)a	2.3		62.25
	trap2	-567.7	0.00	63.75
	trap1	-786.8	143.57	
		-786.7	142.44	
		-786.3	137.99	
	avg	-786.6	141.31	
	2055	-786.9	144.71	
81	sin3b197-a1(4-6)b	2.5		66.42
	trap2	-710.7	0.34	65.72
	trap1	-788.4	162.99	
		-788.6	165.60	
		-788.6	165.60	
	avg	-788.5	164.73	
	2055	-788.4	162.99	

82	sin3b197-a1(8-10)	3.8			8.95
	trap2	-593.7	0.00		
	trap1	-768.5	33.63		
		-768.9	34.72		
		-768.6	33.90		
	avg	-768.7	34.08		
83	sin3b197-a1(20-22)	3.9			68.54
	trap2	-708.8	0.30		
	trap1	-794.8	270.77		
		-795.0	275.10		
		-794.5	264.40		
	avg	-794.8	270.05		
84	sin3b197-a2(0-10)a	2.6			25.49
	trap2	-632.1	0.00		
	trap1	-776.9	65.48		
		-777.4	68.13		
		-777.3	67.59		
	avg	-777.2	67.05		
	2350	-777.1	66.52		
85	sin3b197-a2(0-10)b	5.2			24.16
	trap2	-707.7	0.27		
	trap1	-784.9	123.49		
		-785.0	124.47		
		-785.3	127.47		
	avg	-785.1	125.13		
	2350	-784.3	117.75		
86	sin5b197-a2(0-10)a	3.3	0.00		258.23
	trap2	-680.4	0.03		
	trap1	-809.2	848.31		
		-809.3	855.06		
		-809.5	868.73		
	avg	-809.3	857.33		
87	sin5b197-a2(0-10)b	3.6			272.39
	trap2	-708.4	0.29		
	trap1	-811.3	1002.03		
		-811.2	994.12		
		-811.0	978.47		
	avg	-811.2	991.49		
88	sin198-a(0015)a			485.3 uM spike system1	
	0101	-799.5	393.07		
		-799.7	399.36		
		-799.6	396.20		
		-799.6	396.20		0.86
89	sin198-a(0015)b			485.3 uM spike system2	
	0106	-799.0	377.79		
		-799.1	380.80		
		-799.0	377.79		
		-799.0	378.79		0.82

JULY 18, 1991 Sunny, getting warmer...

[S--]uM	log[S--]	mV
2.911	0.464	-735.50
7.280	0.862	-748.00
29.118	1.464	-766.00
72.795	1.862	-778.20
291.180	2.464	-795.60
1052.616	3.022	-812.50

Regression Output:

Constant	-721.95
Std Err of Y Est	0.32663
R Squared	0.99990
No. of Observations	6.00
Degrees of Freedom	4.00
X Coefficient(s)	-29.99
Std Err of Coef.	0.15

Y = -29.9932(logX) - 721
logX = (Y + 721.951)/-29.99

No.	Sample ID wet wt (g)	g or mV	[S--]	SpkAdd	Recovery Meas/Add	uM/g or Recovery Sys/Ben
90	bench spike			485.3		
		-798.0	343.20			
		-798.9	367.75			
		-799.0	370.58			
		-798.6	360.29		0.74	
91	sysspike1048-sys1			10.0 ml july 17 spike		
	trap2	-525.8	0.00			
	trap1	-798.8	364.93			
		-798.9	367.75			
		-799.0	370.58			
	avg	-798.9	367.75		1.02	
92	sysspike1048-sys2			10.0 ml july 17 spike		
	trap2	-708.8	0.36			
	trap1	-798.8	364.93			
		-798.9	367.75			
		-798.9	367.75			
	avg	-798.9	366.81		1.02	1.00
93	sin5b197-a1(0-2)a	1.2				148.78
	trap2	-625.3	0.00			
	trap1	-788.7	168.06			
		-789.1	173.30			
		-789.0	171.98			
	avg	-788.9	171.10			
94	sin5b197-a1(0-2)b	2.9				186.65
	trap2	-708.6	0.36			
	trap1	-803.7	531.60			
		-803.9	539.82			
		-803.8	535.70			
	avg	-803.8	535.70			
95	sin5b197-a1(4-6)a	2.8				650.19
	trap2	-648.0	0.00			
	trap1	-819.4	1774.34			
		-819.5	1788.01			
		-819.6	1801.79			
	avg	-819.5	1788.01			
96	sin5b197-a1(4-6)b	2.5				682.65
	trap2	-708.0	0.34			
	trap1	-819.1	1733.94			
		-819.2	1747.30			
		-819.0	1720.68			
	avg	-819.1	1733.94			

97	sin5b197-a1(8-10)	2.1			874.53
	trap2	-678.1	0.03		
	trap1	-819.9	1843.77		
		-820.2	1886.73		
		-820.0	1857.98		
	avg	-820.0	1862.74		
98	sin5b197-a1(20-22)	3.2			573.80
	trap2	-710.0	0.40		
	trap1	-819.8	1825.46		
		-819.8	1829.67		
		-819.6	1801.79		
		-819.7	1818.93		
99	sin2b199-a2(0-2)a	2.6			59.41
	trap2	-689.0	0.08		
	trap1	-787.6	154.45		
		-787.7	155.64		
		-787.8	156.84		
	avg	-787.7	155.64		
100	sin2b199-a2(0-2)b	2.5			284.16
	trap2	-707.0	0.32		
	trap1	-807.2	695.47		
		-807.3	700.83		
		-807.3	700.83		
	avg	-807.3	699.04		
101	sin2b199-a2(4-6)a	1.3	0.00		289.54
	trap2	-799.4	382.14		
		-799.5	385.08		
		-799.6	388.05		
	avg	-799.5	385.08		
		-799.2	376.31		
102	sin2b199-a2(4-6)b	1.2			364.70
	trap2	-708.9	0.37		
		-801.1	435.41		
		-801.2	438.77		
		-801.2	438.77		
	avg	-801.2	437.64		
		-800.4	412.63		
			0.00		
103	bench spike 2300			485.3 uM spike	
		-802.5	484.81		
		-802.6	488.55		
		-802.7	492.32		
		-802.8	496.11		
	avg	-802.7	490.43		
	2200	-802.1	470.15		

JULY 19, 1991: clear and sunny, still cool

[S--]uM	log[S--]	mV
2.911	0.464	-735.40
7.280	0.862	-747.60
29.118	1.464	-765.70
72.795	1.862	-777.70
291.180	2.464	-795.20
1052.616	3.022	-812.00

Regression Output:

Constant	-721.78
Std Err of Y Est	0.23592
R Squared	0.99995
No. of Observations	6.00
Degrees of Freedom	4.00
X Coefficient(s)	-29.88
Std Err of Coef.	0.11

Y = -29.8768(logX) - 721
logX = (Y + 721.781)/-29.87

No.	Sample ID wet wt (g)	g or mV	[S--]	SpkAdd	Recovery Meas/Add	uM/g or Recovery Sys/Ben
104	bench spike 7/18 210			485.3		
		-802.5	503.19			
		-802.7	511.00			
			0.00			
105	sysspike0930			485.3		
	trap2	-659.0	0.01			
	trap1	-802.1	487.91			
		-802.3	495.49			
		-802.5	503.19			
	avg	-802.3	495.49			1.02
106	sysspike0930-sys2			485.3 uM spike		
	trap2	-708.4	0.36			
	trap1	-802.2	491.69			
		-802.5	503.19			
		-802.4	499.32			
	avg	-802.4	498.04		1.03	1.01
107	sin1a199-a1(0-2)a	7.2			0.73	
	trap2	-679.5	0.04			
	trap1	-743.2	5.21			
		-743.4	5.29			
	avg	-743.3	5.25			
			0.00			
108	sin1a199-a1(0-2)b	7.9			0.94	
	trap2	-706.7	0.31			
	trap1	-747.5	7.26			
		-747.9	7.49			
		-747.8	7.43			
	avg	-747.7	7.39			
109	sin2b197-a1(0-10)a	4.2			80.80	
	trap2	-678.0	0.03			
	trap1	-797.0	329.34			
		-797.4	339.65			
		-797.3	337.04			
	avg	-797.2	335.31			
110	sin2b197-a1(0-10)b	5.8			81.99	
	trap2	-704.7	0.27			
	trap1	-801.7	473.10			
		-801.9	480.45			
		-801.9	480.45			
	avg	-801.8	477.99			

111	sin1a199-a2(0-10)a	14.0		6.05	
	trap2	-680.0	0.04		
	trap1	-779.0	82.26		
		-779.5	85.49		
		-779.5	85.49		
	avg	-779.3	84.40		
112	sin1a199-a2(0-10)b	7.3	0.00	7.53	
	trap2	-704.7	0.27		
	trap1	-773.7	54.67		
		-773.9	55.52		
		-773.5	53.84		
	avg	-773.7	54.67		
113	sin2b199-a2(20-22)	4.3		483.31	
	trap2	-688.4	0.08		
	trap1	-821.0	2093.81		
		-821.0	2093.81		
		-820.8	2061.79		
	avg	-820.9	2083.08		
114	sin2b199-a2(4-6)	4.2		202.16	
	trap2	-708.3	0.35		
	trap1	-809.1	836.83		
		-809.2	843.30		
		-809.1	836.83		
	avg	-809.1	838.98		
115	sin1a199-a1(8-10)	6.0		18.50	
	trap2	-691.8	0.10		
	trap1	-782.6	108.56		
		-783.0	111.96		
		-783.2	113.70		
	avg	-782.9	111.38		
116	sin2b199-a2(8-10)	5.4		341.99	
	trap2	-707.4	0.33		
	trap1	-819.4	1850.91		
		-819.5	1865.23		
		-819.5	1865.23		
	avg	-819.5	1860.44		
117	sin1a199-a1(4-6)	10.1		3.40	
	trap2	-684.6	0.06		
	trap1	-767.2	33.13		
		-767.7	34.43		
		-767.9	34.97		
	avg	-767.6	34.17		
118	sin2b199-a2(0-2)c	8.2		154.10	59.40
	trap2	-710.8	0.43		
	trap1	-814.3	1249.35		
		-814.5	1268.76		
		-814.4	1259.01		
	avg	-814.4	1259.01		
119	benchspike1713			483.5 uM spike	
	1716	-801.5	465.86		
		-801.7	473.10		
		-801.6	469.47		
		-801.6	469.47		
	avg	-801.6	469.47		

120 benchspike2100 7/18		0.00				
1720	-802.6	507.08				
	-803.0	522.95				
	-803.1	527.00				
avg	-802.9	518.94				
121 sysspike1730sys1			483.5 uM spike			
trap2	-570.9	0.00				
trap1	-801.3	458.74				
	-801.7	473.10				
	-801.6	469.47				
avg	-801.5	467.06		0.97	0.99	
122 sysspike1730sys2			483.5 uM spike			
trap2	-708.1	0.35				
trap1	-801.9	480.45				
	-802.2	491.69				
	-801.8	476.76				
avg	-802.0	482.92		1.00	1.03	1.03

Appendix C

RAW DATA OF SEM CONCENTRATIONS OF Cu, Pb, AND Zn

SEM concentrations of Cu, Pb, nad Zn in sediment samples collected from Sinclair Inlet, WA, were analyzed on January 24–30, 1992, at the Ocean Sciences Laboratory of NCCOSC, RDT&E Division, San Diego, CA. Table B-1 provides the raw and calculated data for copper. Table B-2 provides the raw and calculated data for lead and zinc. A Summary of all the SEM data is provided in table B-3.

Table C-1. Raw and calculated data for the determination of SEM concentrations of copper measured by GFAA. For each batch the sample sequence number (seq#), the sample identification number (ID#), the station location (Sta), the core depth of sample in cm (depth), the absorbance units measured with the GFAA (ABS), the concentration (ppb) determined from the regression standard curve (CONC), the concentration (ppb) of the second dilution (d_2), the concentration of the first dilution (d_1), the concentration of the extract ($C_{extract}$), the weight of the sample (G_w), the dry to wet weight ratio of the sample (R), the centrifuged volume (C_{vol}), the weight of storage vial and sample (W_{sto}), the calculated volume of the extract (V_{ext}), the mass of the metal in the extract (M_{ext}), and the concentration of the sediment sample (C_{sed}) in µg/g and µmol/g (dry weight) are given. **(A)** Batch number RUN1 24 JAN 1992. **(B)** Batch number RUN2 25 JAN 1992. **(C)** Batch number RUN3 25 JAN 1992. **(D)** Batch number RUN4 25 JAN 1992. Quality Assurance (QA) data are presented for each batch.

(A) COPPER RUN1 24 JAN 1992 CONC = (ABS–BLANK)/0.002542 BLANK = 0.004

seq#	ID#	Sta	depth	ABS	CONC [ppb]	d_2 [ppb]	d_1 [ppb]	$C_{extract}$ [ppm]	G_w g	R d/w	C_{vol} ml	W_{sto} ml	V_{ext} ml	M_{ext} µg	C_{sed} µg/g	C_{sed} µmol/g
1	NB	Blank		0.006	2.36											
2	B	Blank		0.004	1.57											
3	1	4a	4–6b	0.220	84.97	849.72	4248.62	4.25	4.14	0.3071	45.0	30.40	71.13	302.20	237.69	3.74
4	2	3a	0–2b	0.367	142.80	1428.01	7140.05	7.14	5.96	0.1957	45.0	22.63	61.59	439.73	377.01	5.93
5	3	1b	0–2a	0.070	25.96	259.64	1298.19	1.30	6.82	0.6376	45.0	23.45	61.55	79.90	18.37	0.29
6	5	2b	0–2c	0.431	167.98	1679.78	8398.90	8.40	8.17	0.2947	45.0	23.77	60.52	508.32	211.12	3.32
7	6	1a	0–2a	0.030	10.23	102.28	511.41	0.51	7.18	0.7123	45.0	27.58	65.30	33.39	6.53	0.10
8	I4	5a	0–2a	0.172	66.09	660.90	6608.97	6.61	6.97	0.3686	45.0	32.19	70.09	463.25	180.31	2.84
9	7	FB190	2300	0.026	8.65	86.55	432.73	0.43								
10	8	3a	4–6a	0.248	95.99	959.87	4799.37	4.80	4.01	0.233	6 45.0	31.05	71.91	345.10	368.41	5.80
11	9	1a	0–10	0.068	25.18	251.77	1258.85	1.26	13.96	0.7688	45.0	41.05	71.96	90.58	8.44	0.13
12	10	FB193	1800	0.007	1.18	11.80	59.01	0.06								
13	11	2a	0–10	0.172	66.09	660.90	3304.48	3.30	3.48	0.3779	45.0	33.80	75.17	248.40	188.88	2.97
14	DUP12	3a	0–10	0.276	107.00	1070.02	5350.12	5.35	5.82	0.3377	45.0	38.79	77.81	416.27	211.80	3.33
15	12	3a	0–10	0.279	108.18	1081.83	5409.13	5.41	5.82	0.3377	45.0	38.79	77.81	420.86	214.13	3.37
16	13	4a	0–10	0.422	164.44	1644.37	8221.87	8.22	10.90	0.4349	45.0	39.49	73.45	603.88	127.39	2.00
17	14	5a	0–10	0.355	138.08	1380.80	6904.01	6.90	7.27	0.4245	45.0	38.36	75.94	524.26	169.88	2.67
18	15	4a	0–2b	0.201	77.50	774.98	3874.90	3.87	4.14	0.2402	45.0	31.68	72.40	280.55	282.13	4.44
19	4	5a	0–2a	0.341	132.57	1325.73	6628.64	6.63	6.97	0.3686	45.0	32.19	70.09	464.63	180.85	2.85
20	S1	120ref		0.344	133.75											
21	B2	Blank		0.003	1.18											

QA Check:

I4	actual/reference	.172/.173	=	99.4%
DUP:	(DUP12/12) – 1	(.276/.279) – 1	=	3.6%
S1 120:	actual/reference	.344/.332	=	103.6%
BLANKS:	values ≤ 2x(0.004)			YES

(Contd)

Table C-1. Continued.

(B) COPPER RUN1 25 JAN 1992 CONC = (ABS – BLANK)/0.002542 BLANK = 0.004

seq#	ID#	Sta	depth	ABS	CONC [ppb]	d_2 [ppb]	d_1 [ppb]	$C_{extract}$ [ppm]	G_w g	R d/w	C_{vol} ml	W_{sto} ml	V_{ext} ml	M_{ext} µg	C_{sed} µg/g	C_{sed} µmol/g
0	Instr. zero			–0.001												
1	B Blank			0.004	1.57											
2	S1 120ref			0.352	138.47											
3	17	1b	0–10	0.058	21.24	212.43	1062.16	1.06	4.76	0.5895	35.0	41.56	71.62	76.07	27.11	0.43
4	18	FB200 1700b		0.001	0.39	3.93	19.67	0.02								
6	20	3b	0–10	0.099	37.37	373.72	1868.61	1.87	2.61	0.5801	35.0	27.57	59.84	111.81	73.85	1.16
7	21	4b	0–10	0.159	60.98	609.76	3048.78	3.05	4.94	0.3044	35.0	27.60	57.55	175.45	116.68	1.84
8	I4 Reference		0.171	65.70												
9	22	4b	0–10	0.150	57.44	574.35	2871.75	2.87	5.47	0.3044	35.0	23.68	53.12	152.55	91.62	1.44
10	23	5b	0–10	0.529	206.53	2065.30	10326.51	10.33	3.32	0.3958	35.0	24.97	56.54	583.88	444.34	6.99
11	24	FB198	0015	0.005	0.39	3.93	19.67	0.02								
12	25	4b	0–2b	0.037	12.98	129.82	649.10	0.65	1.51	0.2307	35.0	16.17	49.59	32.19	92.40	1.45
13	26	FB192 1210		0.002	0.79	7.87	39.34	0.04								
14	DUP27	3a	4–6b	0.174	66.88	668.76	3343.82	3.34	3.75	0.2336	35.0	39.23	70.30	235.08	268.36	4.22
15	27	3a	4–6b	0.182	70.02	700.24	3501.18	3.50	3.75	0.2336	35.0	39.23	70.30	246.15	280.99	4.42
16	28	1a	8–10	0.071	26.36	263.57	1317.86	1.32	6.02	0.6102	35.0	40.75	69.56	91.67	24.95	0.39
17	29	1a	4–6	0.062	22.82	228.17	1140.83	1.14	10.06	0.7829	35.0	26.17	51.03	58.22	77.39	0.12
* 18	30	5a	8–10	1.818	713.61	7136.11	35680.57	35.68	8.23	0.4072	35.0	29.62	56.28	2008.23	599.25	9.43
19	31	4a	8–10	0.398	155.00	1549.96	7749.80	7.75	5.63	0.3633	35.0	40.23	69.43	538.05	263.06	4.14
20	32	5a	4–6a	0.715	279.70	2797.01	13985.05	13.99	5.96	0.3899	35.0	36.70	65.59	917.24	394.71	6.21
21	S1	180ref		0.505	197.09											
22	B2	Blank		0.003	1.18	11.80	59.01	0.06								
rerun	30(5ul)	5a	8–10	0.980	383.95	3839.50	19197.48	19.20								
rerun	30(5ul)	5a	8–10	0.919	59.95	3599.53	17997.64	18.00								
rerun	30(5ul)	5a	8–10	0.927	363.10	3631.00	18155.00	18.15								
(avg)*2		5a	8–10	0.942	369.00	3690.01	18450.04	18.45	*2 8.23	0.4072	35.0	29.62	56.28	2076.87	619.73	9.75

QA Check:

I4:	actual/reference	.171/.173	=	98.8%
DUP:	(DUP27/27) – 1	(.174/.182) – 1	=	4.6%
S1 120:	actual/reference	.352/.332	=	106.0%
S1 180:	actual/reference	.505/.498	=	101.5%
BLANKS:	values ≤ 2x(0.004)			YES

* Sample number 30 was off scale. At the end of the batch, the sample was rerun using a 5-µl sample volume. The average of the 3 reanalyses was multiplied by 2 to obtain a comparable concentration.

(Contd)

Table C-1. Continued.

(C) COPPER RUN3 25 JAN 1992 CONC = (ABS – .176)/0.002542 + 69.23682 (NO BLANK CORRECTION)

seq#	ID#	Sta	depth	ABS	CONC [ppb]	d_2 [ppb]	d_1 [ppb]	$C_{extract}$ [ppm]	G_w g	R d/w	C_{vol} ml	W_{sto} ml	V_{ext} ml	M_{ext} µg	C_{sed} µg/g	C_{sed} µmol/g
0		Instr.	Zero	0.000												
1	B	Blank		0.007	2.75											
2	S1	120ref		0.389	153.03											
3	33	2b	8–10	0.213	83.79	837.92	4189.61	4.19	5.44	0.3786	35.0	37.33	66.73	279.58	135.75	2.14
4	34	FB200	1730a	0.003	1.18	11.80	59.01	0.06								
5	35	5b	4–6a	0.375	147.52	1475.22	7376.08	7.38	5.96	0.3899	35.0	28.82	57.75	425.94	183.29	2.88
6	36	5b	0–2a	0.103	40.52	405.19	2025.96	2.03	1.15	0.2821	35.0	26.57	60.29	122.15	376.53	5.93
7	37	4b	4–6a	0.038	14.95	149.49	747.44	0.75	1.21	0.2828	35.0	29.47	63.12	47.18	137.87	2.17
8	38	1b	20–22	0.135	53.11	531.08	2655.39	2.66	5.95	0.7566	35.0	38.39	67.28	178.65	39.68	0.62
9	39	3a	8–10b	0.140	55.07	550.75	2753.74	2.75	2.16	0.2574	35.0	37.99	70.65	194.56	349.93	5.51
10	I4	Reference		0.188	73.96	739.58	3697.88	3.70								
11	40	2b	20–22	0.494	194.34	1943.35	9716.76	9.72	4.31	0.4112	35.0	40.79	71.30	692.79	390.91	6.15
12	41	4b	8–10	0.084	33.04	330.45	1652.24	1.65	3.45	0.3344	35.0	32.24	63.65	105.16	91.15	1.43
13	42	FB194	1100	0.003	1.18	11.80	59.01	0.06								
14	43	1b	8–10a	0.049	19.28	192.76	963.81	0.96	4.76	0.5895	35.0	40.91	70.97	68.40	24.38	0.38
15	44	3a	0–2a	0.136	53.50	535.01	2675.06	2.68	2.84	0.1957	35.0	39.24	71.22	190.51	342.78	5.39
16	45	5a	4–6b	0.453	178.21	1782.06	8910.31	8.91	4.47	0.3899	35.0	42.83	73.17	651.96	374.08	5.89
17	46	4b	20–22	0.038	14.95	149.49	747.44	0.75	3.80	0.4145	35.0	28.30	59.38	44.38	28.18	0.44
18	DUP47	2a	4–6a	0.124	48.78	487.80	2439.02	2.44	2.04	0.3551	35.0	28.50	61.33	149.58	206.49	3.25
19	47	2a	4–6a	0.128	50.35	503.54	2517.70	2.52	2.04	0.3551	35.0	28.50	61.33	154.41	213.15	3.35
20	48	2b	4–6c	0.253	99.53	995.28	4976.40	4.98	4.15	0.3480	35.0	30.32	61.04	303.76	210.33	3.31
21	49	2a	0–2a	0.327	128.64	1286.39	6431.94	6.43	6.81	0.3209	35.0	38.93	66.96	430.68	197.08	3.10
22	50	5b	20–22	0.481	189.22	1892.21	9461.05	9.46	3.17	0.5095	35.0	16.29	48.05	454.65	281.50	4.43
23	51	4a	0–2a	0.267	105.04	1050.35	5251.77	5.25	5.40	0.2402	35.0	31.75	61.22	321.51	247.87	3.90
24	52	5b	8–10a	0.529	208.10	2081.04	10405.19	10.41	2.13	0.4455	35.0	21.25	54.02	562.14	592.40	9.32
25	53	4a	20–22	0.353	138.87	1388.67	6943.35	6.94	6.45	0.4912	35.0	43.23	71.60	497.12	156.91	2.47
26	S1	180ref		0.549	215.97											
27	B3	Blank		0.005	1.97											
28	S1	180ref		0.562	221.09											
avg S1 180				0.556	218.53											

QA Check:

I4:	actual/reference	.188/.173	=	108.7%
DUP:	(DUP47/47) – 1	(.124/.128) – 1	=	3.1%
S1 120:	actual/reference	.389/.332	=	117.2% **
S1 180:	actual/reference	.556/.498	=	111.6%
BLANKS:	values ≤ 2x(0.004)			YES

** Exceeded QA criteria.

(Contd)

Table C-1. Continued.

(D) COPPER RUN4 25 JAN 1992 CONC = (ABS)/0.002542 (NO BLANK CORRECTION)

seq#	ID#	Sta	depth	ABS	CONC [ppb]	d_2 [ppb]	d_1 [ppb]	$C_{extract}$ [ppm]	G_w g	R d/w	C_{vol} ml	W_{sto} ml	V_{ext} ml	M_{ext} µg	C_{sed} µg/g	C_{sed} µmol/g
0	Instr.	Zero		0.002												
1	B	Blank		0.006	2.36											
2	S1	120ref		0.410	161.29											
*3	54	5a	8–10a	1.697	667.58	6675.85	33379.23	33.38	6.33	0.4072	35.0	21.12	49.72	1659.50	643.82	10.13
4	55	3a	8–10a	0.333	131.00	1309.99	6549.96	6.55	4.20	0.2574	35.0	43.56	74.16	485.77	449.34	7.07
5	56	3b	8–10	0.218	85.76	857.59	4287.96	4.29	3.81	0.5225	35.0	31.81	62.86	269.54	135.40	2.13
6	57	3b	4–6a	0.141	55.47	554.68	2773.41	2.77	2.27	0.5123	35.0	19.09	51.74	143.49	123.38	1.94
7	58	4b	4–6b	0.074	29.11	291.11	1455.55	1.46	2.32	0.2828	35.0	27.70	60.25	87.70	133.67	2.10
8	59	4b	0–2a	0.052	20.46	204.56	1022.82	1.02	2.29	0.2307	35.0	23.38	55.99	57.26	108.39	1.71
9	I4	Reference		0.198	77.89	778.91	3894.57	3.89								
10	60	2b	0–2a	0.135	53.11	531.08	2655.39	2.66	2.62	0.2947	35.0	29.48	61.73	163.91	212.28	3.34
11	61	2a	8–10a	0.149	58.62	586.15	2930.76	2.93	5.44	0.3786	35.0	30.87	60.30	176.74	85.81	1.35
12	62	3a	20–22	0.244	95.99	959.87	4799.37	4.80	4.59	0.1727	35.0	40.83	71.06	341.04	430.23	6.77
13	63	2a	18–20	0.162	63.73	637.29	3186.47	3.19	3.73	0.3838	35.0	34.71	65.83	209.75	146.52	2.31
14	64	5a	0–2b	0.462	181.75	1817.47	9087.33	9.09	7.87	0.3686	35.0	31.52	58.53	531.90	183.36	2.89
15	65	3b	0–2a	0.154	60.58	605.82	3029.11	3.03	2.75	0.3639	35.0	28.69	60.81	184.20	184.07	2.90
16	DUP66	2b	4–6a	0.081	31.86	318.65	1593.23	1.59	1.20	0.3480	35.0	20.26	53.97	85.98	205.89	3.24
17	66	2b	4–6a	0.082	32.26	322.58	1612.90	1.61	1.20	0.3480	35.0	20.26	53.97	87.04	208.43	3.28
18	16	FB192 2000		0.027	10.62	106.22	531.08	0.53								
19	67	3a	30–32	0.471	185.29	1852.87	9264.36	9.26	5.25	0.1727	35.0	40.17	69.75	646.15	712.66	11.21
20	68	3b	20–22	0.126	49.57	495.67	2478.36	2.48	4.59	0.1727	35.0	25.80	56.10	139.05	175.41	2.76
21	S1	180ref		0.574	225.81											
22	B3	Blank		0.004	1.57	15.74	78.68	0.08								
rerun	54(5ul)5a		8–10a	0.908	357.20	3571.99	17859.95	17.86								
rerun	54(5ul)5a		8–10a	0.840	330.45	3304.48	16522.42	16.52								
rerun	54(5ul)5a		8–10a	0.809	318.25	3182.53	15912.67	15.91								
rerun	54(5ul)5a		8–10a	0.858	337.53	3375.30	16876.48	16.88								
avg	54(5ul)5a		8–10a	0.854	335.86	3358.58	16792.88	16.79	*2 6.33	0.4072	35.0	21.12	49.72	1669.76	647.80	10.19
rerun	S1 120ref			0.411												
rerun	S1 180ref			0.577												

QA Check:

I4:	actual/reference	.198/.173	=	114.5%
DUP:	(DUP66/66) – 1	(.081/.082) – 1	=	1.2%
S1 120:	actual/reference	.410/.332	=	123.5%**
S1 180:	actual/reference	.574/.498	=	115.3%
BLANKS:	values ≤ 2x(0.004)			YES

* Sample number 54 was off scale. At the end of the batch the sample was rerun usinga 5-µl sample volume. The average of the 4 reanalyses was multiplied by 2 to obtain a comparable concentration.

** QA criteria exceeded.

(Contd)

Table C-2. Raw and calculated data for the determination of SEM concentrations of lead and zinc measured by Graphite Furnace Atomic Absorption (GFAA). For each batch the sample sequence number (seq#), the sample identification number (ID#), the station location (Sta), the core depth of sample in cm (depth), the absorbance units measured with the GFAA (ABS), the concentration (ppb) determined from the regression standard curve (CONC), the concentration (ppb) of the second dilution (d_2), the concentration of the first dilution (d_1), the concentration of the extract ($C_{extract}$), the weight of the sample (G_w), the dry to wet weight ratio of the sample (R), the centrifuged volume (C_{vol}), the weight of storage vial and sample (W_{sto}), the calculated volume of the extract (V_{ext}), the mass of the metal in the extract (M_{ext}), and the concentration of the sediment sample (C_{sed}) in µg/g and µmol/g (dry weight) are given. **(A)** Lead batch number RUN1 29 JAN 1992. **(B)** Lead batch number RUN2 30 JAN 1992. **(C)** Zinc batch number RUN1 30 JAN 1992. Quality Assurance (QA) data are presented for each batch.

(A) LEAD RUN1 29 JUN 92 CONC = ABS/0.001185 (NO BLANK CORRECTION)

seq#	ID#	Sta	depth	ABS	CONC [ppb]	d_2 [ppb]	d_1 [ppb]	$C_{extract}$ [ppm]	G_w g	R d/w	C_{vol} ml	W_{sto} ml	V_{ext} ml	M_{ext} µg	C_{sed} µg/g	C_{sed} µmol/g
1	MB	Blank		0.001	0.84											
2	9	1a	0–10	0.065	54.85	548.52	2742.62	2.74	13.96	0.7123	35.0	41.05	61.96	169.92	17.09	0.08
3	10	FB190	1800	0.001	0.84	8.44	42.19	0.04								
4	11	2a	0–10	0.077	64.98	649.79	3248.95	3.25	3.48	0.3779	45.0	3.80	75.17	244.22	185.71	0.90
5	12	3a	0–10	0.103	86.92	869.20	4345.99	4.35	5.82	0.3377	45.0	38.79	77.81	338.14	172.05	0.83
6	13	4a	0–10	0.233	196.62	1966.24	9831.22	9.83	10.90	0.4349	45.0	39.49	73.45	722.08	152.32	0.74
7	14	5a	0–10	0.271	228.69	2286.92	11434.60	11.43	7.27	0.4245	45.0	38.36	75.94	868.29	281.35	1.36
8	15	4a	0–2b	0.080	67.51	675.11	3375.53	3.38	4.14	0.2402	45.0	31.68	72.40	244.40	245.77	1.19
9	M1	120ref		0.171	144.30	1443.04	7215.19	7.22								
10	16	FB190	2000	0.003	2.53	25.32	126.58	0.13								
11	17	1b	0–10	0.047	39.66	396.62	1983.12	1.98	4.76	0.5895	35.0	41.56	71.62	142.03	50.61	0.24
12	18	FB200	1700	0.000	0.00	0.00	0.00	0.00								
13	19	2b	0–10	0.149	125.74	1257.38	6286.92	6.29	4.15	0.3679	35.0	32.67	63.38	98.45	260.98	1.26
14	20	3b	0–10	0.036	30.38	303.80	1518.99	1.52	2.61	0.5801	35.0	27.57	59.84	90.89	60.03	0.29
15	21	4b	0–10	0.067	56.54	565.40	2827.00	2.83	4.94	0.3044	35.0	27.60	57.55	162.69	108.19	0.52
16	22	4b	0–10	0.076	64.14	641.35	3206.75	3.21	5.47	0.3044	35.0	23.68	53.12	170.34	102.30	0.49
17	DUP27	3a	4–6b	0.076	64.14	641.35	3206.75	3.21	3.75	0.2336	35.0	39.23	70.30	225.45	257.36	1.24
18	27	3a	4–6b	0.072	60.76	607.59	3037.97	3.04	3.75	0.2336	35.0	39.23	70.30	213.58	243.81	1.18
19	23	5b	0–10	0.188	158.65	1586.50	7932.49	7.93	3.32	0.3958	35.0	24.97	56.54	448.52	341.33	1.65
20	24	FB198	0015	0.000	0.00	0.00	0.00	0.00								
21	25	4b	0–2b	0.015	12.66	126.58	632.91	0.63	1.51	0.2307	35.0	16.17	49.59	31.38	90.09	0.43
22	26	FB190	1210	0.001	0.84	8.44	42.19	0.04								
23	5	2b	0–2c	0.125	105.49	1054.85	5274.26	5.27	8.17	0.2947	45.0	23.77	60.52	319.2	132.58	0.64
24	6	1a	0–2a	0.029	24.47	244.73	1223.63	1.22	7.18	0.7123	45.0	27.58	65.30	79.90	15.62	0.08
25	4	5a	0–2a	0.173	145.99	1459.92	7299.58	7.30	6.97	0.3686	45.0	32.19	70.09	511.66	199.16	0.96
26	2	3a	0–2b	0.100	84.39	843.88	4219.41	4.22	5.96	0.1957	45.0	22.63	61.59	259.86	222.79	1.08
27	60	2b	0–2a	0.037	31.22	312.24	1561.18	1.56	2.62	0.2947	35.0	29.48	61.73	96.37	124.81	0.60
28	B2	Blank		0.000	0.00	0.00	0.00	0.00								

QA Check:

DUP:	(DUP27/27) – 1	(.076/.072) – 1	=	4.6%
M1 120:	actual/reference	.171/.171	=	106.0%
BLANKS:	values ≤ 2x(0.001)			YES

(Contd)

Table C-2. Continued.

(B) LEAD RUN2 0201 JAN 30 1992. CONC = ABS/0.001185 (NO BLANK CORRECTION)

seq#	ID#	Sta	depth	ABS	CONC [ppb]	d_2 [ppb]	d_1 [ppb]	$C_{extract}$ [ppm]	G_w g	R d/w	C_{vol} ml	W_{sto} ml	V_{ext} ml	M_{ext} µg	C_{sed} µg/g	C_{sed} µmol/g
1	MB	Blank		0.001	0.84	8.44	42.19	0.04								
2	M1	120ref		0.174	146.84	1468.35	7341.77	7.34								
3	3	1b	0–2a	0.043	36.29	362.87	1814.35	1.81	6.82	0.6376	45.0	23.45	61.55	111.67	25.68	0.40
4	49	2a	0–2a	0.116	97.89	978.90	4894.51	4.89	6.81	0.3209	35.0	38.93	66.96	327.74	149.97	
5	44	3a	0–2a	0.050	42.19	421.94	2109.70	2.11	2.84	0.1957	35.0	39.24	71.22	150.25	270.34	
6	51	4a	0–2a	0.086	72.57	725.74	3628.69	3.63	5.40	0.2402	35.0	31.75	61.22	222.14	171.27	
7	36	5b	0–2a	0.027	22.78	227.85	1139.24	1.14	1.15	0.2821	35.0	26.57	60.29	68.69	211.73	
8	dup47			lost												
9	47	2a	4–6a	0.039	32.91	329.11	1645.57	1.65	2.04	0.3551	35.0	28.50	61.33	100.92	139.31	
10	9	4b	0–2a	0.020	16.88	168.78	843.88	0.84	2.29	0.2307	35.0	23.38	55.99	47.24	89.43	
11	64	5a	0–2b	0.221	186.50	1864.98	9324.89	9.32	7.87	0.3686	35.0	31.52	58.53	545.81	188.15	
12	M1	180ref		0.248	209.28	2092.83	10464.14	10.46								
13	b2	Blank		0.000	0.00	0.00	0.00	0.00								
rerun	51	4a	0–2a	0.088	74.26	742.62	3713.08	3.71	5.40	0.2402	35.0	31.75	61.22	227.31	175.25	
rerun	51	4a	0–2a	0.084	70.89	708.86	3544.30	3.54	5.40	0.2402	35.0	31.75	61.22	216.98	167.28	

QA Check:

DUP:	(lost)		
M1 120:	actual/reference	.174/.171	= 101.8%
M1 180:	actual/reference	.248/.239	= 103.8%
BLANKS:	values ≤ 2x(0.001)		YES

(Contd)

Table C-2. Continued.

(C) ZINC RUN 1 30 JAN 1992 CONC = (ABS – Blank)/0.00274 (Blank = 0.0595)

seq#	ID#	Sta	depth	ABS	CONC [ppb]	d_2 [ppb]	d_1 [ppb]	$C_{extract}$ [ppm]	G_w g	R d/w	C_{vol} ml	W_{sto} ml	V_{ext} ml	M_{ext} µg	C_{sed} µg/g	C_{sed} µmol/g
0	B	BLANK		0.075	27.29											
1	MB	BLANK		0.044	16.01											
2	9	1a	0–10	0.312	91.89	918.85	4594.25	4.59	13.96	0.7123	35.0	41.05	61.96	284.64	28.62	0.44
3	10	FB190	1800	0.085	9.28	92.79	463.97	0.46								
4	11	2a	0–10	0.498	159.57	1595.71	7978.53	7.98	3.48	0.3779	45.0	33.80	75.17	599.74	456.04	6.98
5	12	3a	0–10	0.465	147.56	1475.62	7378.09	7.38	5.82	0.3377	45.0	38.79	77.81	574.06	292.08	4.47
6	13	4a	0–10	0.646	213.43	2134.28	10671.40	10.67	10.90	0.4349	45.0	39.49	73.45	783.79	165.34	2.53
7	14	5a	0–10	0.863	292.39	2923.94	14619.72	14.62	7.27	0.4245	45.0	38.36	75.94	1110.15	359.73	5.50
8	15	4a	0–2b	0.427	133.73	1337.34	6686.68	6.69	4.14	0.2402	45.0	31.68	72.40	484.14	486.85	7.45
9	16	FB190	2000	0.177	42.76	427.58	2137.92	2.14								
10	17	1b	0–10	0.268	75.87	758.73	3793.67	3.79	4.76	0.5895	35.0	41.56	71.62	271.69	96.82	1.48
11	M1	180ref		0.523	168.67	1686.68	8433.41	8.43								
12	18	FB200	1700	0.086	9.64	96.43	482.17	0.48								
13	21	4b	0–10	0.376	115.17	1151.75	5758.73	5.76	4.94	0.3044	35.0	27.60	57.55	331.40	220.38	3.37
14	22	4b	0–10	0.385	118.45	1184.50	5922.49	5.92	5.47	0.3044	35.0	23.68	53.12	314.60	188.94	2.89
15	23	5b	0–10	0.734	245.45	2454.51	12272.56	12.27	3.32	0.3958	35.0	24.97	56.54	693.92	528.07	8.08
16	24	FB198	0015	0.085	9.28	92.79	463.97	0.46								
17	25	4b	0–2b	0.174	41.67	416.67	2083.33	2.08	1.51	0.2307	35.0	16.17	49.59	103.31	296.55	4.54
18	26	FB190	1210	0.435	136.64	1366.45	6832.24	6.83								
19	19	2b	0–10	0.551	178.86	1788.57	8942.87	8.94	4.15	0.3679	35.0	32.67	63.38	566.78	371.23	5.68
20	20	3b	0–10	0.27	76.60	766.01	3830.06	3.83	2.61	0.5801	35.0	27.57	59.84	229.17	151.36	2.32
21	DUP27	3a	4–6b	0.353	106.80	1068.05	5340.25	5.34	3.75	0.2336	35.0	39.23	70.30	375.44	428.58	6.56
22	27	3a	4–6b	0.341	102.44	1024.38	5121.91	5.12	3.75	0.2336	5.0	39.23	70.30	360.09	411.06	6.29
23	5	2b	0–2c	0.534	172.67	1726.71	8633.55	8.63	8.17	0.2947	45.0	23.77	60.52	522.52	217.02	3.32
24	6	1a	0–2a	0.201	51.49	514.92	2574.60	2.57	7.18	0.7123	45.0	27.58	65.30	168.12	32.87	0.50
25	4	5a	0–2a	0.928	316.05	3160.48	15802.40	15.80	6.97	0.3686	45.0	32.19	70.09	1107.66	431.14	6.59
26	2	3a	0–2b	0.436	137.01	1370.09	6850.44	6.85	5.96	0.1957	45.0	22.63	61.59	421.90	361.72	5.53
27	3	1b	0–2a	0.356	107.90	1078.97	5394.83	5.39	6.82	0.6376	45.0	23.45	61.55	332.04	76.36	1.17
28	49	2a	0–2a	0.559	181.77	1817.69	9088.43	9.09	6.81	0.3209	35.0	38.93	66.96	608.56	278.48	4.26
29	44	3a	0–2a	0.334	99.89	998.91	4994.54	4.99	2.84	0.1957	35.0	39.24	71.22	355.71	640.00	9.79
30	51	4a	0–2a	0.441	138.83	1388.28	6941.41	6.94	5.40	0.2402	35.0	31.75	61.22	424.95	327.62	5.01
31	36	5b	0–2a	0.244	67.14	671.40	3356.99	3.36	1.15	0.2821	35.0	26.57	60.29	202.40	623.91	9.54
32	59	4b	0–2a	0.194	48.94	489.45	2447.23	2.45	2.29	0.2307	35.0	23.38	55.99	137.01	259.34	3.97
33	64	5a	0–2b	1.048	359.72	3597.16	17985.81	17.99	7.87	0.3686	35.0	31.52	58.53	1052.75	362.91	5.55

QA Check:

DUP:	(DUP27/27) – 1	–(.353/.341) – 1	=	3.5%
M1 180:	actual/reference	.523/.545	=	96.0%
BLANKS:	values ≤ 2x(0.0595)			YES

(Contd)

Table C-3. SEM for Cu, Pb, and Zn and AVS concentrations measured in sediment cores collected from Sinclair Inlet. The SEM/AVS value is calculated for composite and surface samples.

Station	Depth (cm)	SEM Metal	Sed (ppm)	Sed (µmol/g)	AVS (µmol/g)	SEM/AVS
1a	0–10	Cu	8.44	0.13	0.79	0.827
1a	0–10	Pb	17.09	0.08		
1a	0–10	Zn	28.62	0.44		
1a	0–2	Cu	6.53	0.10	0.10	6.809
1a	0–2	Pb	15.62	0.08		
1a	0–2	Zn	32.87	0.50		
1a	4–6	Cu	7.39	0.12	0.43	0.271
1a	8–10	Cu	24.95	0.39	3.03	0.130
1b	0–10	Cu	27.11	0.43	10.46	0.206
1b	0–10	Pb	50.61	0.24		
1b	0–10	Zn	96.82	1.48		
1b	0–2	Cu	18.37	0.29	3.34	0.557
1b	0–2	Pb	25.68	0.40		
1b	0–2	Zn	76.36	1.17		
1b	08–10	Cu	24.38	0.38	10.46	
1b	20–22	Cu	39.68	0.62	3.93	
2a	0–10	Cu	188.88	2.97	73.56	0.147
2a	0–10	Pb	185.71	0.90		
2a	0–10	Zn	456.04	6.98		
2a	0–2	Cu	197.08	3.10	70.77	0.114
2a	0–2	Pb	149.97	0.72		
2a	0–2	Zn	278.48	4.26		
2a	04–6	Cu	206.49	3.25	156.09	
2a	04–6	Cu	213.15	3.35		
2a	04–6	Pb	139.31	0.67		
2a	08–10	Cu	85.81	1.35	133.96	
2a	18–20	Cu	146.52	2.31		
2b	0–10	Cu	191.88	3.02	21.96	0.453
2b	0–10	Pb	260.98	1.26		
2b	0–10	Zn	372.23	5.68		
2b	0–2	Cu	211.12	3.32	52.30	0.139
2b	0–2	Pb	132.58	0.64		
2b	0–2	Zn	217.02	3.32		
2b	0–2	Cu	212.28	3.34	20.16	
2b	0–2	Pb	124.81	0.60		
2b	4–6	Cu	208.43	3.28	83.19	
2b	4–6	Cu	205.89	3.24	83.19	
2b	4–6	Cu	210.33	3.31	82.02	
2b	8–10	Cu	135.75	2.14	90.34	
2b	20–22	Cu	390.91	6.15	117.54	

(Contd)

Table C-3. SEM for Cu, Pb, and Zn and AVS concentrations measured in sediment cores collected from Sinclair Inlet. The SEM/AVS value is calculated for composite and surface samples. Continued.

Station	Depth (cm)	SEM Metal	Sed (ppm)	Sed (µmol/g)	AVS (µmol/g)	SEM/AVS
3a	0–10m	Cu	214.13	3.37		
3a	0–10m	Cu	211.80	3.33	3.46	2.500
3a	0–10m	Pb	172.05	0.83		
3a	0–10m	Zn	292.08	4.47		
3a	0–2	Cu	377.01	5.93	69.57	0.180
3a	0–2	Pb	222.79	1.08		
3a	0–2	Zn	361.72	5.53		
3a	0–2	Cu	342.78	5.39	69.06	0.239
3a	0–2	Pb	270.34	1.30		
3a	0–2	Zn	640.00	9.79		
3a	4–6	Cu	368.41	5.80	105.29	
3a	4–6	Cu	268.36	4.22	71.12	
3a	4–6	Cu	280.99	4.42		
3a	4–6	Pb	243.81	1.18		
3a	4–6	Pb	257.36	1.24		
3a	4–6	Zn	428.58	6.56		
3a	4–6	Zn	411.06	6.29		
3a	8–10	Cu	449.34	7.07	54.66	
3a	8–10	Cu	349.93	5.51	55.90	
3a	20–22	Cu	430.23	6.77	0.39	
3a	30–32	Cu	712.66	11.21	0.45	
3b	0–10	Cu	73.85	1.16	67.06	0.056
3b	0–10	Pb	60.03	0.29		
3b	0–10	Zn	151.36	2.32		
3b	0–2	Cu	184.07	2.90	6.09	
3b	04–6	Cu	123.38	1.94	12.15	
3b	08–10	Cu	135.40	2.13	1.71	
3b	20–22	Cu	175.41	2.76	9.99	
4a	0–10	Cu	127.39	2.00	20.14	0.262
4a	0–10	Pb	152.32	0.74		
4a	0–10	Zn	165.34	2.53		
4a	0–2	Cu	247.87	3.90	41.16	0.237
4a	0–2	Pb	171.27	0.83		
4a	0–2	Pb	175.25	0.85		
4a	0–2	Pb	167.28	0.81		
4a	0–2	Zn	327.62	5.01		
4a	0–2	Cu	282.13	4.44	37.11	0.352
4a	0–2	Pb	245.77	1.19		
4a	0–2	Zn	486.85	7.45		
4a	4–6	Cu	237.69	3.74	86.08	
4a	8–10	Cu	263.06	4.14	34.20	
4a	20–22	Cu	156.91	2.47	10.70	

(Contd)

Table C-3. SEM for Cu, Pb, and Zn and AVS concentrations measured in sediment cores collected from Sinclair Inlet. The SEM/AVS value is calculated for composite and surface samples. Continued.

Station	Depth (cm)	SEM Metal	Sed (ppm)	Sed (µmol/g)	AVS (µmol/g)	SEM/AVS
4b	0–10	Cu	91.62	1.44	41.67	0.116
4b	0–10	Pb	102.30	0.49		
4b	0–10	Zn	188.94	2.89		
4b	0–10	Cu	116.68	1.84	45.66	0.125
4b	0–10	Pb	108.19	0.52		
4b	0–10	Zn	220.38	3.37		
4b	0–2	Cu	92.40	1.45	23.04	0.279
4b	0–2	Pb	90.09	0.43		
4b	0–2	Zn	296.55	4.54		
4b	0–2	Cu	108.39	1.71	23.75	0.257
4b	0–2	Pb	89.43	0.43		
4b	0–2	Zn	259.34	3.97		
4b	4–6	Cu	137.87	2.17	37.40	
4b	4–6	Cu	133.67	2.10	43.80	
4b	8–10	Cu	91.15	1.43	28.54	
4b	20–22	Cu	28.18	0.44	14.52	
5a	0–10	Cu	169.88	2.67	97.98	0.097
5a	0–10	Pb	281.35	1.36		
5a	0–10	Zn	359.73	5.50		
5a	0–2	Cu	180.31	2.84		
5a	0–2	Cu	180.85	2.85	66.12	0.157
5a	0–2	Pb	199.16	0.96		
5a	0–2	Zn	431.14	6.59		
5a	0–2	Cu	183.36	2.89	56.77	0.165
5a	0–2	Pb	188.15	0.91		
5a	0–2	Zn	362.91	5.55		
5a	4–6	Cu	394.71	6.21	90.86	
5a	4–6	Cu	374.08	5.89	58.75	
5a	8–10	Cu	306.92	4.83	280.66	
5a	8–10	Cu	344.48	5.42		
5a	8–10	Cu	643.82	10.13		
5a	8–10	Cu	323.90	5.10		
5a	8–10	Cu	318.69	5.02		
average			387.56	6.10		
5a	8–10	Cu	599.25	9.43	268.38	
5a	8–10	Cu	302.27	4.76		
5a	8–10	Cu	304.91	4.80		
5a	8–10	Cu	322.42	5.07		
5a	8–10	Cu	619.73	9.75		
average			429.71	6.76		
5b	0–10	Cu	444.34	6.99	65.24	0.256
5b	0–10	Pb	341.33	1.65		
5b	0–10	Zn	528.07	8.08		
5b	0–2	Cu	376.53	5.93	52.74	0.313
5b	0–2	Pb	211.73	1.02		
5b	0–2	Zn	623.91	9.54		
5b	4–6	Cu	183.29	2.88	90.86	
5b	8–10	Cu	592.40	9.32	196.30	
5b	20–22	Cu	281.50	4.43	112.62	

Appendix D

DETERMINATIONS OF ORGANIC MATTER CONTENT BY LOSS ON IGNITION FOR SEDIMENT SAMPLES FROM SINCLAIR INLET

Station	Depth	Rep	Dish #	Dish wt	g Preburn	g Postburn	F_{om}	AVS µmol/g
1a	0–2	a1	34	1.0	11.40	11.20	0.019	0.12
1a	0–10	a2	3	1.4	9.61	9.52	0.012	0.88
1a	0–10	a2	2	1.4	15.82	15.68	0.010	0.88
1a	4–6	a1	7	1.0	9.69	9.57	0.014	0.43
1a	8–10	a1	18	1.0	6.88	6.52	0.062	3.03
1b	0–10	a3	20	1.0	8.91	8.41	0.064	10.46
1b	0–2	a2	26	1.0	9.57	9.23	0.040	3.05
1b	20–22	a2	30	1.0	11.61	11.28	0.032	3.93
1b	4–6	a2	13	1.0	12.20	11.69	0.046	4.66
1b	8–10	a1	11	1.5	9.82	9.12	0.084	10.09
2a	0–10	a1	10	1.0	7.85	7.27	0.085	71.31
2a	0–2	a2	24	1.0	6.10	5.51	0.116	70.77
2a	18–20	a2	31	1.0	8.41	7.69	0.097	139.29
2a	4–6	a2	1	1.4	6.39	5.71	0.138	152.34
2a	8–10	a2	29	1.0	7.06	6.05	0.167	133.96
2b	0–10	a1	6	1.5	5.82	5.52	0.069	22.13
2b	0–2	a2	9	1.0	5.36	4.82	0.125	56.30
2b	20–22	a2	6	1.0	6.59	5.89	0.125	117.54
2b	4–6	a2	13	1.5	8.12	7.32	0.121	82.02
2b	8–10	a2	15	1.2	9.22	8.24	0.123	90.34
3a	0–9	a3	23	1.0	8.30	7.60	0.096	3.46
3a	20–22	4	28	1.0	5.28	4.97	0.074	0.39
3a	30–32	4	35	1.0	6.61	6.31	0.054	0.45
3a	4–6	a2	14	0.9	6.60	5.90	0.122	105.29
3a	8–10	a4	11	1.0	5.50	5.05	0.101	55.28
3b	0–10	a2	3	1.5	10.44	10.10	0.038	4.43
3b	0–10	a2	2	1.5	10.91	10.59	0.034	4.43
3b	0–2	a1	4	1.5	8.95	8.31	0.086	6.19
3b	20–22	a1	33	1.0	12.19	11.71	0.043	9.99
3b	4–6	a1	22	1.0	9.49	8.91	0.069	12.56
3b	8–10	a1	4	1.4	9.75	9.21	0.065	1.71
4a	0–10	a	8	1.5	7.19	6.33	0.151	20.14
4a	0–2	a1	17	1.0	5.10	4.58	0.128	39.13
4a	20–22	a	25	1.0	6.89	6.39	0.085	10.70
4a	4–6	a1	27	1.0	6.20	5.51	0.133	85.14
4a	8–10	a	21	1.0	6.98	6.27	0.119	34.20
4b	0–10	a1	12	1.5	11.44	9.89	0.156	43.67
4b	0–10	a1	36	1.0	6.62	5.72	0.160	43.67
4b	0–2	a2	1	1.5	4.88	4.45	0.127	23.39
4b	20–22	a2	14	1.0	6.02	5.60	0.084	14.52
4b	4–6	a2	5	1.0	5.60	4.88	0.158	40.60
4b	8–10	a2	5	1.5	6.34	5.75	0.122	28.54
5a	0–10	a5	32	1.0	7.89	7.11	0.113	97.98
5a	4–6	a	10	1.5	6.32	5.90	0.087	90.86
5a	grab	a3	8	1.0	7.22	6.54	0.110	68.55
5b	0–10	a2	19	1.0	6.75	6.26	0.085	67.03
5b	0–2	a1	16	1.0	6.30	5.71	0.112	59.45
5b	20–22	a1	15	1.0	8.31	7.80	0.070	112.62
5b	4–6	a1	9	1.5	10.85	10.00	0.091	165.28
5b	8–10	a1	12	1.0	7.40	6.91	0.077	196.30

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
September 1993

3. REPORT TYPE AND DATES COVERED
Final: June 1991–January 1992

4. TITLE AND SUBTITLE
ACID VOLATILE SULFIDES AND SIMULTANEOUSLY EXTRACTED COPPER, LEAD, AND ZINC IN SEDIMENTS OF SINCLAIR INLET, WASHINGTON

5. FUNDING NUMBERS
ME8352

6. AUTHOR(S)
Robert K. Johnston

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Naval Command, Control and Ocean Surveillance Center (NCCOSC)
RDT&E Division
San Diego, CA 92152–5001

8. PERFORMING ORGANIZATION REPORT NUMBER
TR 1552

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Engineering Field Activity Northwest
Naval Facilities Engineering Command
Silverdale Washington

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Acid volatile sulfides (AVS) and simultaneously extracted metal (SEM) concentrations of copper (Cu), lead (Pb), and zinc (Zn) were measured in the marine sediments of Sinclair Inlet, Puget Sound, Washington, as part of a project to evaluate the flux of metals between the sediment and bottom water of the Inlet. The AVS samples were collected from the same stations used to measure metal fluxes with a benthic chamber. The stations represented a range of previously measured heavy metal sediment concentrations in the Inlet.

Two sediment cores (10 to 30 cm depth) were collected from each station; one core was selected to determine the AVS profile (2-cm increments), and the other was homogenized to obtain a composite AVS value for the top 10 cm. The AVS measured in composite samples ranged from 0.8 to 98.0 μmol/g. For nine of the ten stations composite AVS concentrations were 2.2 to 10.3 times higher than the SEM concentrations of Cu, Pb, and Zn, and 1.1 to 6.2 times higher than the sum of divalent metal concentrations (Cd, Cu, Hg, Ni, Pb, Ag, and Zn) measured in bulk sediment grabs collected from the same stations. One station had a composite AVS concentration lower than the composite SEM concentration, resulting in SEM/AVS = 2.5. Seven of the ten stations had high AVS concentrations at the surface (> 20 μmol/g), which increased at intermediate depths and decreased towards the bottom of the core. Simultaneously extracted Cu profiles were relatively uniform with depth and ranged from 0.1 to 11.2 μmol/g. There was not a clear relationship between AVS and metal flux measured with the benthic chamber.

14. SUBJECT TERMS

acid volatile sulfide (AVS)	lead	organic matter
cadmium	manganese	sediment core
copper	metal flux	silver
divalent metal	mercury	simultaneously extracted metal (SEM)
iron	nickel	zinc

15. NUMBER OF PAGES
91

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAME AS REPORT

NSN 7540-01-280-5500

Standard form 298 (FRONT)