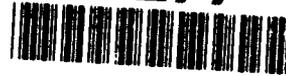


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Naval Command,
Control and Ocean
Surveillance Center RDT&E Division

San Diego, CA
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Technical Document 2434
February 1993

An Evaluation of Contaminant Flux Rates From Sediments of Sinclair Inlet, WA, Using a Benthic Flux Sampling Device

D. B. Chadwick
S. H. Lieberman
C. E. Reimers
D. Young



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**NAVAL COMMAND, CONTROL AND
OCEAN SURVEILLANCE CENTER
RDT&E DIVISION
San Diego, California 92152-5001**

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ADMINISTRATIVE INFORMATION

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SUMMARY OF FINDINGS

The objective of this project was to demonstrate the Benthic Flux Sampling Device (BFSD) on site to determine the mobility of contaminants in sediments off the Puget Sound Naval Shipyard (PSNS) in Sinclair Inlet, WA. Quantification of toxicant flux from the sediments will support ongoing assessment studies and facilitate the design of appropriate remediation strategies, if required.

The sampling in Sinclair Inlet focused on identifying contaminant fluxes from the sediments around the PSNS. From 30 June 1991 to 29 July 1991, we performed 10 deployments of the BFSD to characterize flux rates of contaminants from seven sites near the shipyard and three reference sites in Sinclair Inlet. Target contaminants included the trace metals arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn). Two sites were also sampled for organic contaminant release, including polynuclear aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs).

Several ancillary measurements were also performed to support the flux-rate measurements. Bulk-sediment chemical analyses were performed at each of the 10 sites to provide a baseline for interpreting flux data. To document the geochemical processes responsible for contaminant migration from the sediment, scientists from Scripps Institute of Oceanography (SIO) performed *in situ* microprofile measurements of oxygen, pH, sulfide, CO₂, and resistivity through the sediment-water interface. Time-series samples were also analyzed for silica as a check on BFSD performance. We performed analytical chemical analysis to determine Acid Volatile Sulfides (AVS) in sediments, which is believed to be a determining factor in mobility and bioavailability of trace metals. Hydrographic and water-quality surveys were performed in the inlet to document receiving water conditions during the BFSD deployments.

Trace metal flux rates were characterized as *release rates*, if the flux was positive, or as *uptake rates*, if the flux was negative, based on an 80-percent confidence interval of the slope from a linear regression of concentration vs. time. Levels of Cr and Hg fell below detection limits in all water samples, and, thus, no results could be obtained for these trace metals. The most consistent release rates were measured for Ni, Zn, and As. Release of Ni was observed at sites 2B, 3B, 4B, and 5A (see figure 5 for site locations), while uptake was not measured at any site; and the remaining six sites had no distinguishable flux (1A,1B,2A,3A,4A,5B). The maximum release rate of Ni was 565 $\mu\text{g}/\text{m}^2/\text{day}$ at shipyard site 5A. Release of Zn was measured at five sites (1B,2A,3A,5A,5B) with a maximum release of 837 $\mu\text{g}/\text{m}^2/\text{day}$, again at site 5A. Uptake of Zn was observed at site 1A, and four sites (2B,4A,4B,5B) showed no consistent Zn flux. Release was measured at four sites (1B,2B,3A,4B), while uptake was not found at any site; and the remaining sites (1A,2A,3B,4A,5A,5B) showed no flux. The maximum As release was 292 $\mu\text{g}/\text{m}^2/\text{day}$ at site 2B.

For Cu, Cd, and Pb, flux rates were not as consistently positive; and at several sites we observed sediment uptake of these metals. Cu release was measured only at site 3A (346 $\mu\text{g}/\text{m}^2/\text{day}$), while uptake was observed at four sites (1A,2A,2B,3B), and no flux was

measured at the remaining five sites (1B,4A,4B,5A,5B). Similarly, release of Cd was found at only 2 of the 10 sites (1A,5B), with uptake at 2 sites (2A,2B) and no detectable flux at 6 sites (1B,3A,3B,4A,4B,5A). The maximum Cd release rate was $68 \mu\text{g}/\text{m}^2/\text{day}$ at site 5B. Measurement of flux rates for Pb was hampered by the low levels present in many samples. Insufficient data were available to calculate a flux for six sites (1A,1B,2B,3A,4A,5A). Of the remaining sites, none showed a release of Pb, while two showed uptake (2A,3B) and two showed no flux (4B,5B).

Results for the PAH and PCB fluxes were obtained at sites 3B and 5B. At site 3B, release of several PAH compounds was observed and in particular for the more soluble, lower molecular weight PAHs such as naphthalene, acenaphthene, fluorene, and phenanthrene. Of the 24 PAH compounds measured, 11 showed a significant (80-percent CI) release, while the remainder had no detectable flux. The release rates for the compounds with detectable fluxes ranged from $28 \text{ ng}/\text{m}^2/\text{day}$ for Dibenzo[a,h]anthracene to a maximum of $6600 \text{ ng}/\text{m}^2/\text{day}$ for C1-Naphthalene. At site 5B, PAH release was observed for eight compounds predominantly of medium molecular weight (phenanthrene, fluoranthene, pyrene, and chrysene), while a small but statistically significant uptake was found for Benzo-b-fluoranthene. No detectable flux was found for the remaining 15 compounds. Small sample volumes and low ambient-water concentrations limited our ability to measure flux rates of PCB congeners. Only PCB-110 could be quantified, and these values can only be interpreted as upper limits, since all but one of them lacked second-ion confirmation from the GC/MS analysis. No detectable flux was observed at either site, and PCB concentrations based on the Aroclor 1254 equivalents were generally below $1 \text{ ng}/\text{l}$.

These results suggest that for most of the measured compounds, no release is taking place. For the trace metals, this may be related to the strongly reducing characteristics of the sediments adjacent to the shipyard as reflected in the shallow oxygen penetration, and the relatively high AVS and organic content. For Zn, Ni, and As, where measurable release was found, only Zn appeared to be strongly tied to shipyard sources, while Ni and As also exhibited release at sites removed from the shipyard. Bulk sediment results for the trace metals suggest that Zn and Hg at some sites are elevated relative to published criteria (State of WA, 1991). Together with the flux measurements, this suggests that Zn loading may represent a significant environmental issue and that Hg probably warrants further investigation. For PAHs and PCBs, the limited release is probably attributable to low-bulk levels, high-organic loading, and the high-particle affinity of many of these compounds. The release of lower molecular-weight PAHs at shipyard site 3B may have been mediated by bioturbation. The source of these compounds is attributed to recent input, since they are generally weathered or volatilized quickly in the marine environment. At site 5B, where the more moderate weight PAHs were released, the fluxes appeared to be more strongly coupled to the bulk sediment levels.

In general, where release of contaminants was found, the measured rates do not represent a significant source relative to other major inputs such as sewer discharges, nonpoint source runoff, and marinas. They may, however, represent an exposure pathway for benthic biota with a subsequent potential for toxicological effects and/or bioaccumulation.

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INTRODUCTION

OBJECTIVE

The objective of this project was to demonstrate the Benthic Flux Sampling Device (BFSD) on site to determine the mobility of contaminants in sediments off the Puget Sound Naval Shipyard in Sinclair Inlet, WA. Quantification of the flux of toxicants from the sediments will support ongoing assessment studies and, if necessary, the design of appropriate remediation strategies. (Refer to the last chapter in this document for a list of acronyms and abbreviations used in this study.)

BACKGROUND

Preliminary assessment and Site Investigation (SI) studies indicate that sediments adjacent to the Puget Sound Naval Shipyard (PSNS) in Sinclair Inlet may contain elevated levels of trace metals and organic compounds (GeoEngineers, 1989). Representatives from the Engineering Field Activity, NW, are currently conducting an extensive assessment of the area. Plans now call for chemical analyses and biological assessment of sediment samples collected at the site. However, these analyses do not address the potential for release of contaminants back into the water column from the sediment; nor do they address the natural factors that control toxicant migration and bioavailability. The bulk concentration of a toxic substance in sediment is not necessarily a valid measure for predicting biological risk (Di Toro, 1989). Bioassay methods may also represent an unrealistic departure from natural conditions, that is, where indicator species are exposed to sediment removed from the site and placed in a laboratory environment.

Previous studies indicate that biological uptake, accumulation, and toxicity result primarily from the fraction of the toxicant pool that is readily solubilized (Anderson and Morel, 1982). In surface sediments, production of this soluble fraction will in most cases cause it to migrate through the pore water and across the sediment-water interface. For these reasons, benthic toxicant fluxes can provide important supplemental information when trying to determine the environmental significance of contaminants in marine sediments. This approach provides a direct measure of the contribution of contaminated sediment to water-column loadings and also provides a unique *in situ* indicator of bioavailability and, hence, an estimate of the potential for environmental harm.

The Marine Environment Branch of the Naval Command, Control and Ocean Surveillance Center, Research, Development, Test and Evaluation Division (NRaD) has recently developed an instrument for *in situ* measurement of contaminant release rates from in-place sediments (Reimers et al., 1991; Chadwick et al., 1992). The device consists of a chamber and associated "landing gear" that can be lowered from a small craft to the bottom and released, isolating a volume of water in contact with the sediment. At preprogrammed times, generally over a period of 2 to 3 days, a microprocessor-based control system onboard the BFSD is then used to control collection of samples from the trapped volume within the chamber. Next, the chamber and samples are retrieved using a

standard acoustic-release mechanism. The flux is then calculated from the laboratory analysis of the change—over time—in concentration of the toxicant within the chamber. The microprocessor is also used to record data from a suite of sensors (temperature, salinity, oxygen, and pH) that monitor (and control if necessary) conditions within the dome during the flux rate measurement.

STUDY SITE

Sinclair Inlet is one of several bays located in the western-central Puget Sound basin (figure 1). The inlet is bordered by two population centers, Bremerton on the north, and Port Orchard on the south. The Bremerton shoreline is dominated by the piers and shipyard facilities of the PSNS, while the Port Orchard shoreline is characterized by several small marinas, and light commercial and residential development. A sewage outfall projects roughly 200 m into the inlet from the northwest shoreline.

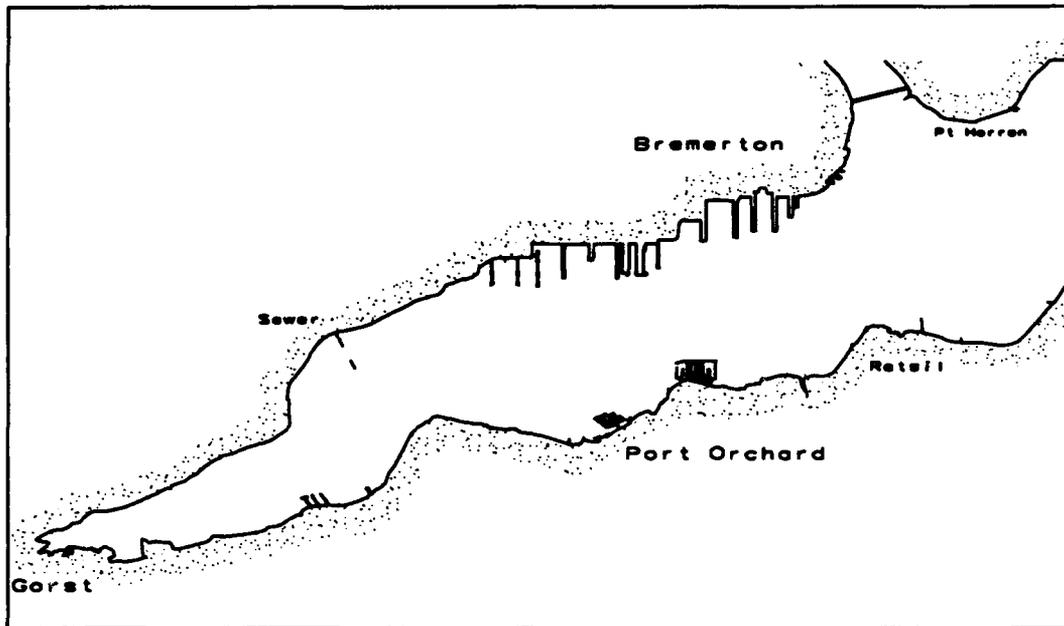


Figure 1. Study site in Sinclair Inlet. The Puget Sound Naval Shipyard is located along the southern shore of the City of Bremerton.

SELECTION OF ANALYTICAL PARAMETERS

The survey in Sinclair Inlet focused on identifying contaminant fluxes from the sediments around the PSNS. From 30 June 1991 to 29 July 1991, we deployed the BFSD 10 times to characterize flux rates of contaminants from seven sites near the shipyard and three reference sites in Sinclair Inlet. Target contaminants for which the BFSD had been tested prior to the investigation included the trace metals Cd, Cr, Cu, Ni, Pb, and Zn, and several polynuclear aromatic hydrocarbons (PAHs). Methods for As, Hg, and selected PCB congeners were under development during the study. Bulk-sediment data from the Site Investigation (SI) showed elevated levels of As, Cd, Cu, Hg, Pb, and Zn at some sites near the shipyard. Although the SI data showed no significant levels of PAHs or PCBs, previous studies indicated that PAHs and PCBs were present at elevated levels in at least some areas off the shipyard (GeoEngineers, 1989; Weston, 1990). Based on this information, our measurements were focused on flux rates for the trace metals listed in table 1. In addition, two deployments incorporated split samples for selected PAH compounds and PCB congeners (table 1).

Table 1. Target analytes for flux-rate measurements.

Trace Metals	PAHs	PCB Congeners*
		018
Cd	Acenaphthylene (AC)	028+031
Cr	Acenaphthene (AE)	052
Cu	Anthracene (A)	049
Hg*	Fluorene (F)	044
Ni	Phenanthrene (P)	074
Pb	Fluoranthene (FL)	070+076
Zn	Pyrene (PY)	066
	Benzo (a) Anthracene (BA)	095
	Chrysene (C)	101
	Benzo (b) Fluroanthene (BB)	099
	Benzo (k) Fluroanthene (BK)	110
	Benzo (a) Pyrene (BAP)	118
	Indeno (1,2,3,-cd) Pyrene (IP)	105
	Dibenzo (a,h) Anthracene (DA)	136
	Benzo (g,h,i) Perylene (BP)	149
		153
		141
		138
		176
		183
		174
		180
		170+190

* Indicates measurements techniques still under development.

SUPPORTING MEASUREMENTS

Several ancillary measurements were also performed in addition to the flux rate measurements in their support. Bulk sediment chemical analyses were performed at each of the 10 sites to provide a baseline for interpreting flux data. Scientists from Scripps Institute of Oceanography (SIO) performed *in situ* microprofile measurements (Reimers, 1987) of oxygen, pH, sulfide, CO₂, and resistivity through the sediment-water interface. These data were collected to provide a basis for understanding the geochemical processes responsible for contaminant migration from the sediment. Scripps also analyzed time-series samples for silica, a well-characterized nutrient (Berelson et al., 1987), as a check on BFSF performance.

Under an existing memorandum of agreement, the Environmental Protection Agency, Environmental Research Laboratory at Newport, OR (EPA-ERLN), performed detailed sediment and water chemistry for PAHs and PCBs. These data were used to assess release rates for these organic contaminants and to build on previous studies aimed at increasing knowledge of sediment/pore-water interactions.

Researchers from the University of Rhode Island (URI) also performed analytical chemical analyses to determine Acid Volatile Sulfides (AVS) in sediments. Sulfide content in marine sediments is a determining factor in mobility and bioavailability of trace metals (Di Toro et al., 1990). These measurements, in conjunction with sediment flux rate measurements, were designed to help explain the nature of contaminant release rates in the presence of sulfide and to provide a link between chemical measurements and biological measurements performed at the site.

Hydrographic and water quality surveys were also performed in the inlet using a real-time monitoring system aboard the survey boat (Chadwick and Salazar, 1991). This included surface-water mapping throughout the inlet as well as creating vertical profiles at each of the 10 BFSF sites. Measured parameters included temperature, salinity, pH, dissolved oxygen, transmittance, chlorophyll-*a*, oil fluorescence, and bathymetry. These data were compiled into areal maps and profiles to characterize conditions at the site during the BFSF survey.

SELECTION OF SAMPLING SITES

A series of 10 sites was selected based on chemical data from the ongoing Site Investigation (SI) and information from previous studies. Figures 2 and 3 show preliminary bulk sediment concentrations for trace metals from the SI surveys. Because BFSF deployments take approximately 3 days each, all the sites included in the SI could not be sampled. Instead, a series of 10 representative sites was selected within the shipyard and reference areas. The sites were chosen as representative areas with similar contaminant levels in the sediment. Ranking values were assigned for each of the eight target metals based on individual concentration. A cumulative ranking sum was then calculated for each site, and the sites were separated into five groups using a K-means clustering (figure 4). Two sites were then selected (1A,B-5A,B) from each cluster. These sites (figure 5) represent a

gradient in general metal-contamination levels, although individual metals may not follow this trend in all cases (e.g., As). Summary statistics for individual and cumulative sum metals are included in Appendix 1. Flux rate measurements were performed along this gradient to understand the relationship better between bulk sediment concentrations and toxicant mobility.

Sampling for PAHs and PCBs was performed at 2 of the 10 sites. At the shipyard, data from a previous study (Weston, 1990) indicate total PAH levels of approximately 5 ppm in the sediment to the west of pier 4. The first sampling was performed in this area, which corresponds with our station 5B. The second PAH/PCB sampling was done at our station 3B. Microprofile measurements were performed at 5 of the 10 sites, one from each of the cluster groups. Sites 1B, 2B, 3B, 4A, and 5B were selected as representative of these areas. Sample sites for silica analysis were identical to the 10 BFSD sites, as these measurements serve to confirm flux measurements taken by the BFSD. Sediment AVS measurements were performed on cores taken at each of the 10 sites. Bulk sediment samples were collected at each of the 10 sites for analysis of metals, PAHs, and PCBs.

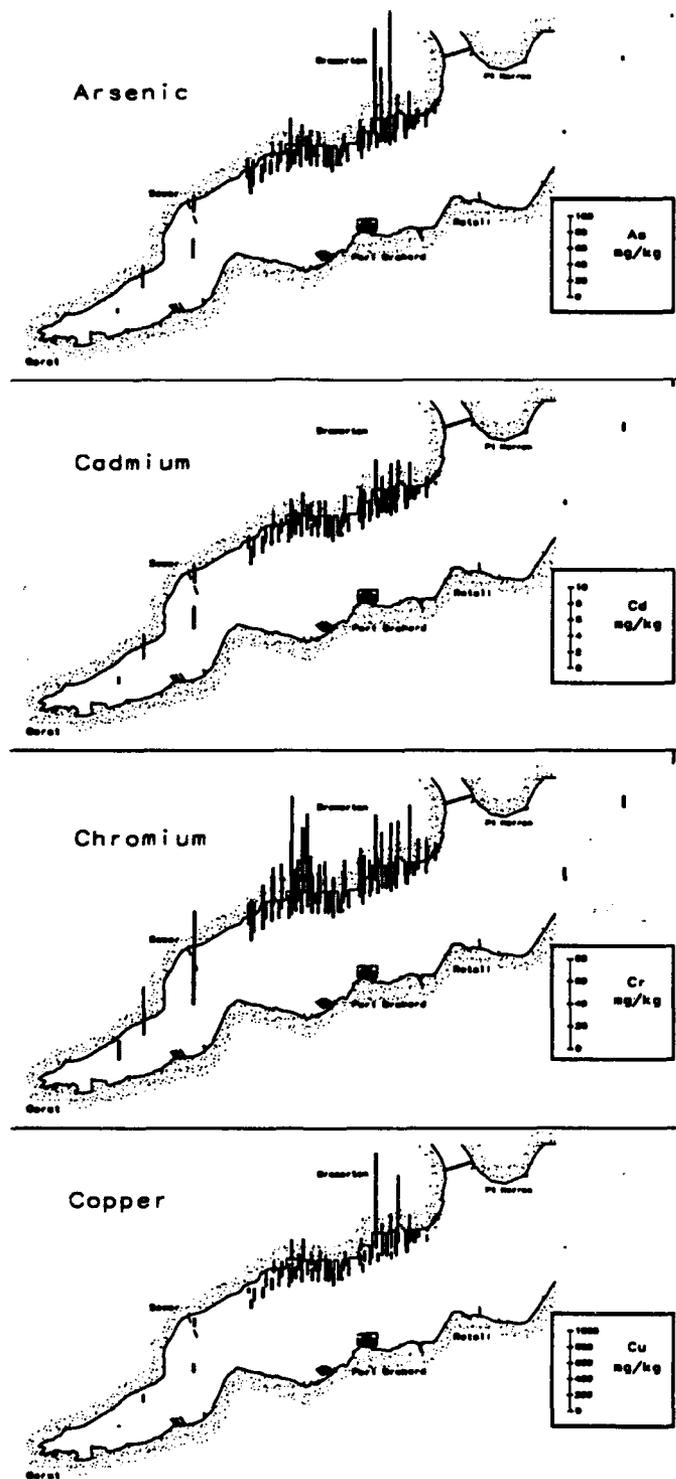


Figure 2. Preliminary SI bulk sediment data for As, Cd, Cr, and Cu.

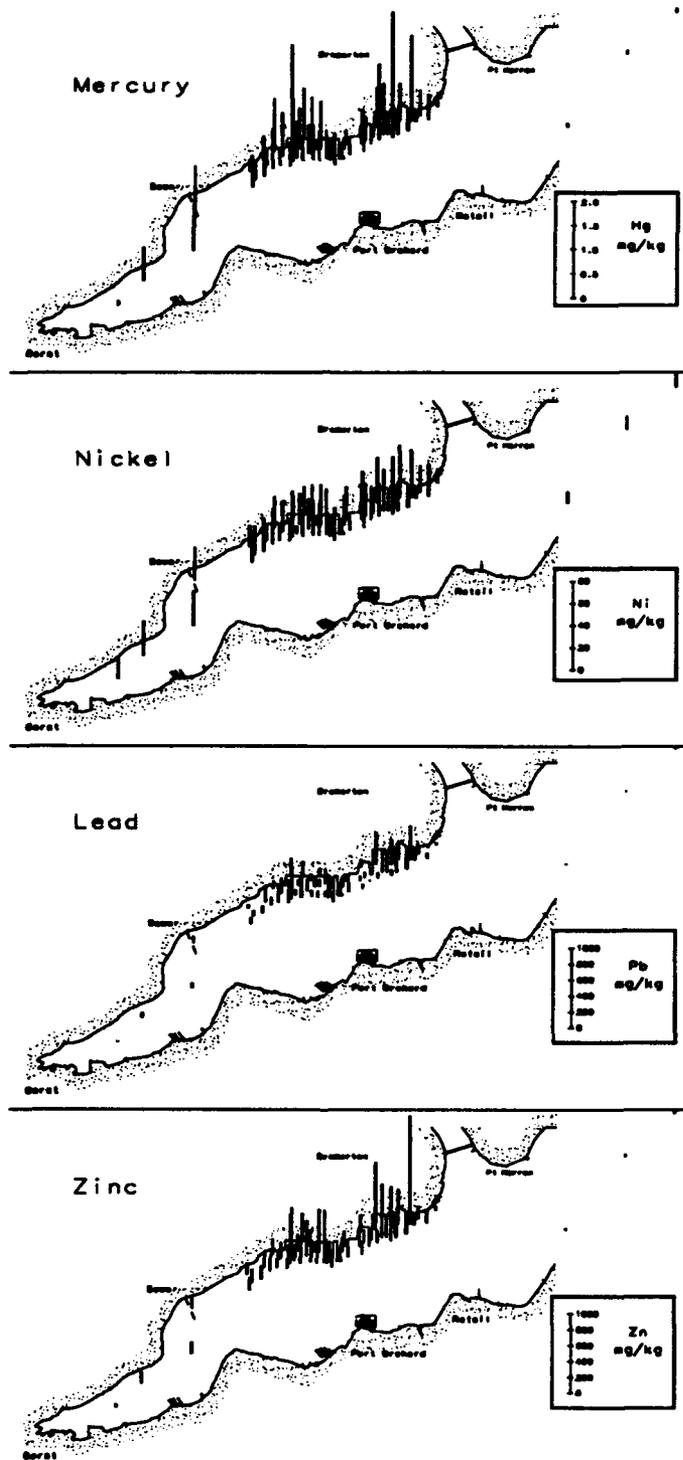


Figure 3. Preliminary SI bulk sediment data for Hg, Ni, Pb, and Zn.

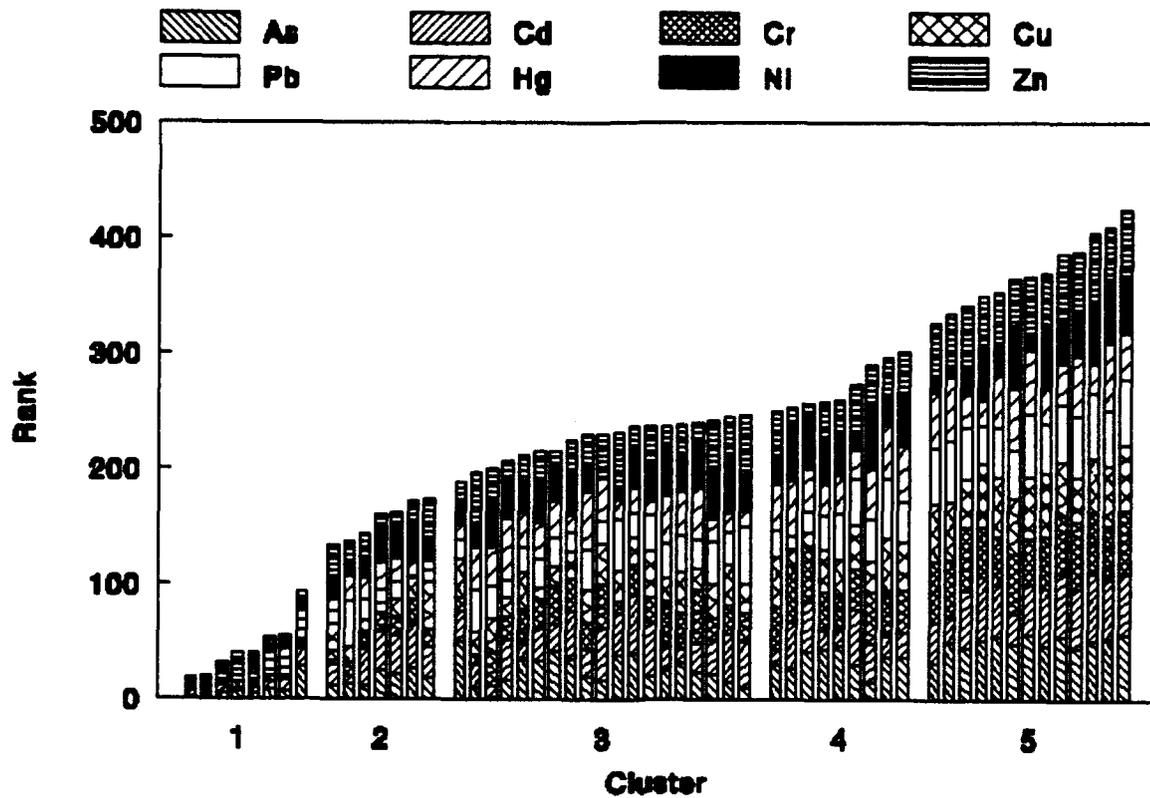


Figure 4. Cumulative rank sum clusters for eight metals: As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn, and their spatial locations in Sinclair Inlet.

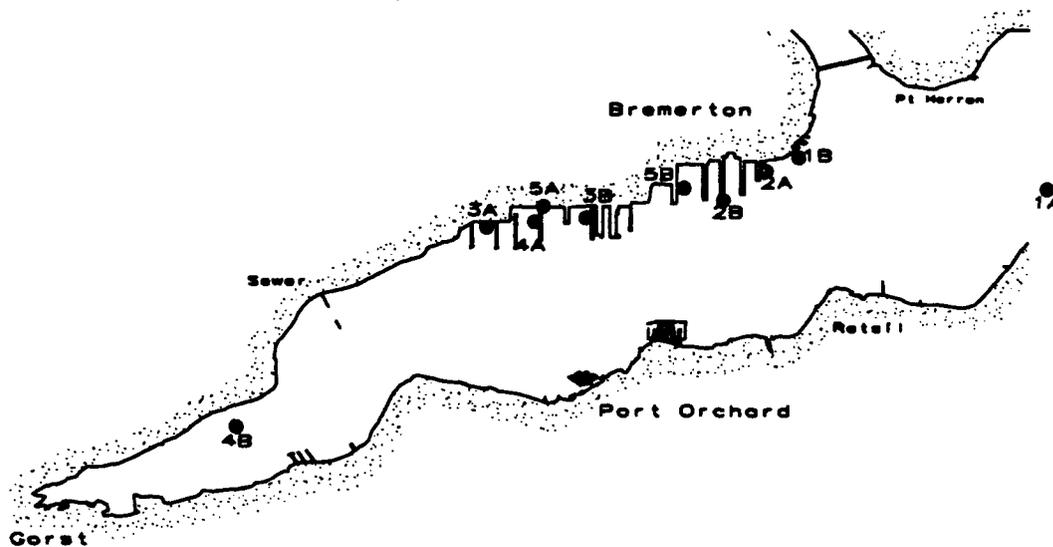


Figure 5. Sampling sites selected for the flux rate study.

INSTRUMENTATION AND METHODS

BFSD SYSTEM DESCRIPTION

The BFSD is an instrument for *in situ* measurement of toxicant flux rates from sediments. A flux out of—or into—the sediment is measured by isolating a volume of water above the sediment, drawing off samples from this volume over time, and analyzing these samples for increase or decrease in toxicant concentration. Increasing concentrations indicate that the toxicant is fluxing out of the sediment. Decreasing concentrations indicate that the toxicant is fluxing into the sediment. Initial tests carried out in conjunction with SIO and EPA-ERLN have shown that the system can be useful for measuring a variety of contaminant and nutrient flux rates.

The prototype BFSD system developed for this purpose is shown in figure 6. The system consists of an open-bottomed chamber mounted in a tripod-shaped framework with associated sampling gear, sensors, control system, power supply, and deployment/retrieval equipment. The entire device is approximately 1.2 by 1.2 m wide from leg to leg. The lower part of the framework contains the chamber, sampling valves, sampling bottles, and batteries. The chamber is box-shaped approximately 40-cm square by 25-cm tall and is constructed of polycarbonate. The top of the chamber is hinged at one edge so it may be left open during deployment to minimize sediment disturbance. The bottom of the chamber forms a knife edge with a flange 5 cm above the base, providing a positive seal between the box and the sediment.

Samples are drawn off through a 4-mm Teflon tube connected to a manifold of valves and into air-filled Teflon sampling bottles (500 ml). Sampling is initiated by the control system that opens the valves at preprogrammed intervals. The bottles then fill by hydrostatic pressure while venting through a check valve mounted at the top of the frame. Sensors for monitoring conditions within the chamber, including temperature, salinity, pH, and dissolved oxygen, are mounted on the chamber lid. A small pump maintains circulation in the flow-through system to the sensors and also is used to mix the chamber volume via a helical diffuser mounted vertically on the central axis of the box. The acquisition and control unit, oxygen-supply bottle, video camera, and retrieval-line canister are mounted on the vertical members of the frame. The oxygen system is used to maintain oxic conditions within the chamber by diffusing oxygen at a constant rate through a coil of thin-walled Teflon tubing. The upper frame houses an acoustically activated retrieval buoy that can be signaled from the surface to initiate retrieval. The BFSD is designed for use in coastal and inland waters to depths of 50 m. Typical deployment periods during the Sinclair study were approximately 2 days.

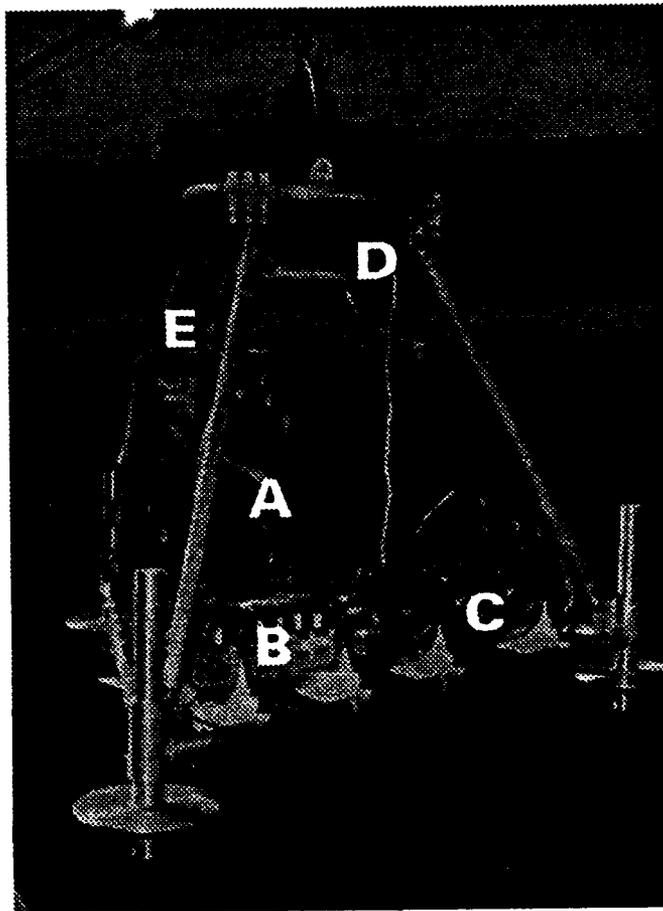


Figure 6. The Benthic Flux Sampling Device showing the polycarbonate chamber with the lid open (A), valve manifold (B), battery case (C), retrieval gear (D), and control/acquisition unit (E).

***IN SITU* SEDIMENT MICROPROFILER**

The microprofiler consists of a series of vertically mounted electrodes attached to the bottom of a pressure case containing the system electronics. Using an electric motor connected to a threaded drive rod, the electrodes are slowly driven down through the sediment-water interface and then several centimeters into the sediment column. For deployment in shallow water, the profiler is mounted in a small tripod framework similar to the one used for the BFSD. The design and calibration of the sensors are described in detail in Revsbech et al. (1983), Revsbech and Jorgensen (1986), Reimers (1987), and Archer et al. (1989). The profiling system is described by Reimers (1987). For this project, the microprofiler was fitted with sensors for measuring mm-scale profiles of dissolved O_2 , pH, ΣH_2S , pCO_2 , and resistivity. The ΣH_2S and pCO_2 sensors are still in development, while the other electrodes have been used extensively in the deep ocean and in San Diego Bay.

SAMPLE COLLECTION AND HANDLING

Sample collection and handling procedures were performed according to Puget Sound Estuary Program (PSEP) protocol (Tetra Tech, 1986) wherever possible. Occasionally, special instrumentation, collection techniques, and analysis methods required deviations from PSEP protocols. A summary of the samples collected is shown in table 2, and collection and handling procedures are described as follows.

Table 2. Sample collection matrix for the 10 sites in Sinclair Inlet.

Site	BFSD Time Series	BFSD t_0	Sediment Bulk Grab	Sediment Core AVS	Sediment Core Pore Water
1A	6	1	1	1	0
1B	6	1	1	1	0
2A	6	1	1	1	0
2B	6	1	1	1	0
3A	6	1	1	1	0
3B	6	4	2	1	1
4A	6	1	1	1	0
4B	6	1	1	1	0
5A	6	1	1	1	0
5B	6	4	2	1	1
Total	60	16	12	10	2

METAL FLUX SAMPLES

Time-series water samples were collected using the BFSD sampling system at each site. These samples filled into acid-washed, 500-ml Teflon (TFE) sampling bottles aboard the BFSD. After each deployment, blank ferrules were fitted in place of the sampling lines, and the samples were shipped (via overnight mail) on ice to NRaD for processing. Samples were filtered and acidified at NRaD immediately upon receipt. Initial (t_0) water samples were collected from outside the BFSD into precleaned 500-ml polyethylene bottles using the Teflon pumping system aboard the survey vessel. Next, these samples were refrigerated until the BFSD deployment was completed and then shipped to NRaD with the corresponding time-series samples. Split samples for silica analysis were taken from

time-series and t_0 samples prior to processing. Detailed procedures for BFSD preparation, deployment, and sample collection are given in Chadwick and Stanley, 1992.

PAH/PCB FLUX SAMPLES

Time-series water samples were collected for PAH/PCB analysis using the BFSD sampling system at sites 3B and 5B. These samples filled into precleaned, 500-ml borosilicate glass sampling bottles aboard the BFSD. After each deployment, blank ferrules were fitted in place of the sampling lines, and the samples were brought ashore for initial processing (split sample for metals, filtration, and preservation) by EPA-ERLN on-site personnel. Triplicate t_0 water samples were collected from outside the BFSD into precleaned 500-ml glass bottles using the Teflon pumping system aboard the survey boat. These samples were handled similarly as the time-series samples. The split samples for metals were transferred into precleaned, 250-ml polyethylene bottles and shipped on ice to NRaD.

BULK SEDIMENT SAMPLES

A bulk sediment grab was acquired at each site using a modified Van Veen grab. Sediment samples were transferred from the grab into precleaned, 500-ml wide-mouth polyethylene jars using a precleaned plastic scoop. The samples were shipped on ice to NRaD with the other BFSD samples. Split samples for PAH/PCB analysis were collected by dipping a precleaned, stainless steel scoop into precleaned 500-ml, wide-mouth glass jars.

SEDIMENT CORES

Sediment cores were collected at each site using a modified Wildco hand corer. Core samples were stored in the plastic collection liners until processed ashore. The cores were used for AVS analysis on site. Solids remaining from the AVS analysis were shipped to NRaD for further analysis of metals. Duplicate cores were collected for pore-water analysis of PAH/PCB at sites 3B and 5B.

HYDROGRAPHIC SURVEYS

Hydrographic data for surface waters were collected at a depth of 1 meter along three transects encompassing the length of the inlet. One transect ran along the northern shore, one roughly down the middle, and the last along the southern shore. Sampling in the western extent of the inlet was limited by shallow water. (The map contours generated in the region west of about $120^{\circ} 40' 40''$ may be distorted by extrapolation.) Vertical profiles were performed at each of the BFSD sampling sites, except for site 5A, where only bottom-water conditions were measured. Surface-water and vertical profile parameters included temperature, salinity, pH, dissolved oxygen, transmittance, chlorophyll-*a*, oil fluorescence, and bathymetry.

SAMPLE PROCESSING, STORAGE, AND ANALYSIS

Sample processing, storage, and analysis was under Puget Sound Estuary Program (PSEP) protocol wherever possible. Occasionally, special instrumentation, collection techniques, and analysis methods required deviations from PSEP protocols. A summary sample analysis matrix is shown in table 3, and the procedures are described as follows.

Table 3. Sample analysis matrix.

Samples	Metals by AA	Metals by ASV	Silica	AVS	PAH/PCB
BFSD Time Series	60	20	60	0	12
BFSD t_0	10	0	10	0	6
Sediment Bulk Grab	10	0	0	0	10
Sed. Core AVS/SEM	70	0	0	70	0
Sed. Pore Water	0	0	0	0	6
Total	150	20	70	70	34

TRACE METAL SAMPLES

The BFSD produced batches of six samples per deployment. After recovery and shipment, the samples were immediately filtered through precleaned 0.45- μ cellulose nitrate membrane-filter units and acidified to pH 2 with high-purity nitric acid. Constituent metals of interest were separated from the seawater matrix and concentrated by APDC chelation/MIBK extraction. The extracts were then analyzed by Graphite Furnace Atomic Absorption (GFAA) using the method of standard additions to develop a standard curve. Additional water samples, including replicates and t_0 samples, were analyzed in a similar fashion. A detailed description of these procedures is included in Appendix 2. The first and last time-series samples from each deployment were also analyzed by Anodic Stripping Voltammetry (Zirino and Lieberman, 1975) as an indicator of speciation for Cu, Cd, Zn, and Pb. Bulk sediment samples were acid digested by a standard microwave-assisted digestion technique (EPA Method 3051). Following digestion, the digestate was analyzed by GFAA following the procedures described above for all elements of interest, except As and Hg. Sample aliquots were digested separately and analyzed for As and Hg by a cold-vapor technique (EPA 7471A). A detailed description of these procedures may be found in the standard methods cited.

PAH/PCB SAMPLES

Water samples from the BFSD were liquid-liquid extracted immediately after collection. Sediment samples from surficial sediments were extracted by sonication with acetonitrile and cleaned using C-18 solid-phase sorbent. Interstitial water from the core

samples was obtained by centrifugation and liquid-liquid extraction. The concentrations of selected PAH compounds and PCB congeners in these three matrices were then determined using high-performance gas chromatography and mass spectrometry. Total PCB concentrations were then estimated from an Aroclor 1254 standard based on PCB congener 110. A detailed description of these protocols may be found in Young, et al., 1991.

AVS SAMPLES

Analysis of acid-volatile sulfides (AVS) followed the standard protocols developed by EPA-ERL, Narragansett (Boothman, 1991). In the method used here, the AVS concentration was determined by sediment sulfides reacting with HCl to form gaseous H₂S and purging the evolved H₂S with nitrogen gas. The purged H₂S was then trapped in a sulfide antioxidant buffer, diluted to volume, and the S²⁻ concentration was measured with a sulfide ion-selective electrode. A detailed description of this procedure can be found in Johnston, 1992. Simultaneously extracted metals (SEM) were analyzed by GFAA for selected elements.

SILICA SAMPLES

Silica samples were split into 50-ml plastic vials from the BFSD time-series samples and t₀ samples following filtration and prior to acidification. Samples were refrigerated until analyzed.

The analysis followed the standard colorimetric method for determining reactive silicate in seawater (Strickland and Parsons, 1968). A detailed description of this procedure is included in Appendix 2.

CALCULATION OF FLUX RATES

Flux rates from BFSD time-series samples were estimated using a linear-regression model. Prior to running the regression, sample concentrations were corrected for dilution effects caused by the intake of outside water, as sample water was removed from the chamber. The concentration of the diluting water was based on the t₀ sample. Some samples were dropped from the regression based on performance criteria for dissolved silica and oxygen outlined in the Results chapter that follows. Following the regression of the time-series concentrations, the flux was calculated from the equation,

$$\text{Flux Rate} = (\text{slope of regression}) \times (\text{chamber volume}) / (\text{chamber area})$$

An 80-percent confidence interval (80-percent CI) was then assigned to the flux rate based on a two-sided T-test ($t_{0.05(2), n-2}$) and the standard error of the regression coefficient. If the mean flux was positive and the lower limit of the 80-percent CI was greater than zero, then the flux was designated a *release rate* with magnitude of mean \pm 80-percent CI. Similarly, if the flux rate was negative with an upper limit of the 80-percent CI less than zero, then the flux was designated an *uptake*. The 80-percent CI was chosen to be conservative in the sense that we would not eliminate potential release rates (as an indicator of environmental impact) unless our confidence in them was quite low.

QA/QC PROCEDURES

QA/QC procedures were under Puget Sound Estuary Program (PSEP) protocol wherever possible. Occasionally, special instrumentation, collection techniques, and analysis methods required deviations from PSEP protocols. Analytical QA/QC procedures are described in the references cited in the preceding Analysis chapter. A copy of the PSEP sample collection QA/QC procedures is included as Appendix 3. Standard log sheets and custody sheets are also included in Appendix 3. Detailed descriptions of analytical QA/QC procedures are described in Appendix 2 for trace metals, Appendix 4 for PAH/PCB, and in Johnston 1992 for AVS. A brief description of the trace-metal analytical QA/QC follows.

METHOD BLANKS

Throughout the analyses, method blanks were employed for verifying contamination-free preparation and reagents. Each batch of extracted and digested samples was accompanied by a blank that was analyzed in parallel with the rest of the samples being carried through the entire preparation and analysis procedure.

INSTRUMENT CALIBRATION

Instruments were calibrated at the start of each analytical batch. With water samples and extracted water samples, the method of standard additions was used to generate each calibration curve. Successive dilution of a standard was used to generate standard curves for analyzing the digestates. Initial calibration was verified by subsequent measurement of an independently prepared standard. The calibration was confirmed at regular intervals during an analytical batch.

METHOD ACCURACY AND PRECISION

Standard reference sediments were digested and analyzed periodically as a check on general method accuracy. Additionally, spiked replicates of field samples were processed with each analytical batch to validate method accuracy within the context of varying matrices. With water and extracted water samples that were analyzed by the method of standard additions, spiked samples were not used. Analytical precision and method-detection limits were determined by replicate storage, preparation, and analysis of standard seawater. Further verification of precision was achieved by splitting 1 in 20 field samples. The limited volume available from each field sample restricted the number of split duplicates available to analyze. Based on these splits, the relative standard deviations for individual trace metals were approximately 21 percent for Cu, 10 percent for Cd, 6 percent for Ni, 4 percent for Pb, and 10 percent for Zn. Cr and Hg precision data were not available, because sample concentrations were below detection limits and As precision was not tested.

RESULTS

HYDROGRAPHIC SURVEYS

Hydrographic and water quality surveys were performed in the inlet using the realtime monitoring system aboard the survey boat. This included surface-water mapping (1-meter deep) throughout the inlet on 4 July 1991, as well as creating vertical profiles at each of the 10 BFSD sites. Measured parameters included temperature, salinity, pH, dissolved oxygen, transmittance, chlorophyll-*a*, oil fluorescence, and bathymetry. These data were compiled into areal maps and profiles to characterize conditions at the site during the BFSD survey.

The surface-water conditions are shown in figures 7-13. In general, we found temperatures ranging from about 14-18°C with the colder water entering the inlet at its northeastern extent via Port Orchard, the warmest water mid-inlet and near the southern shoreline, and a slight cooling in the western extent of the inlet. The salinity ranged from about 28.4-28.9 ppt. Its distribution was similar to the temperature with higher salinity being associated with the cooler water in the outer- and inner-most extent of the inlet, and lower salinity water mid-inlet and along the southern shore. Dissolved oxygen in the surface waters was highest in the western extent (8.2 ml/l) and followed a decreasing trend toward the east and north with lowest levels (6.2 ml/l) associated with the low-temperature, high-salinity plume at the northeastern extent of the inlet. Surface-oxygen levels appeared to be dominated by photosynthesis rather than water temperature, based on similarity to the chlorophyll-*a* distribution. The distribution of pH was similar to that of oxygen with a maximum of about 8.5 at the southwestern extent and a minimum of about 8.2 for the mouth of the inlet. Turbidity was measured as percent transmission with highest turbidity in the western inlet and lowest in the northeast. Chlorophyll-*a* was measured on a relative-fluorescence basis and showed a similar distribution to that of pH and oxygen. Relative oil fluorescence showed highest levels along the southern shoreline with small plumes coinciding with each marina. Lowest oil fluorescence was found along the northern/northeastern extent of the inlet following a similar trend as other measured parameters.

Vertical profiles of hydrographic parameters at the BFSD sampling sites are shown in figures 14-16. Temperature decreased with depth with a difference of about 1-2°C from surface to bottom. Strongest thermoclines were observed in the eastern inlet (sites 1A,1B), while most other sites showed a more gradual decrease with depth. Salinity was generally lowest at the surface and typically tracked temperature as a function of depth, with highest salinity extending from the bottom of the thermocline to the bottom of the inlet. Dissolved oxygen and pH had similar profiles with a maximum occurring at or near

the surface in most cases, then decreasing toward the bottom. Oxygen was present at all stations through the entire water column with no indication of anoxic conditions at any of the sites. Turbidity at most sites was highest (lowest percent transmittance) near the surface, although several sites did not show this distribution. Chlorophyll-*a* fluorescence often showed a subsurface maxima with decreasing concentrations at the bottom and surface, while the oil-fluorescence maximum was generally at the surface with levels decreasing toward the bottom.

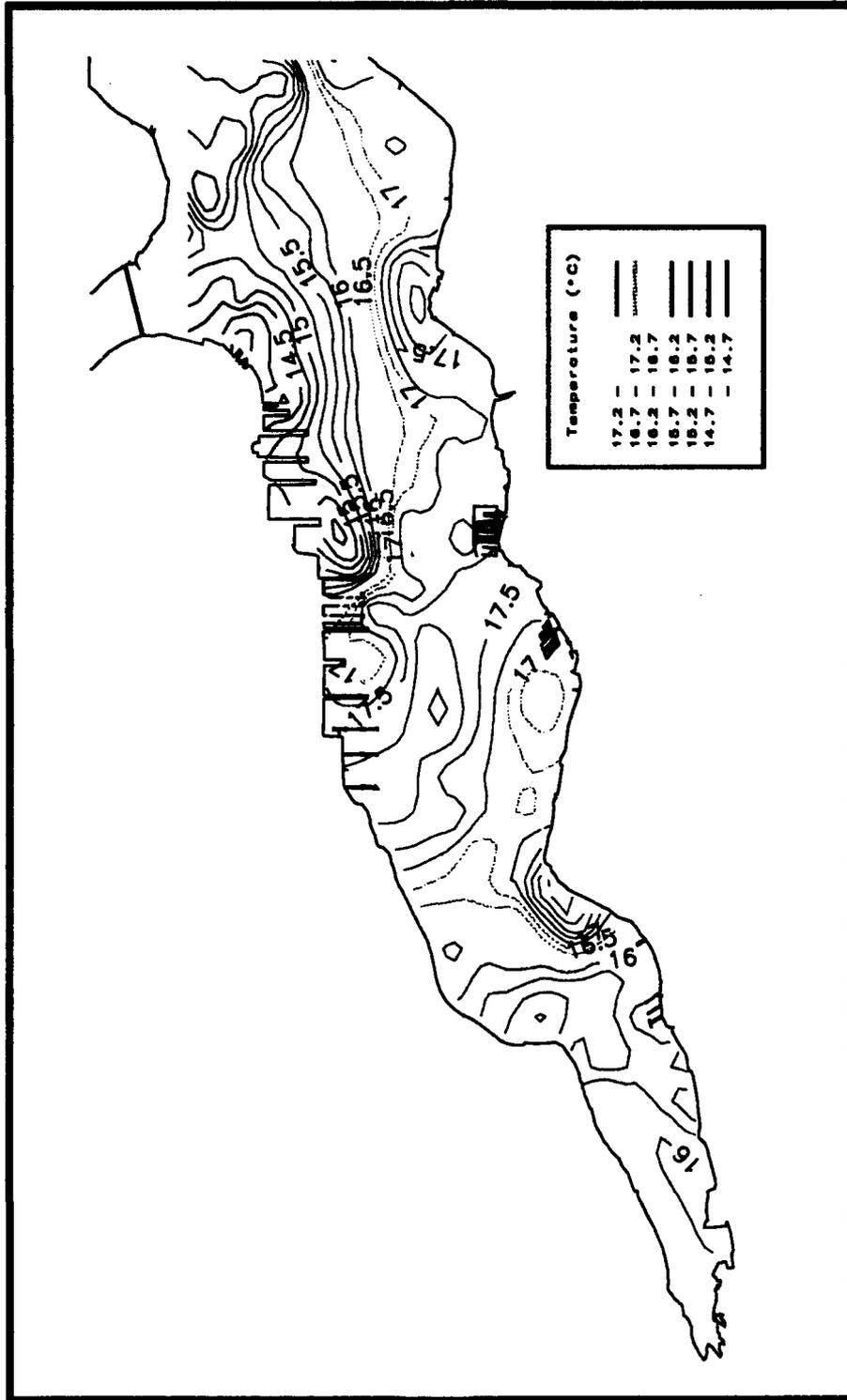


Figure 7. Surface-water temperature distribution in Sinclair Inlet from three east-west transects—performed 7/4/91.

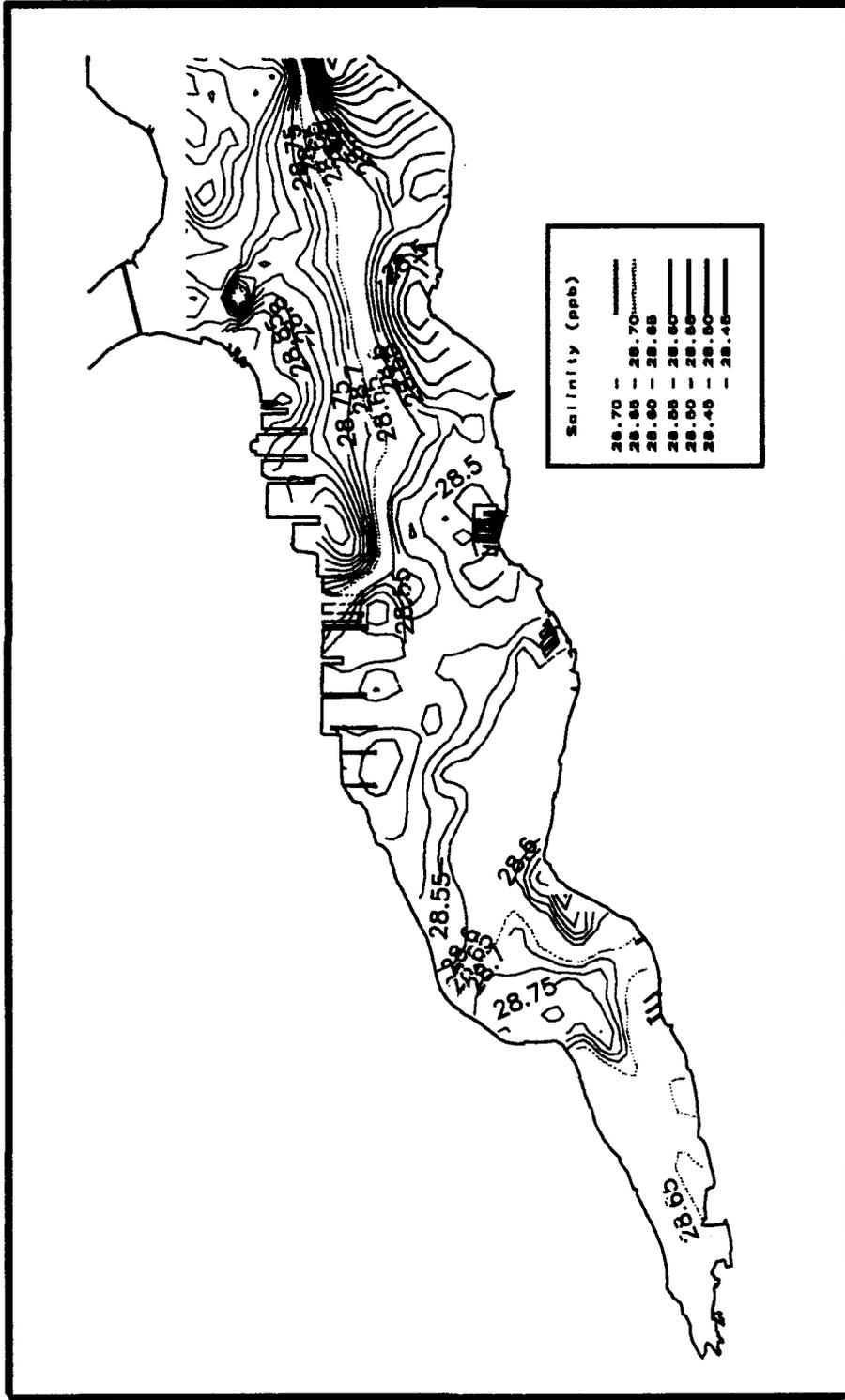


Figure 8. Surface-water salinity distribution in Sinclair Inlet from three east-west transects—performed 7/4/91.

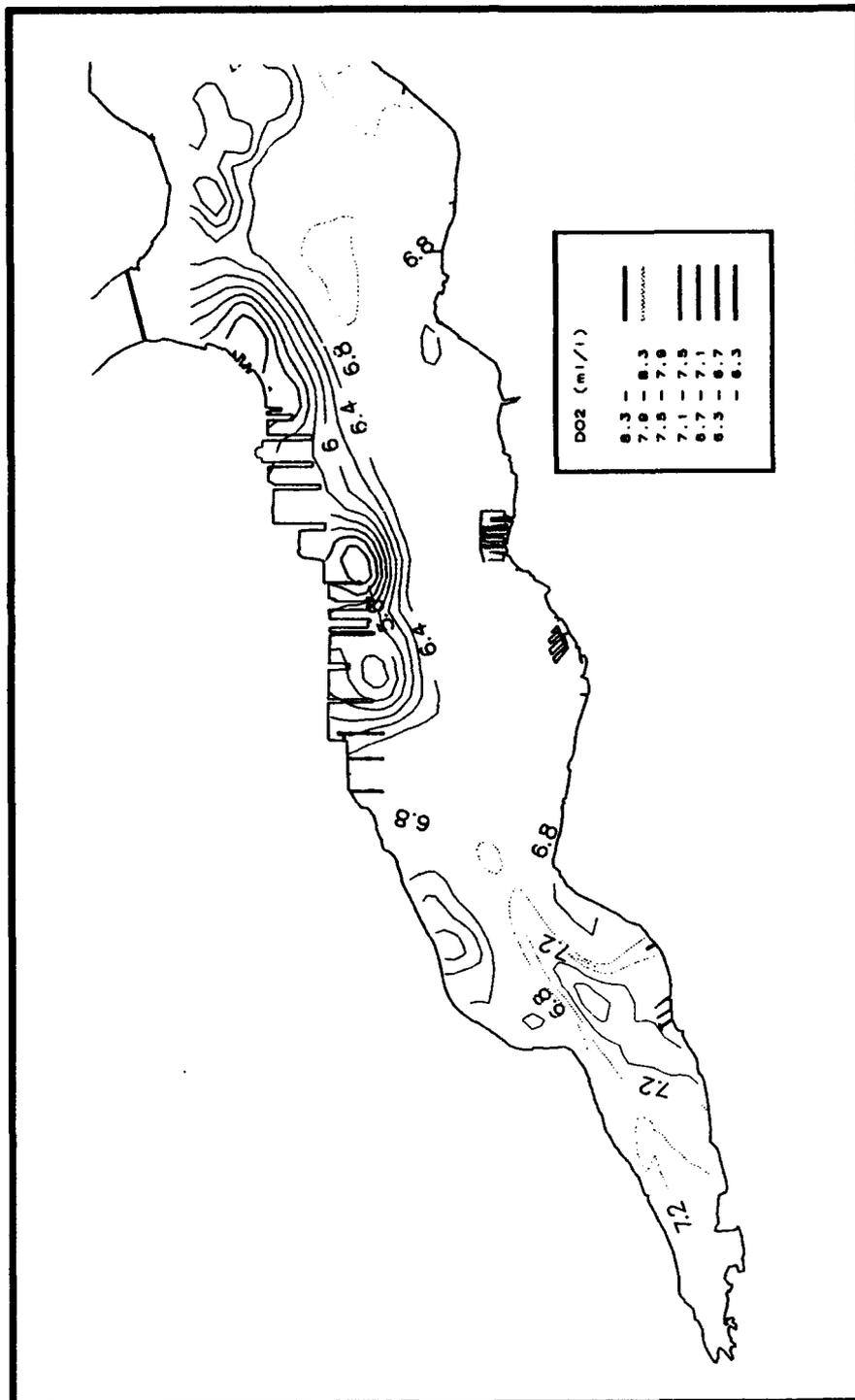


Figure 9. Surface-water dissolved oxygen distribution in Sinclair Inlet from three east-west transects—performed 7/4/91.

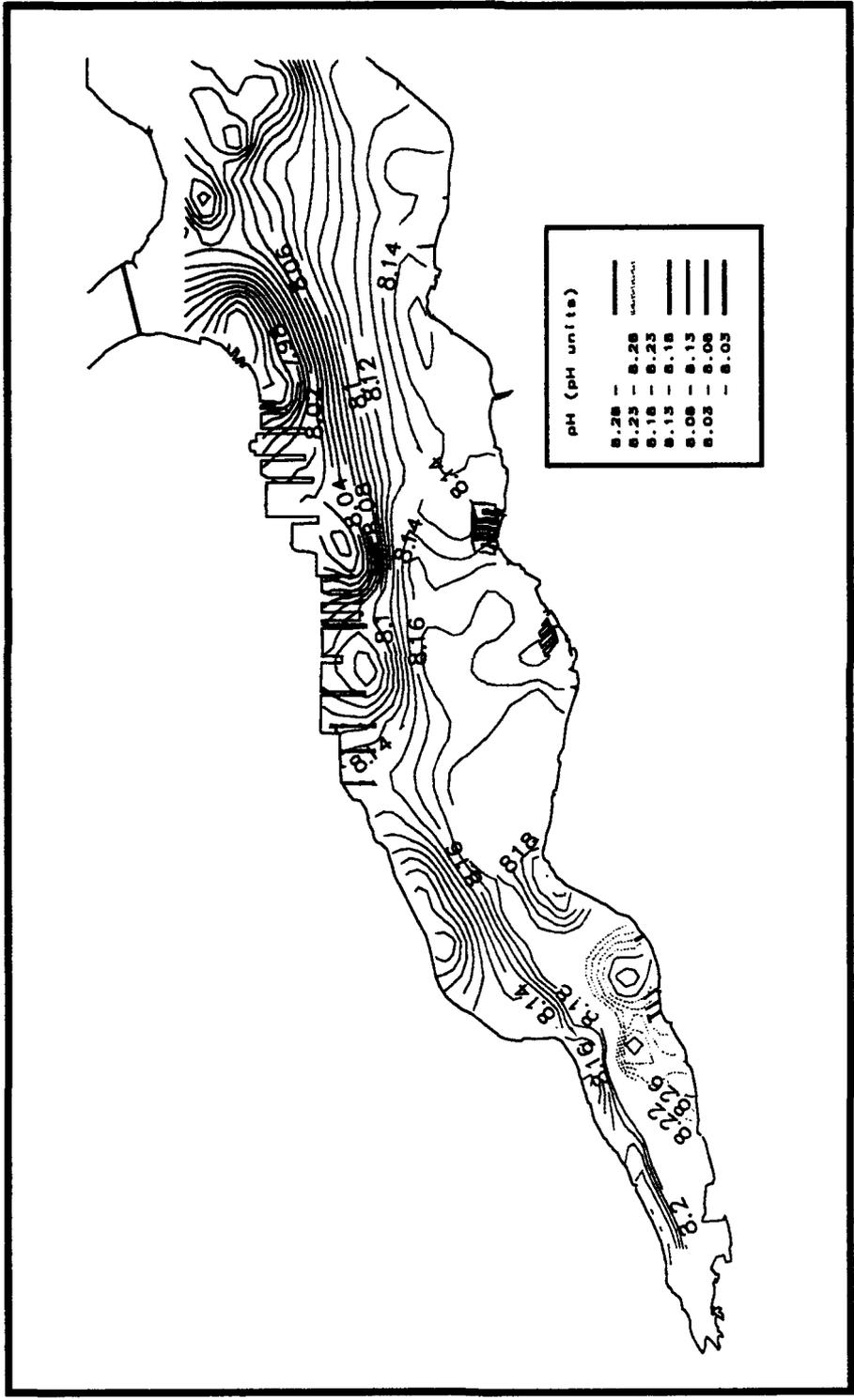


Figure 10. Surface-water pH distribution in Sinclair Inlet from three east-west transects—performed 7/4/91.

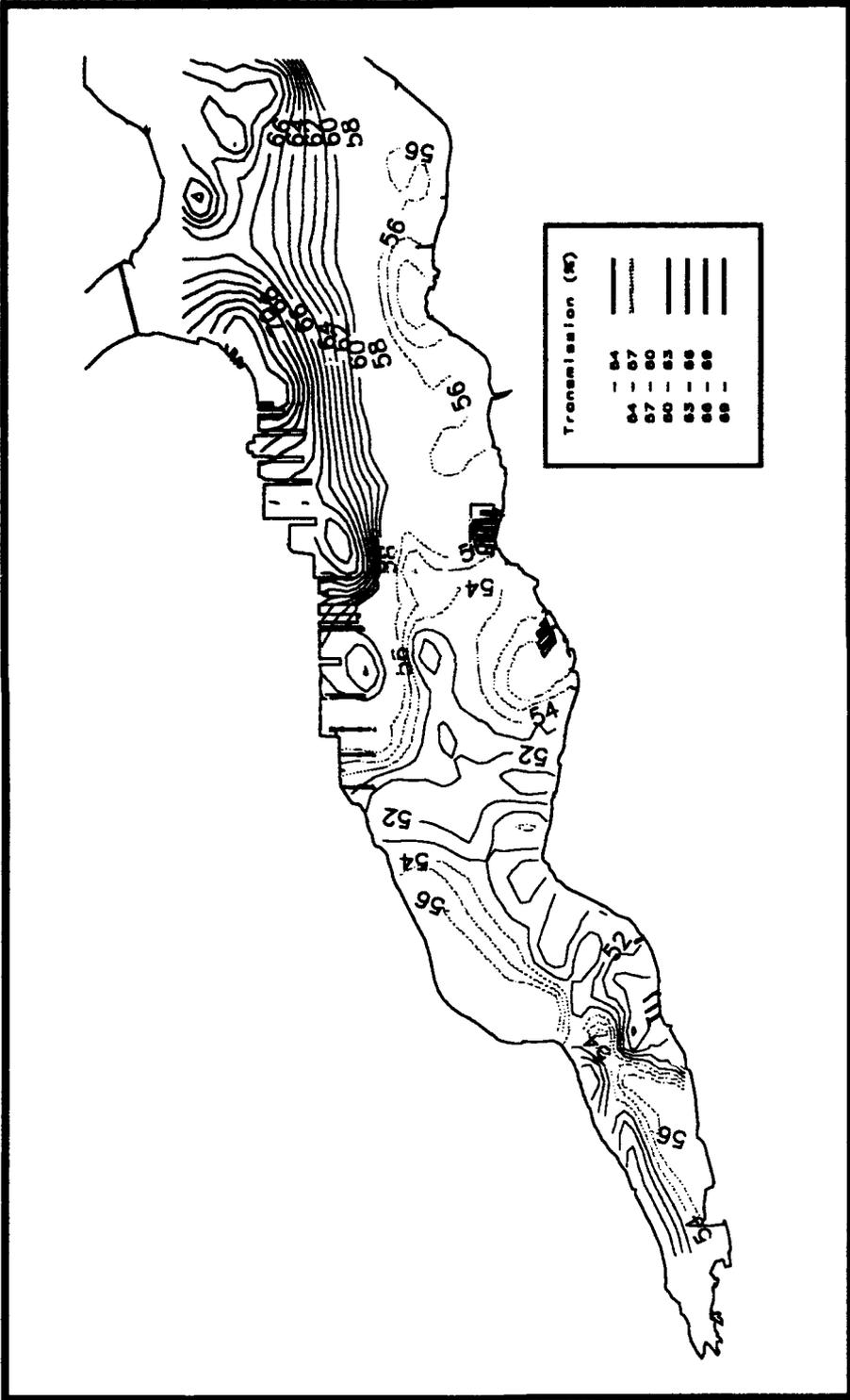


Figure 11. Surface-water turbidity (as % transmittance) in Sinclair Inlet from three east-west transects—performed 7/4/91.

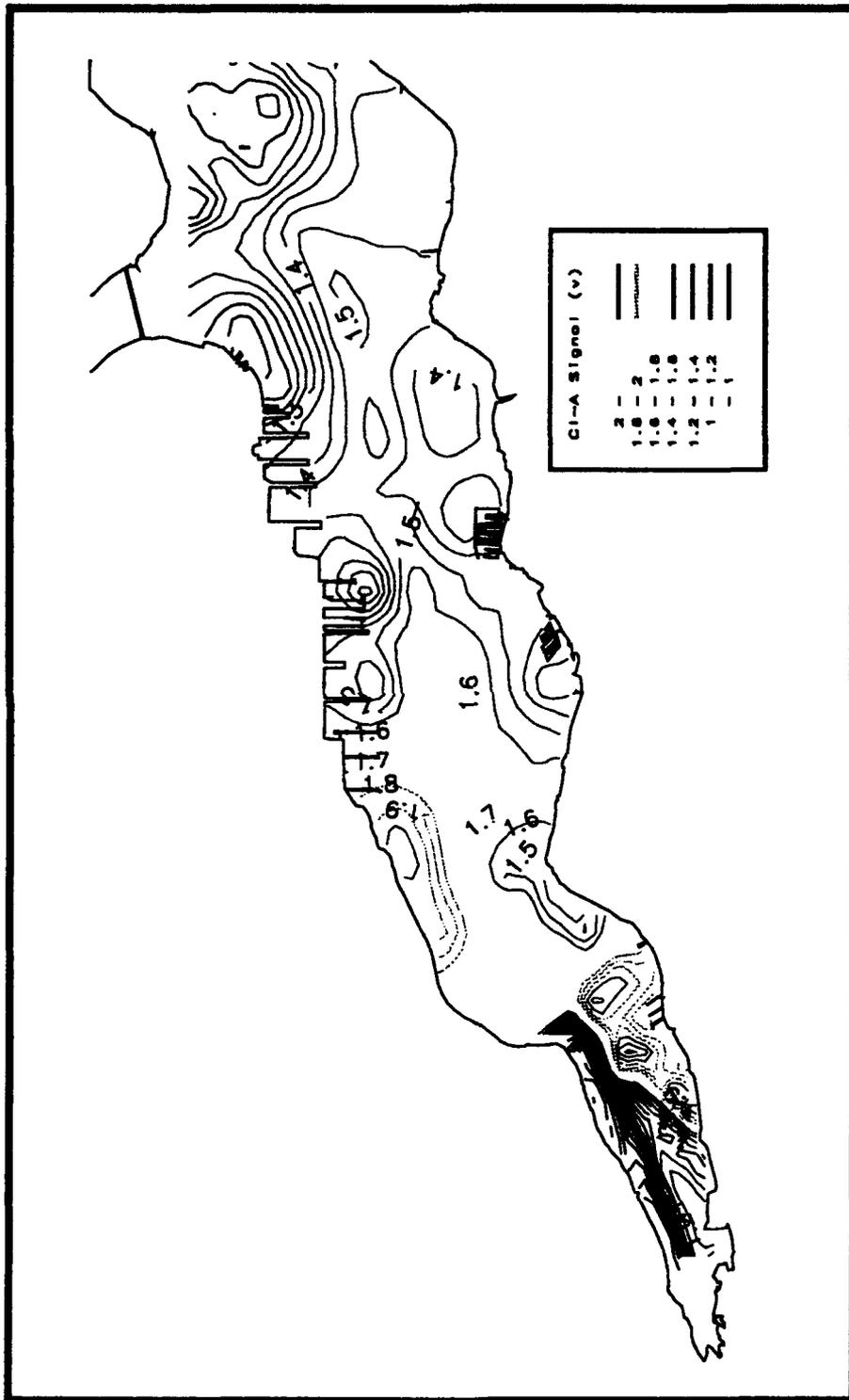


Figure 12. Surface-water chlorophyll-*a* distribution (relative) in Sinclair Inlet from three east-west transects—performed 7/4/91.

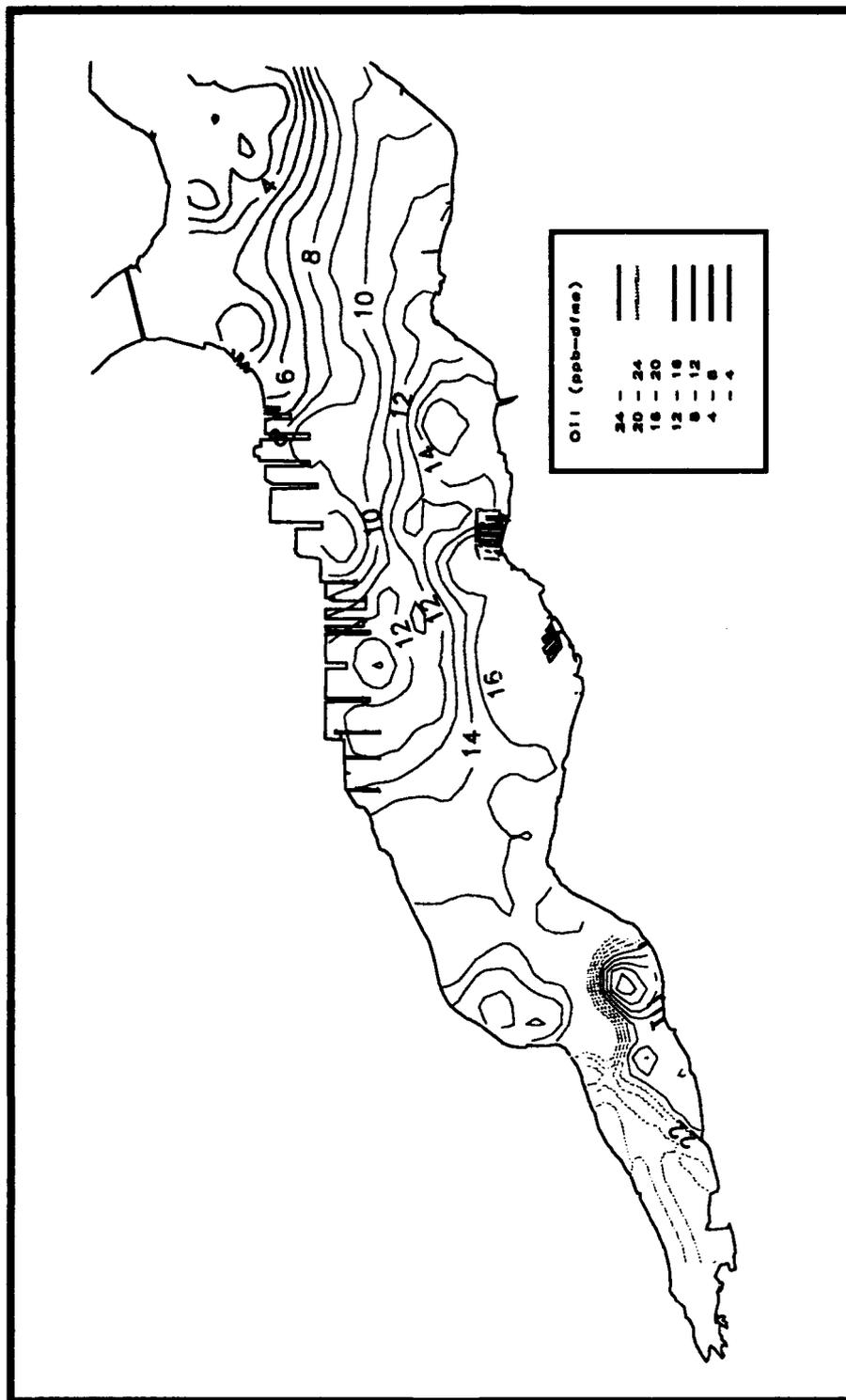


Figure 13. Surface-water oil fluorescence distribution in Sinclair Inlet from three east-west transects—performed 7/4/91.

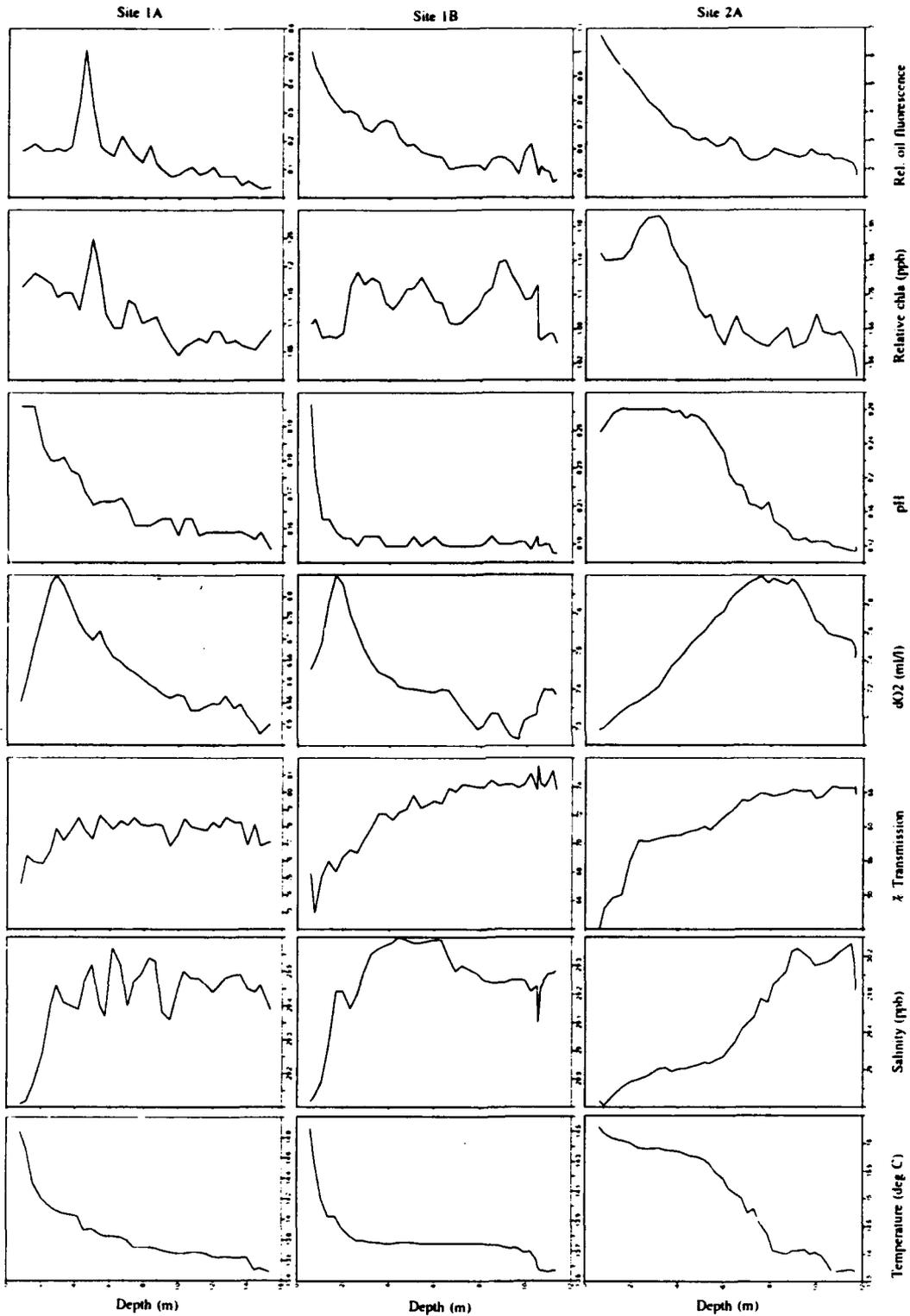


Figure 14. Vertical profiles of temperature, salinity, turbidity, dissolved oxygen, pH, chlorophyll-*a*, and oil at sites 1A, 1B, and 2A.

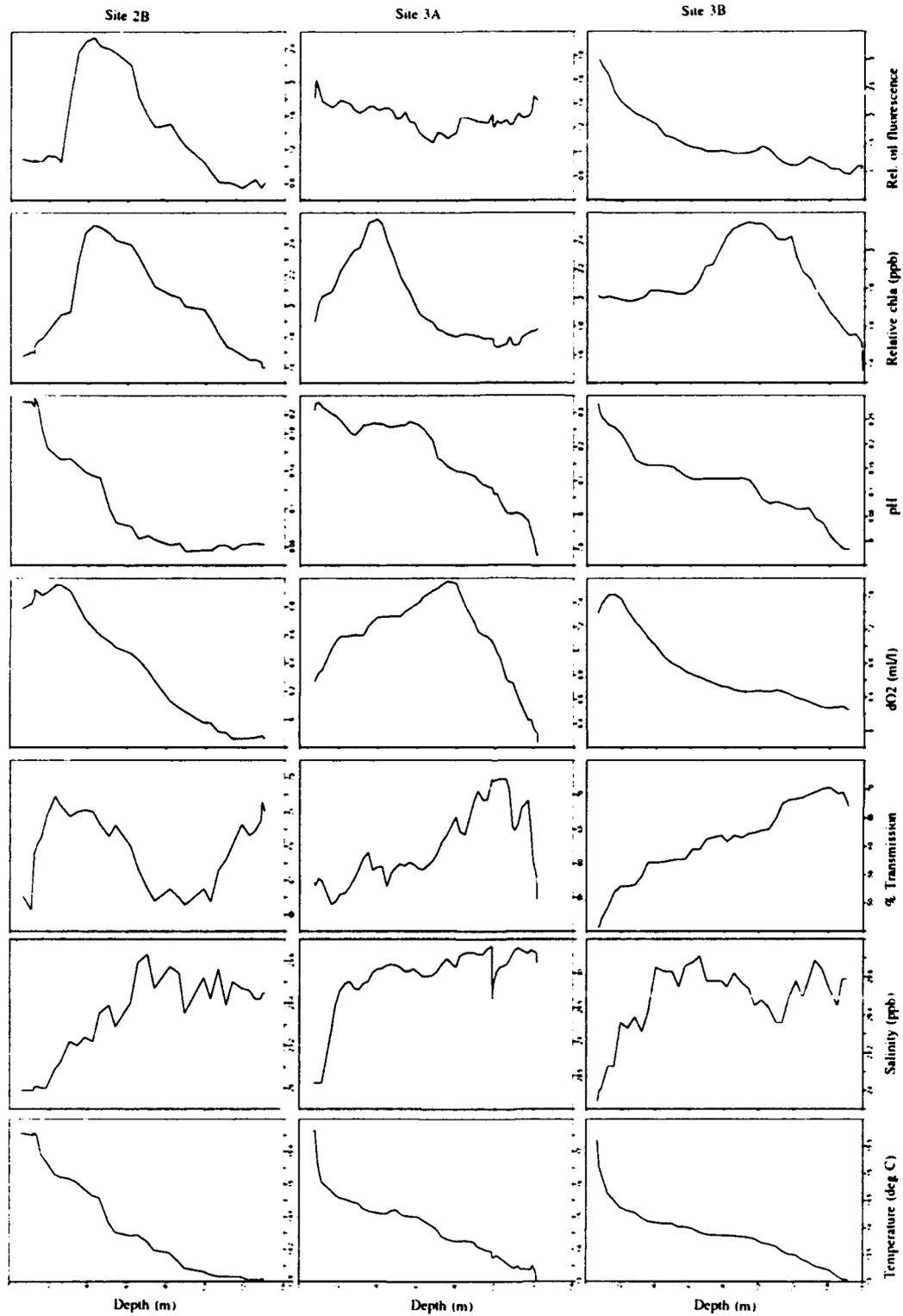


Figure 15. Vertical profiles of temperature, salinity, turbidity, dissolved oxygen, pH, chlorophyll-a, and oil at sites 2B, 3A, and 3B.

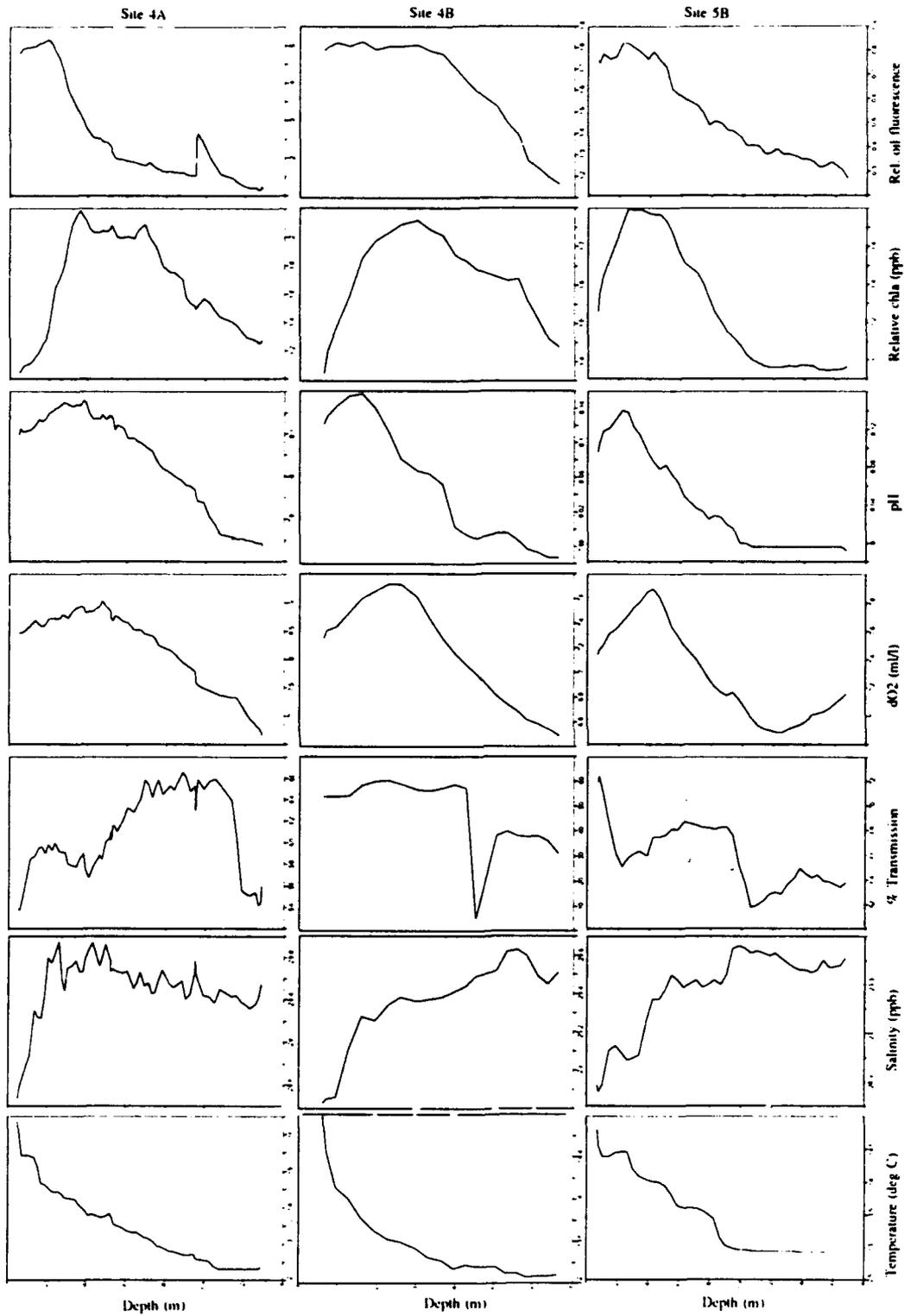


Figure 16. Vertical profiles of temperature, salinity, turbidity, dissolved oxygen, pH, chlorophyll-*a*, and oil at sites 4A, 4B, and 5B.

BFSD PERFORMANCE INDICATORS

A series of 10 BFSD deployments was performed from 30 June 92 to 27 July 1991. At each of the 10 sites, release rates of silica were measured as a check on BFSD performance. The results of these measurements are presented first (figures 17–18) because they are essential in interpreting the release rates for other compounds. A steady increase in dissolved silica over the time of each experiment was used as the primary indicator of a “problem-free” deployment. Based on this criteria, the chamber results from sites 1A, 2A, 2B, 3B, 4A, 4B, and 5A appear problem-free, while the results from 1B, 3A, and 5B are unusual. The silica concentrations for 1B do show an increasing trend for the first 24 hours (samples 1–3) and samples from 3A and 5B increase steadily for the first 32 hours (samples 1–4). Release rates for other compounds were interpreted based on these reduced sample sets.

During each deployment, sensors on the BFSD monitored temperature, salinity, pH, and dissolved oxygen. Results from these measurements are shown in figures 19–28 for Oxygen, pH, and temperature. Oxygen was supplied to the chamber during each deployment to prevent anoxic conditions from developing and disrupting the experiment. The oxygen results show that levels were maintained above zero at all sites except 3B. At 3B, the chamber became anoxic at about hour 29 indicating that samples after this time (samples 5 and 6) may have been influenced by these conditions. At site 1B, oxygen and pH decreased steadily for the first 20 hours but then increased for about 5 hours, indicating a probable disturbance of the chamber seal during this period. This is consistent with the results from the silica measurements. Results from site 3A shows no major deviations in pH or oxygen that could account for the nonuniformity of the silica data at this site. This suggested that the problem at this site may have been related to bottle leakage or some other sampling problem rather than the chamber being poorly sealed. At site 4B, the oxygen level initially decreased for about 6 hours and then increased steadily for the remainder of the experiment. The initial decrease could be related to disturbing the sediment during deployment. The sediment at this most western site was very fine and may have taken longer than usual to resettle. This could also have influenced the concentration of other constituents in the chamber during the first one or two samples.

TRACE-METAL FLUX RATES

Based on the supporting analysis above, results for trace-metal release rates were determined using an abbreviated set of samples. For specific samples, additional outliers were dropped based on a critical-value outlier test in cases where the concentration of a particular sample lies far from the mean of the sample set, indicating probable contamination during collection or processing. In addition, one sample was lost, one was not analyzed for Zn, and some fell below detection. Table 4 shows the samples used to calculate the flux rate at each site. Results for Cu, Cd, Pb, Ni, Zn, and As are shown in figures 29–38. Levels of Cr and Hg fell below detection limits for all water samples, and thus no results could be obtained for these compounds. Calculated release rates, confidence intervals, and r^2 values are summarized in table 5.

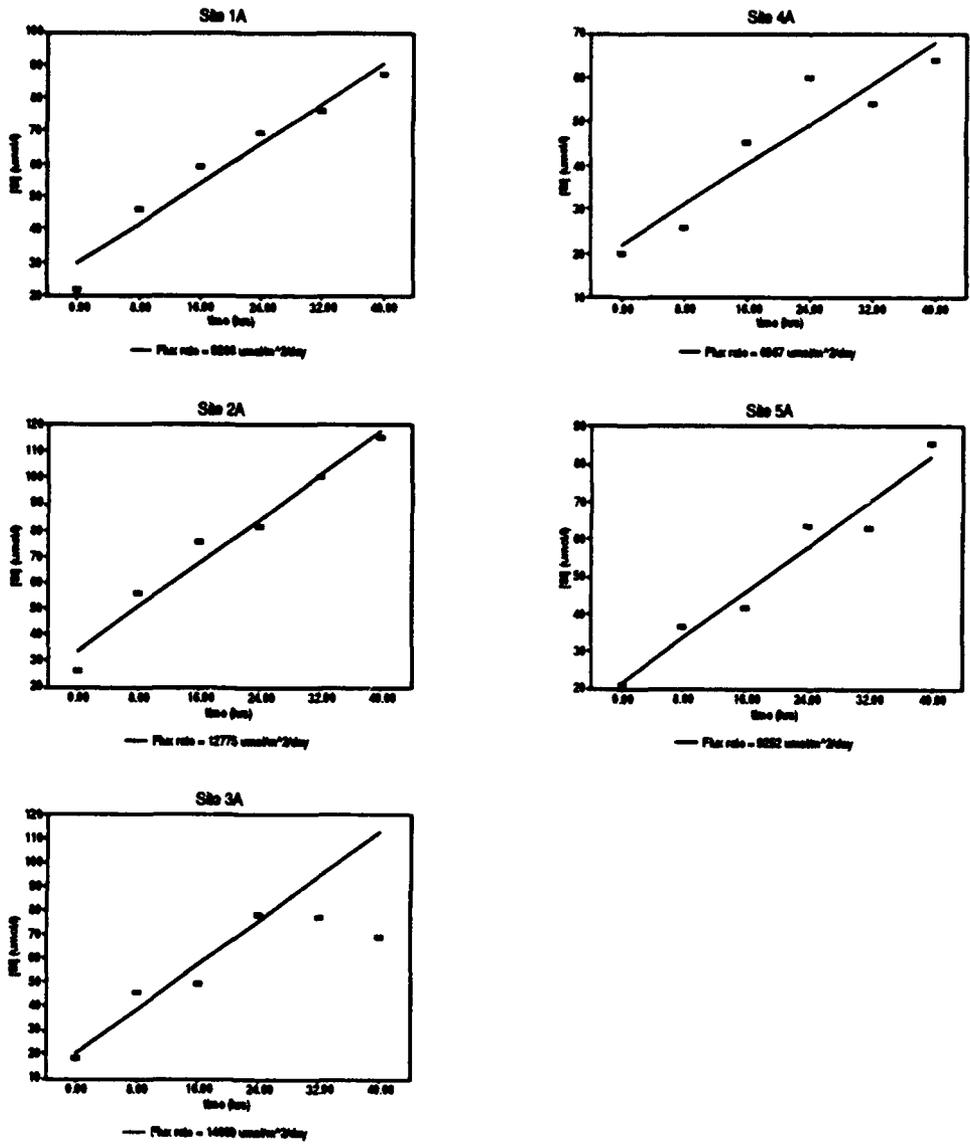


Figure 17. Silica flux data for sites 1A-5A. Sample 6 and possibly 5 at site 3A were considered suspect due to an inconsistent trend in concentration.

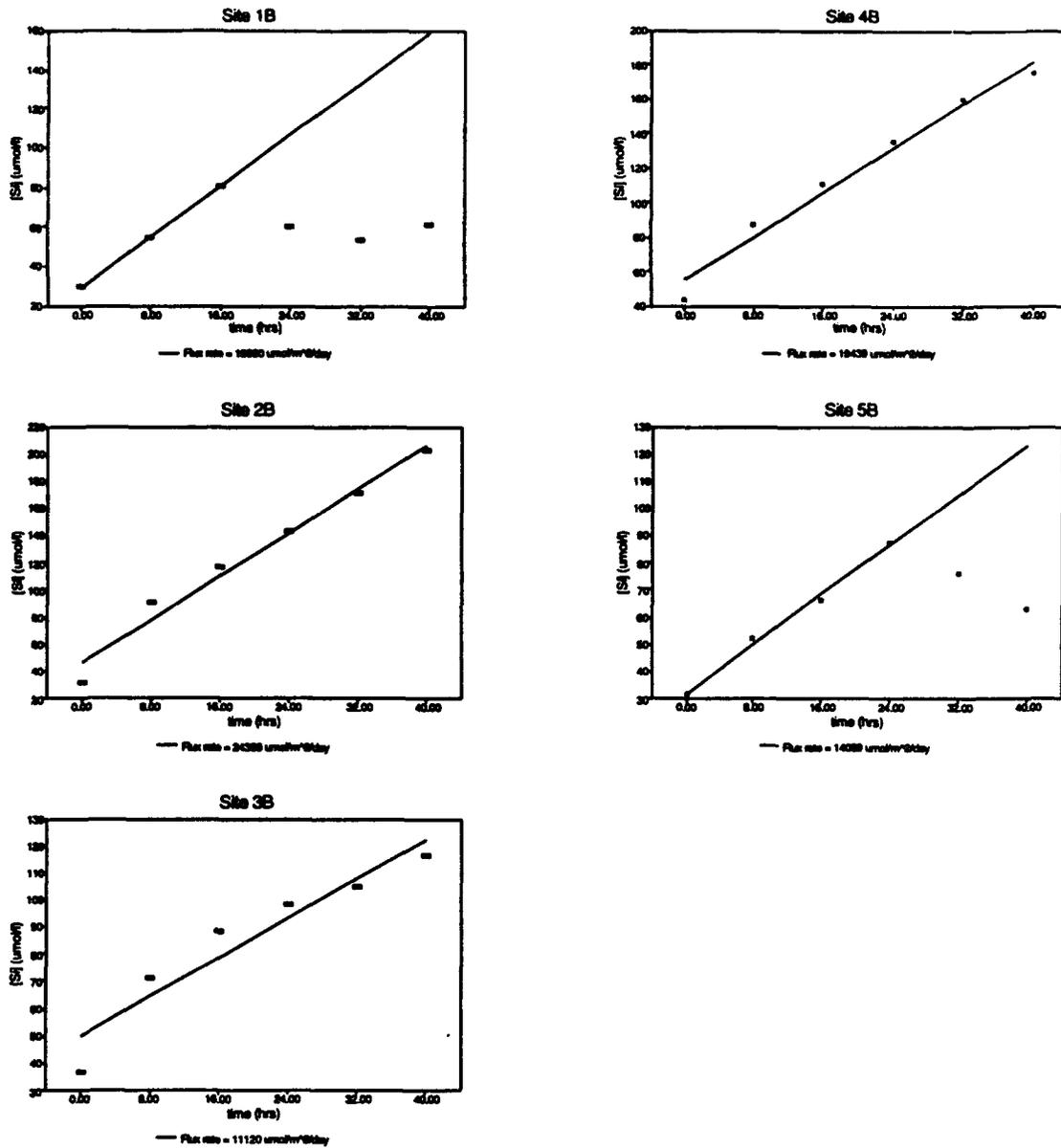


Figure 18. Silica flux data for sites 1B-5B. Samples 4-6 at site 1B and samples 5-6 at site 5B were considered suspect due to an inconsistent trend in concentration.

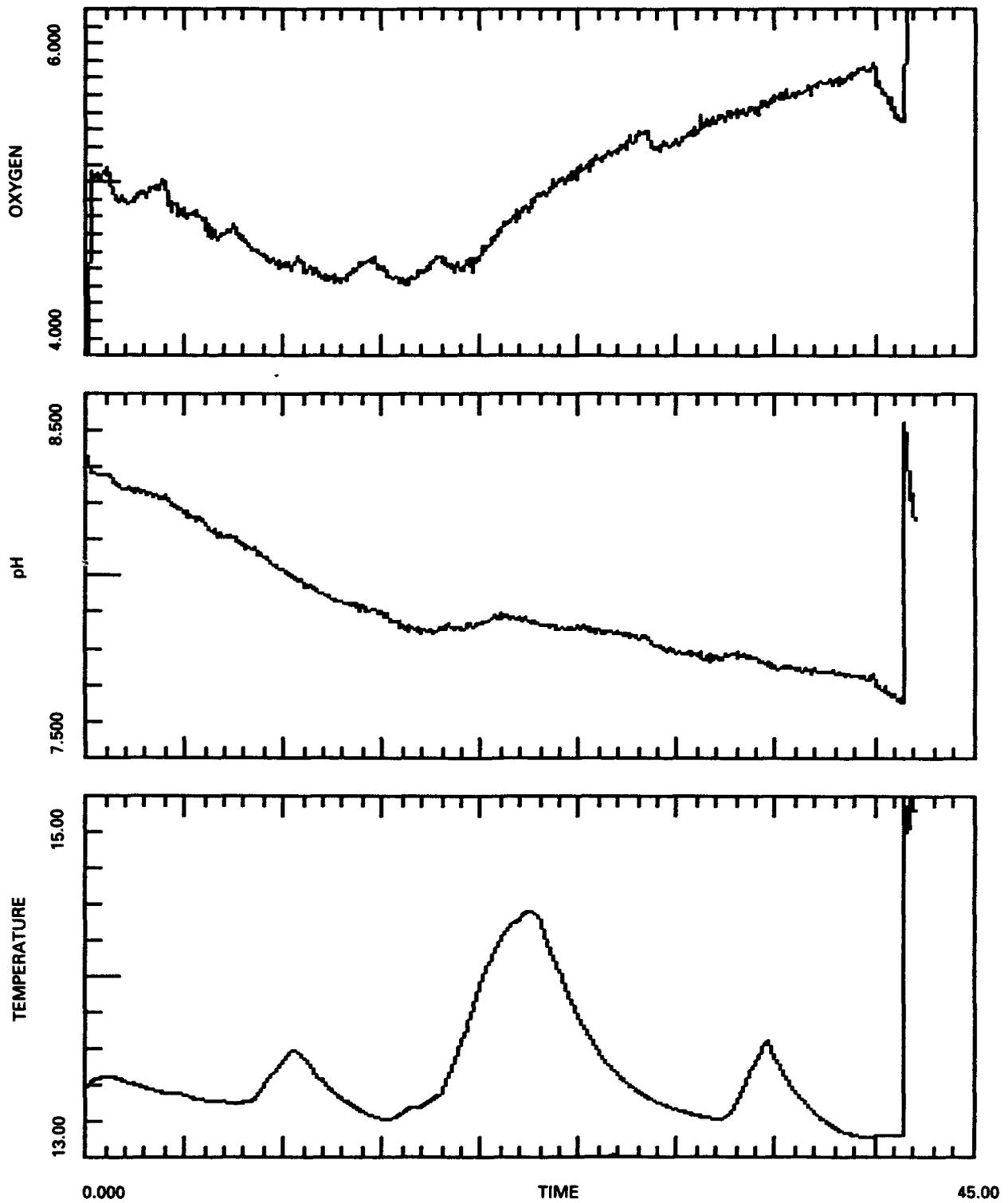


Figure 19. Time-series dissolved oxygen, pH, and temperature inside the flux chamber for the deployment at site 1A.

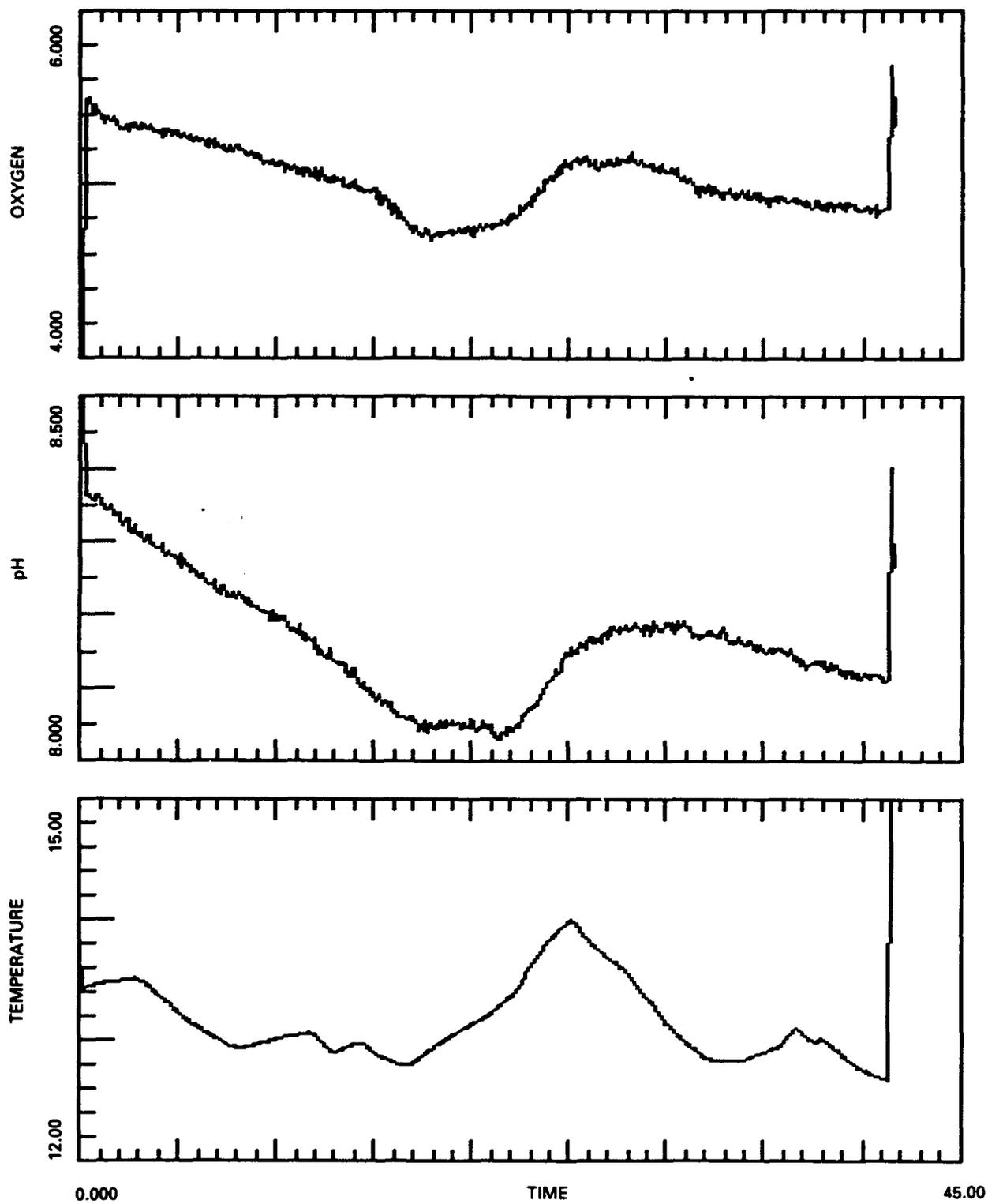


Figure 20. Time-series dissolved oxygen, pH, and temperature inside the flux chamber for the deployment at site 1B.

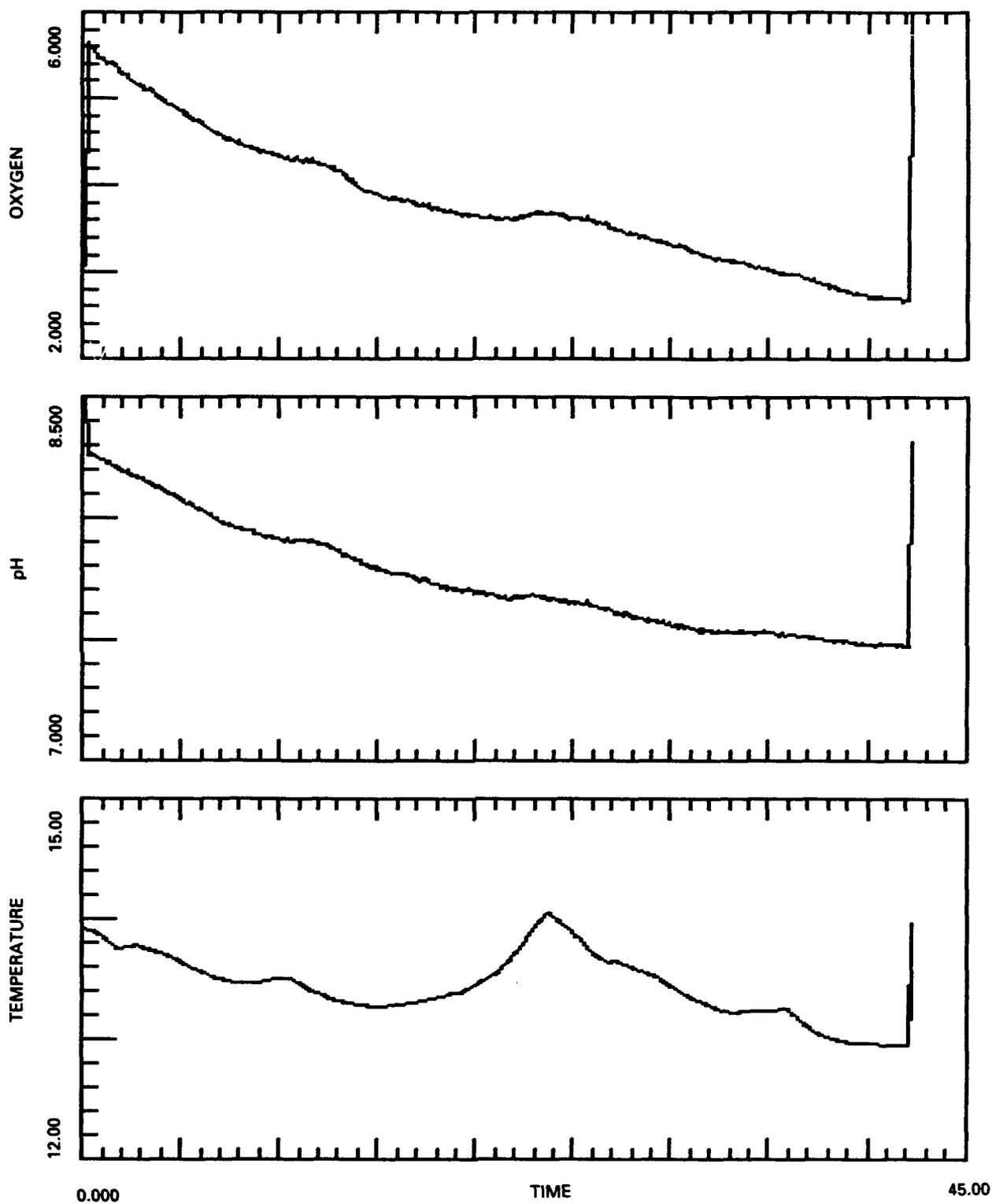


Figure 21. Time-series dissolved oxygen, pH, and temperature inside the flux chamber for the deployment at site 2A.

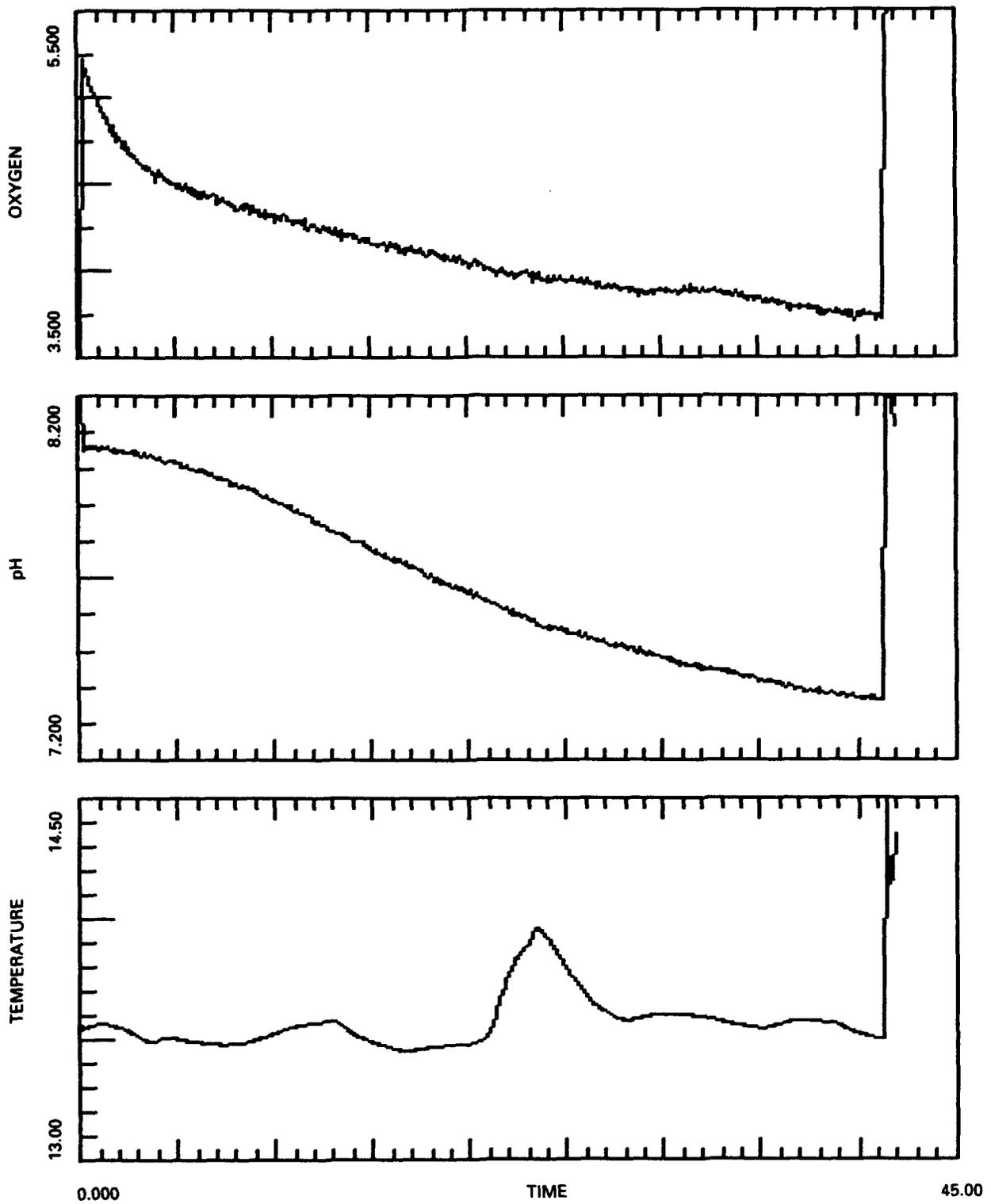


Figure 22. Time-series dissolved oxygen, pH, and temperature inside the flux chamber for the deployment at site 2B.

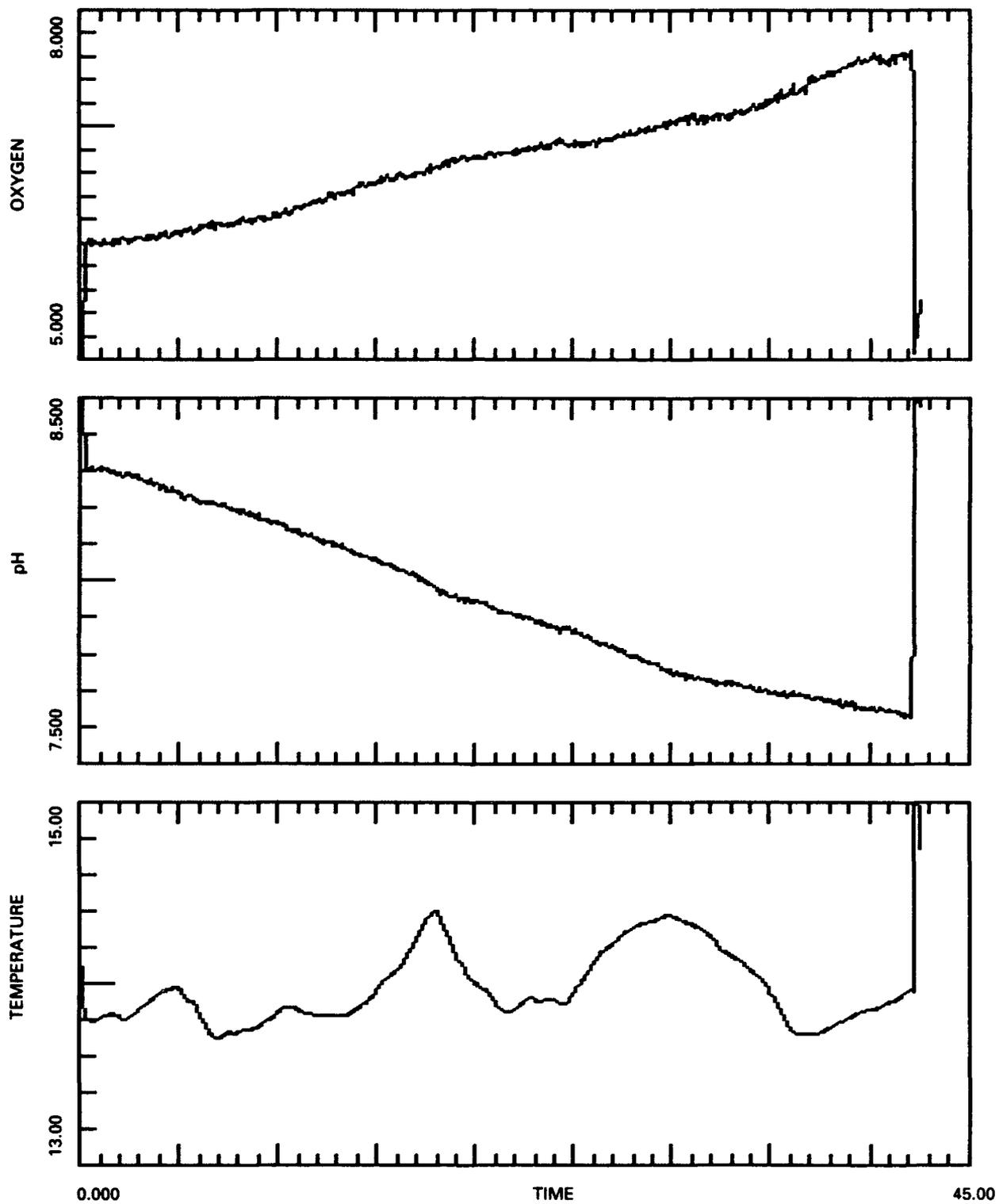


Figure 23. Time-series dissolved oxygen, pH, and temperature inside the flux chamber for the deployment at site 3A.

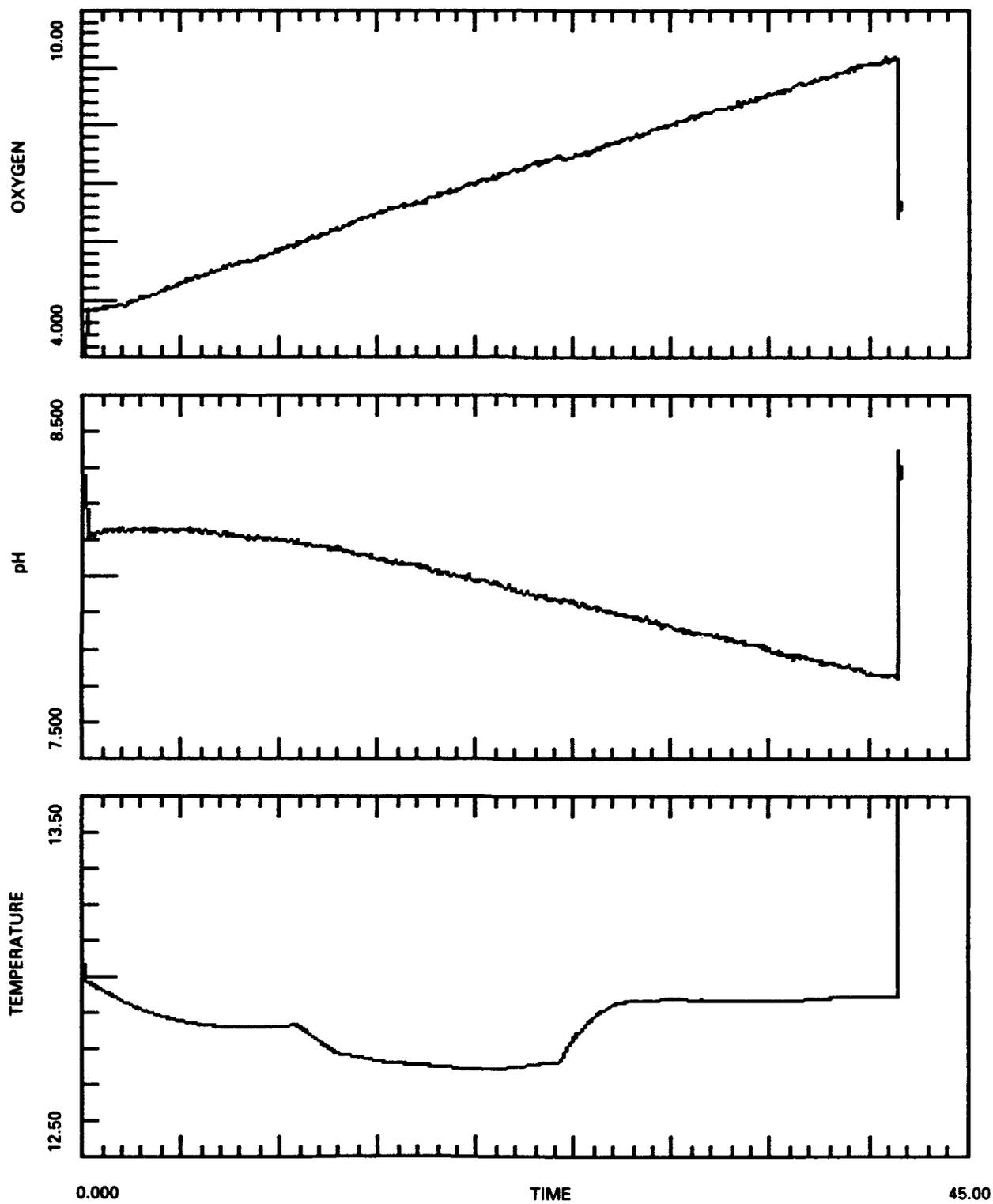


Figure 24. Time-series dissolved oxygen, pH, and temperature inside the flux chamber for the deployment at site 3B.

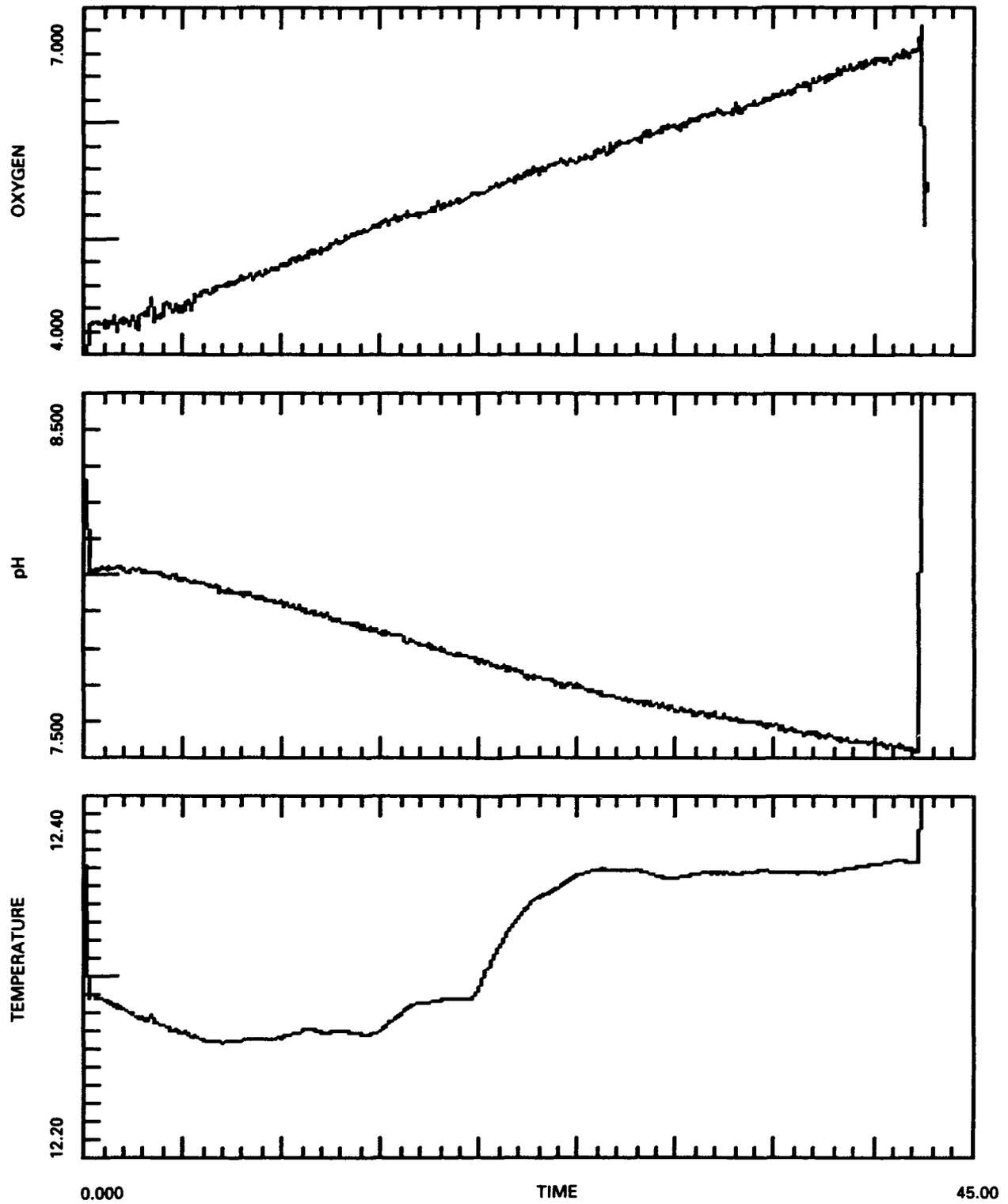


Figure 25. Time-series dissolved oxygen, pH, and temperature inside the flux chamber for the deployment at site 4A.

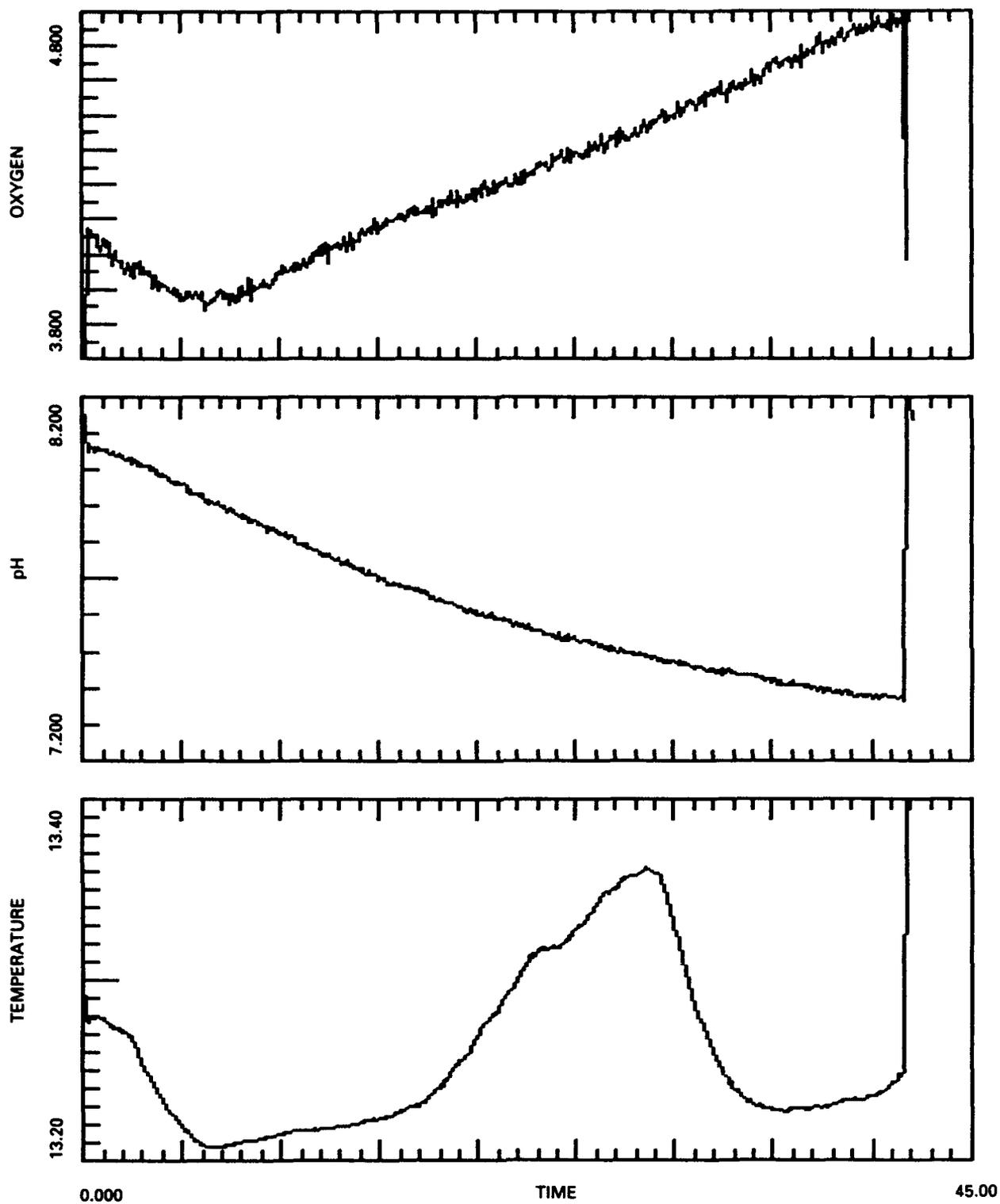


Figure 26. Time-series dissolved oxygen, pH, and temperature inside the flux chamber for the deployment at site 4B.

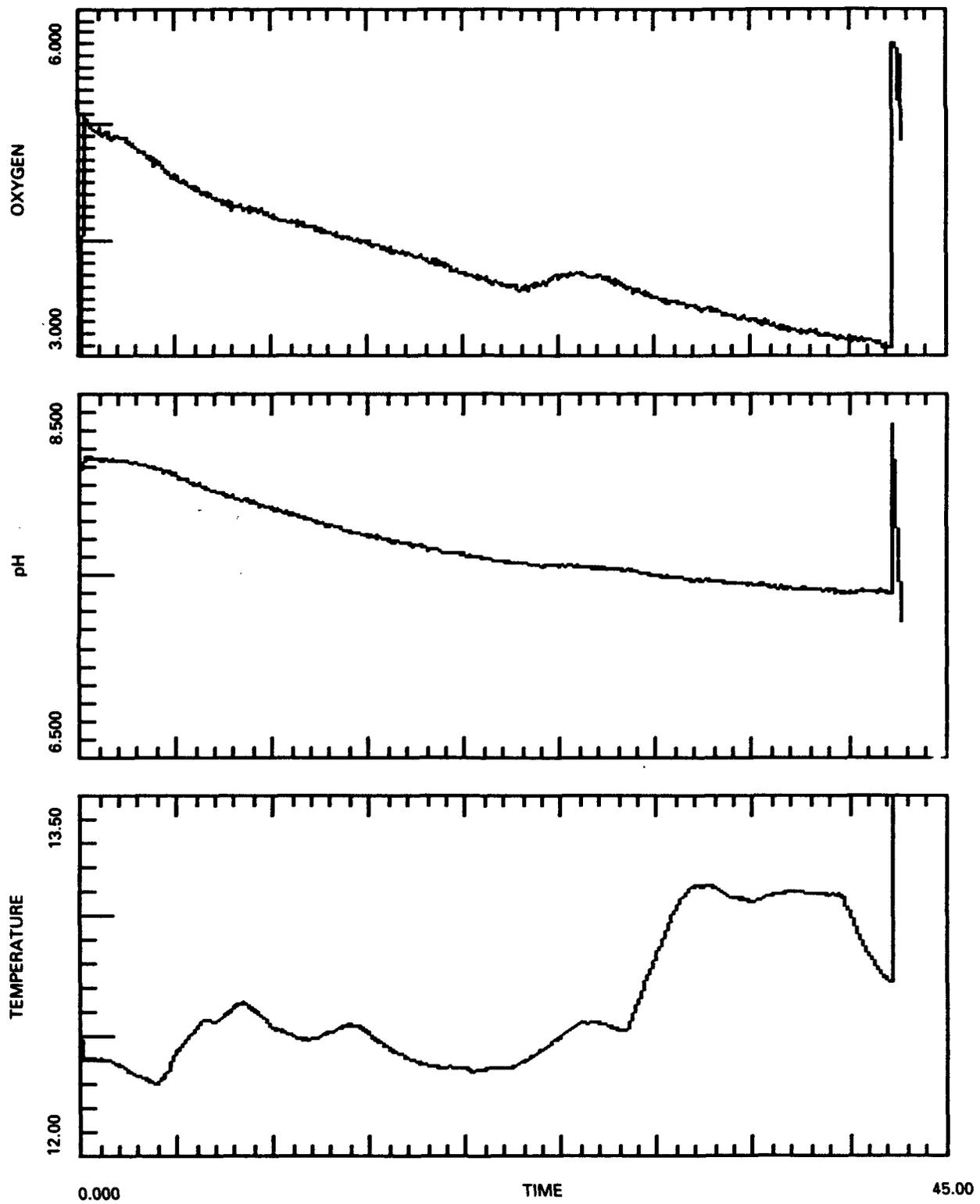


Figure 27. Time-series dissolved oxygen, pH, and temperature inside the flux chamber for the deployment at site 5A.

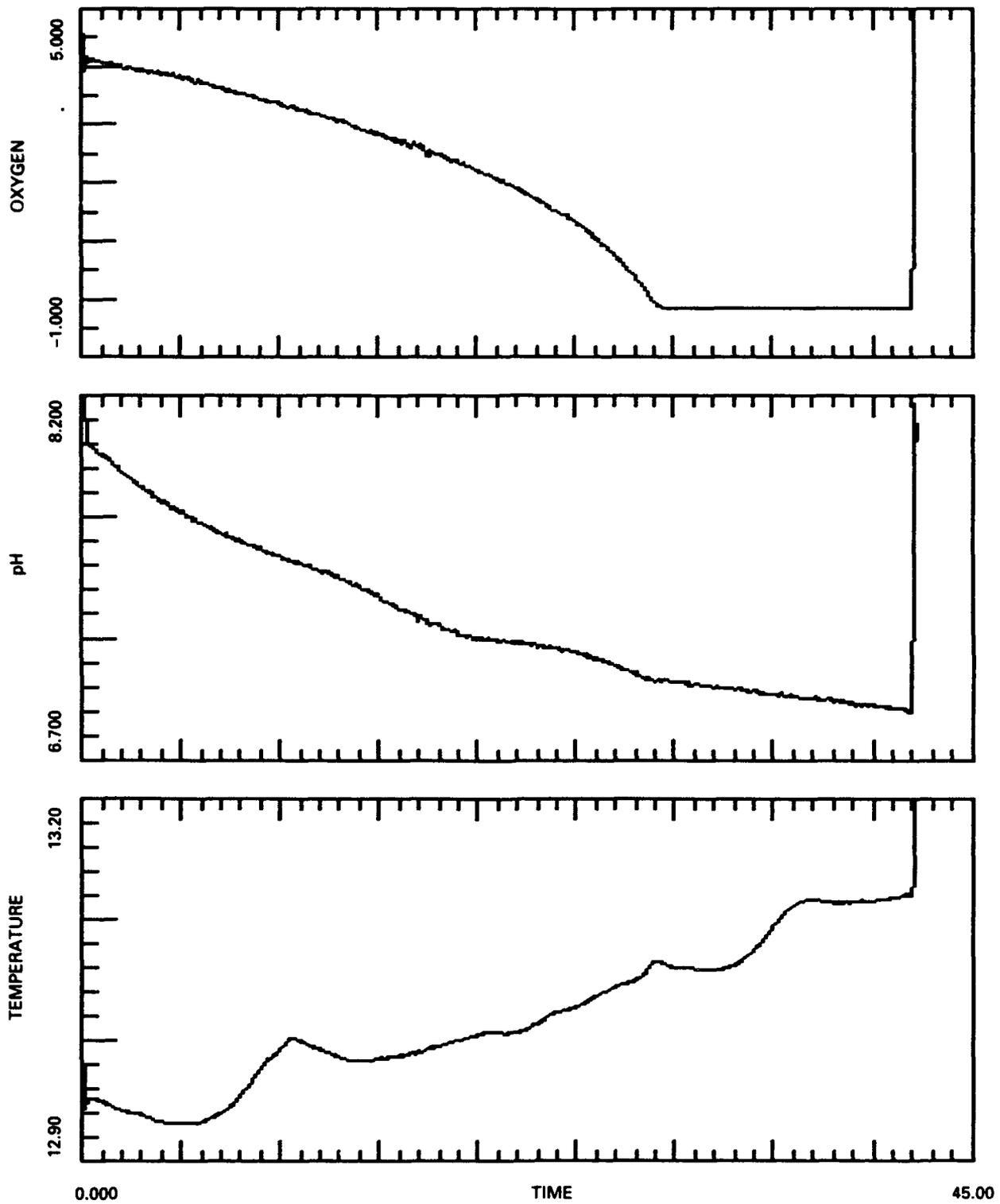


Figure 28. Time-series dissolved oxygen, pH, and temperature inside the flux chamber for the deployment at site 5B.

Table 4. Sample set and performance criterion for calculating metal flux rates.

Site	Performance Criterion		
	Sample Set Based on O ₂ and Si	Samples Dropped Based on Outlier Test	Other Samples Dropped
1A	1-6	5/Ni	--
1B	1-3	--	--
2A	1-6	--	--
2B	1-6	--	--
3A	1-4/5	--	--
3B	1-6	--	--
4A	1-6	--	3/all elements - sample lost
4B	1-6	2/As	--
5A	1-6	1/As	2/Zn - sample not run
5B	1-4	--	--

Trace metal flux rates were characterized as *release rates*, if the flux was positive, or as *uptake rates*, if the flux was negative, based on an 80-percent confidence interval of the slope from a linear regression. The conservative confidence interval of 80 percent was chosen to preclude eliminating even moderately probable fluxes. The most consistent release rates were measured for Ni, Zn, and As. Release of Ni was observed at four sites (2B,3B,4B,5A), while uptake was not measured at any site, and the remaining six sites had no distinguishable flux (1A,1B,2A,3A,4A,5B). The maximum release rate of Ni was 565 $\mu\text{g}/\text{m}^2/\text{day}$ at site 5A. Release of Zn was measured at five sites (1B,2A,3A,5A,5B) with a maximum release of 837 $\mu\text{g}/\text{m}^2/\text{day}$ at site 5A. Uptake of Zn was observed at site 1A, and four sites (2B,4A,4B,5B) showed no consistent Zn flux. Release was measured at four sites (1B,2B,3A,4B), while uptake was not found at any site; and the remaining sites (1A,2A,3B,4A,5A,5B) showed no flux. The maximum As release was 292 $\mu\text{g}/\text{m}^2/\text{day}$ at site 2B. For Cu, Cd, and Pb, flux rates were not as consistently positive; and at several sites, we observed uptake of these metals. Cu release was measured only at site 3A (346 $\mu\text{g}/\text{m}^2/\text{day}$), while uptake was observed at four sites (1A,2A,2B,3B); and no flux was measured at the remaining five sites (1B,4A,4B,5A,5B). Similarly, release of Cd was found at only 2 of the 10 sites (1A,5B), with uptake at 2 sites (2A,2B); and no detectable flux at 6 sites (1B,3A,3B,4A,4B,5A). The maximum Cd release rate was 68 $\mu\text{g}/\text{m}^2/\text{day}$ at site 5B. Measurement of flux rates for Pb was hampered by the low levels present in many samples. Insufficient data were available to calculate a flux for six sites (1A,1B,2B,3A,4A,5A). Of the remaining sites, none showed a release of Pb, while two showed uptake (2A,3B), and two showed no flux (4B,5B).

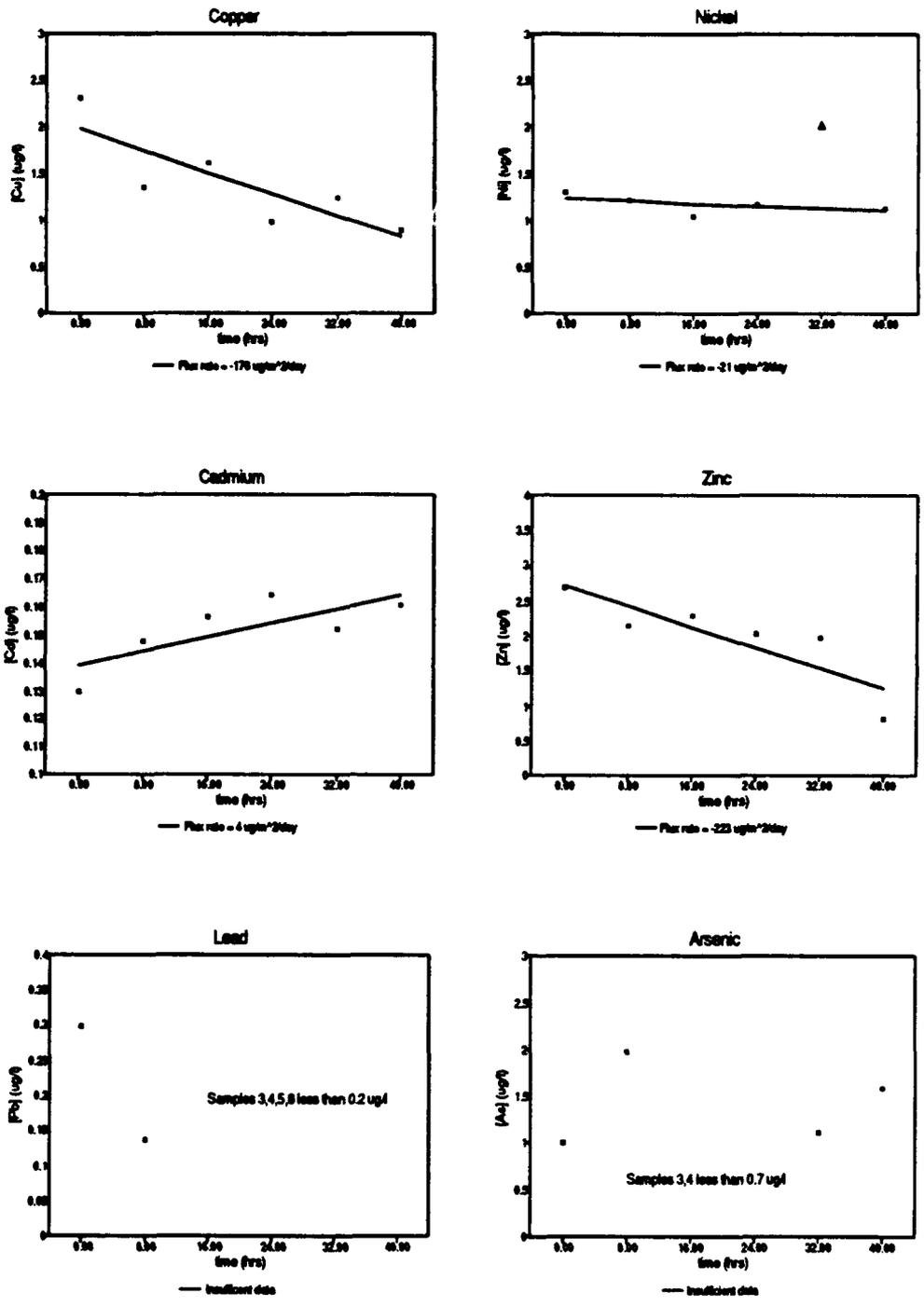


Figure 29. Time-series chamber samples and flux rates at site 1A based on a linear regression over the sampling period. Data not used in the regression are indicated by \blacktriangle (see table 4).

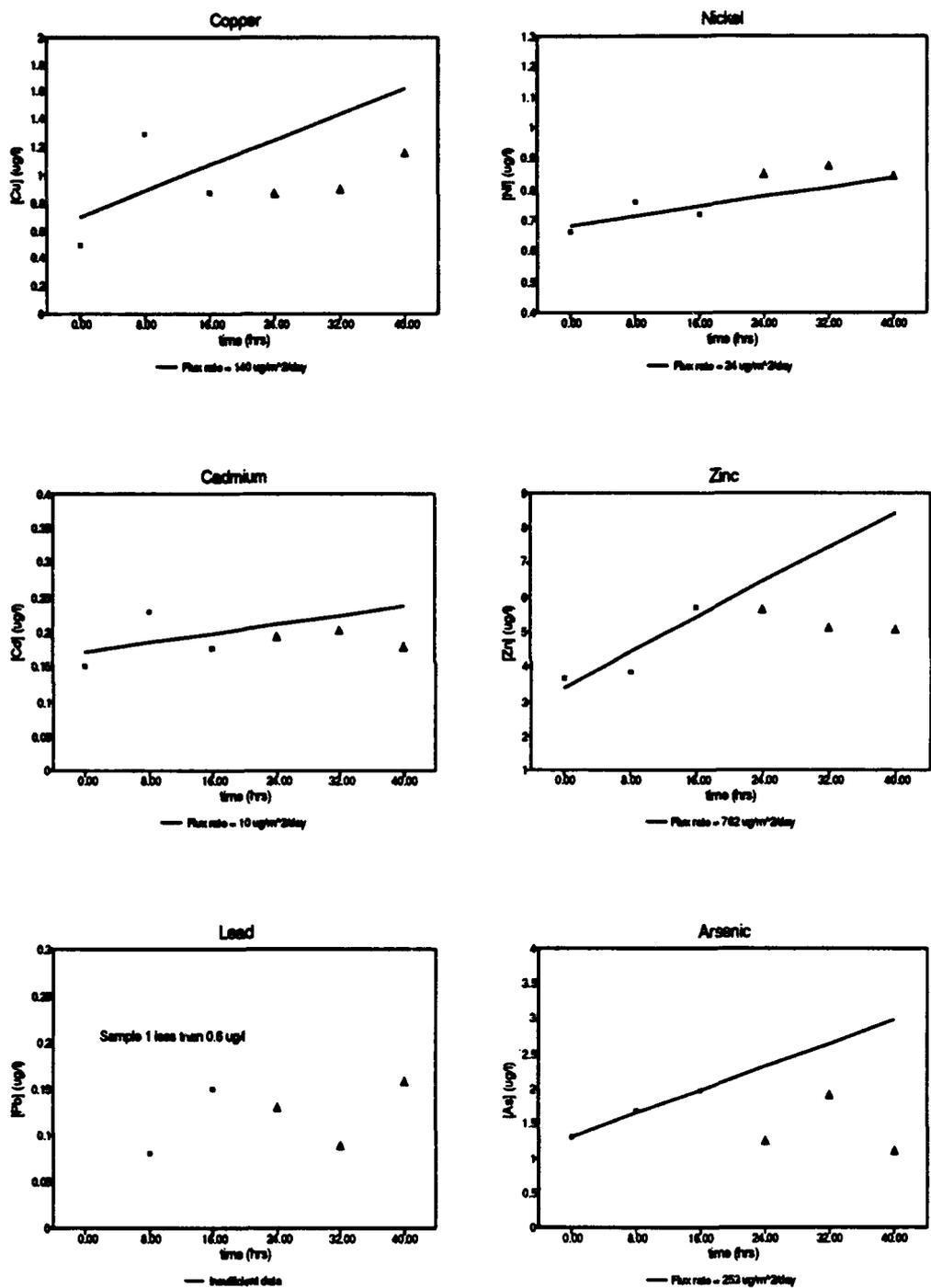


Figure 30. Time-series chamber samples and flux rates at site 1B based on a linear regression over the sampling period. Data not used in the regression are indicated by \blacktriangle (see table 4).

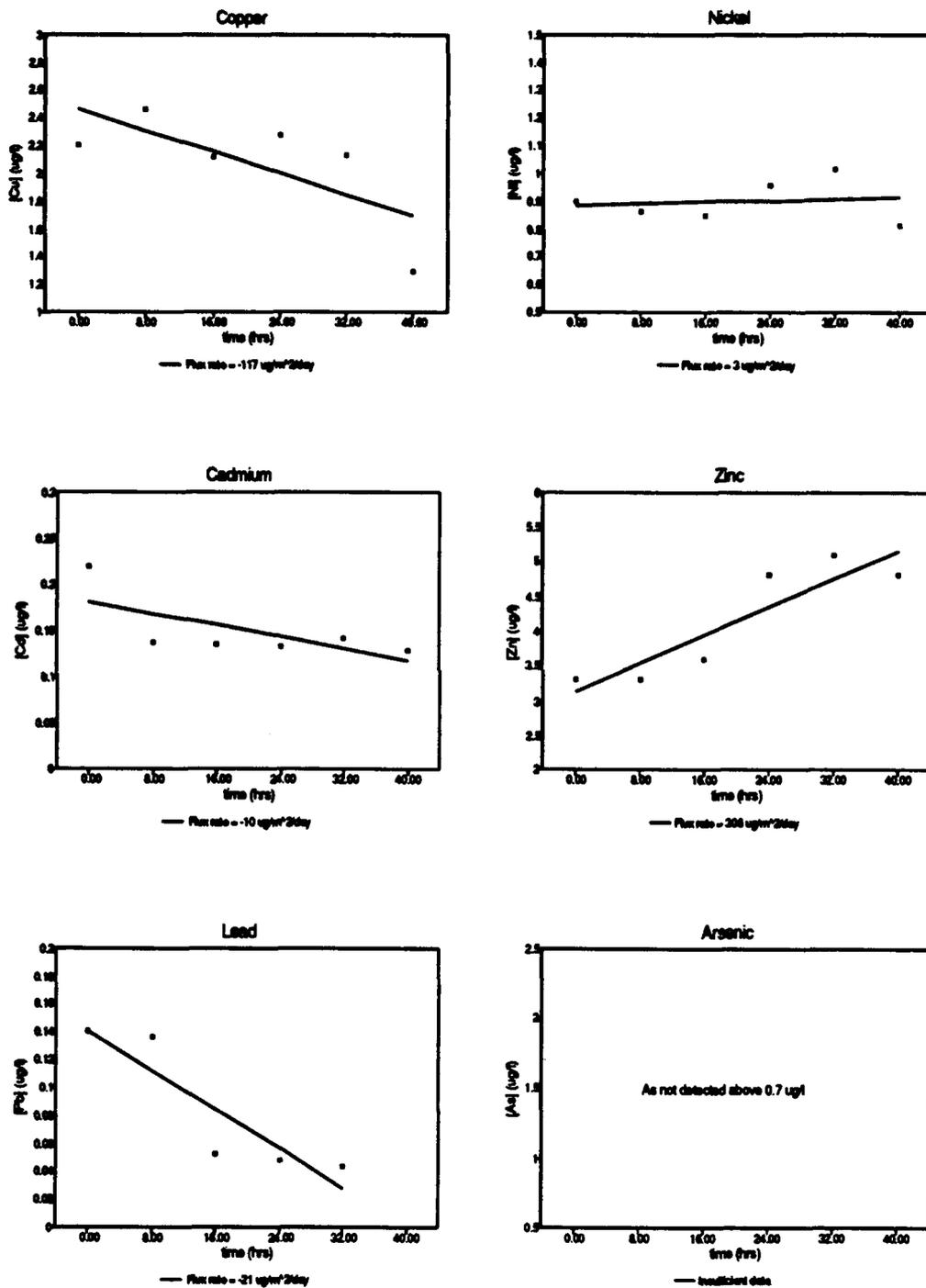


Figure 31. Time-series chamber samples and flux rates at site 2A based on a linear regression over the sampling period. Data not used in the regression are indicated by \blacktriangle (see table 4).

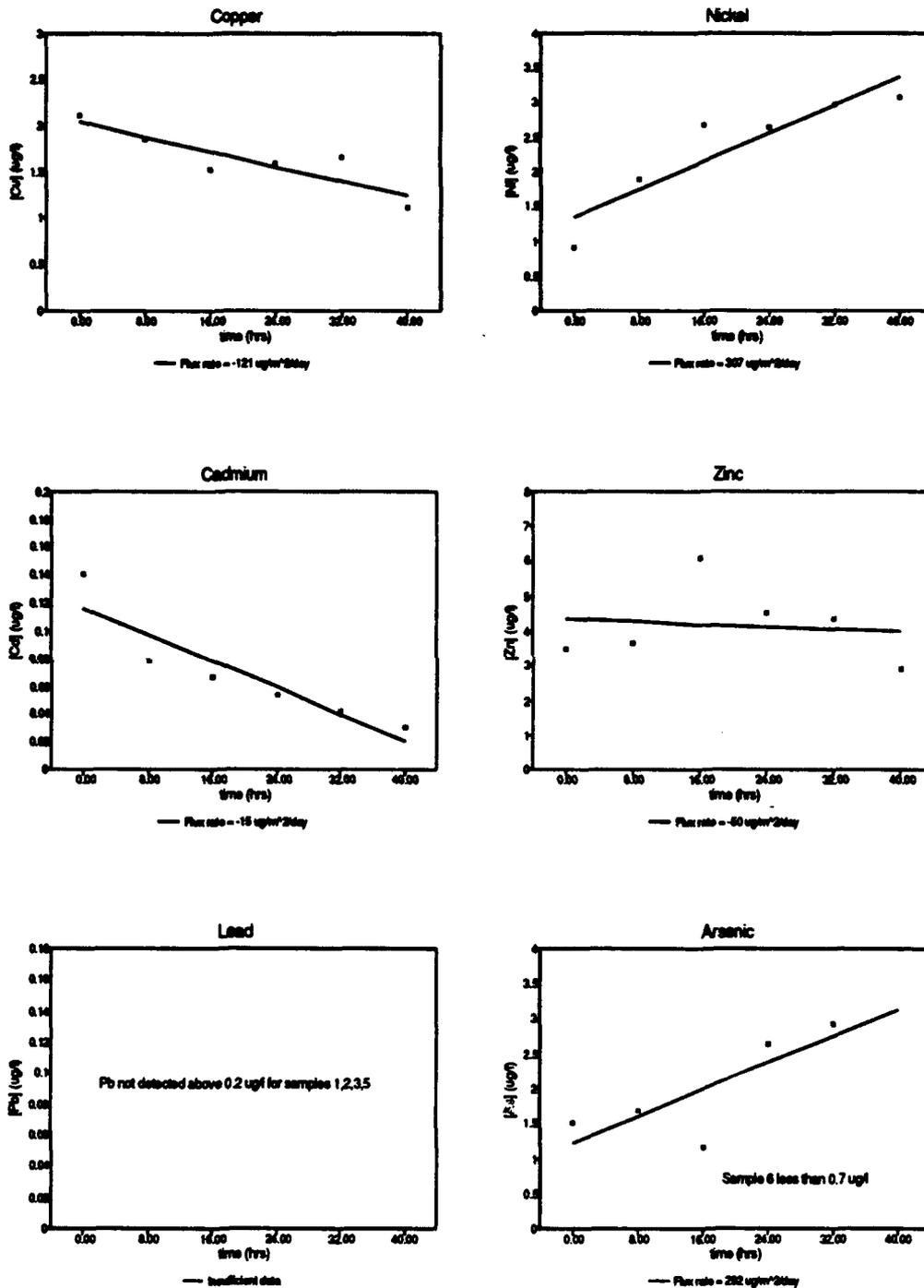


Figure 32. Time-series chamber samples and flux rates at site 2B based on a linear regression using the sampling period. Data not used in the regression are indicated by \blacktriangle (see table 4).

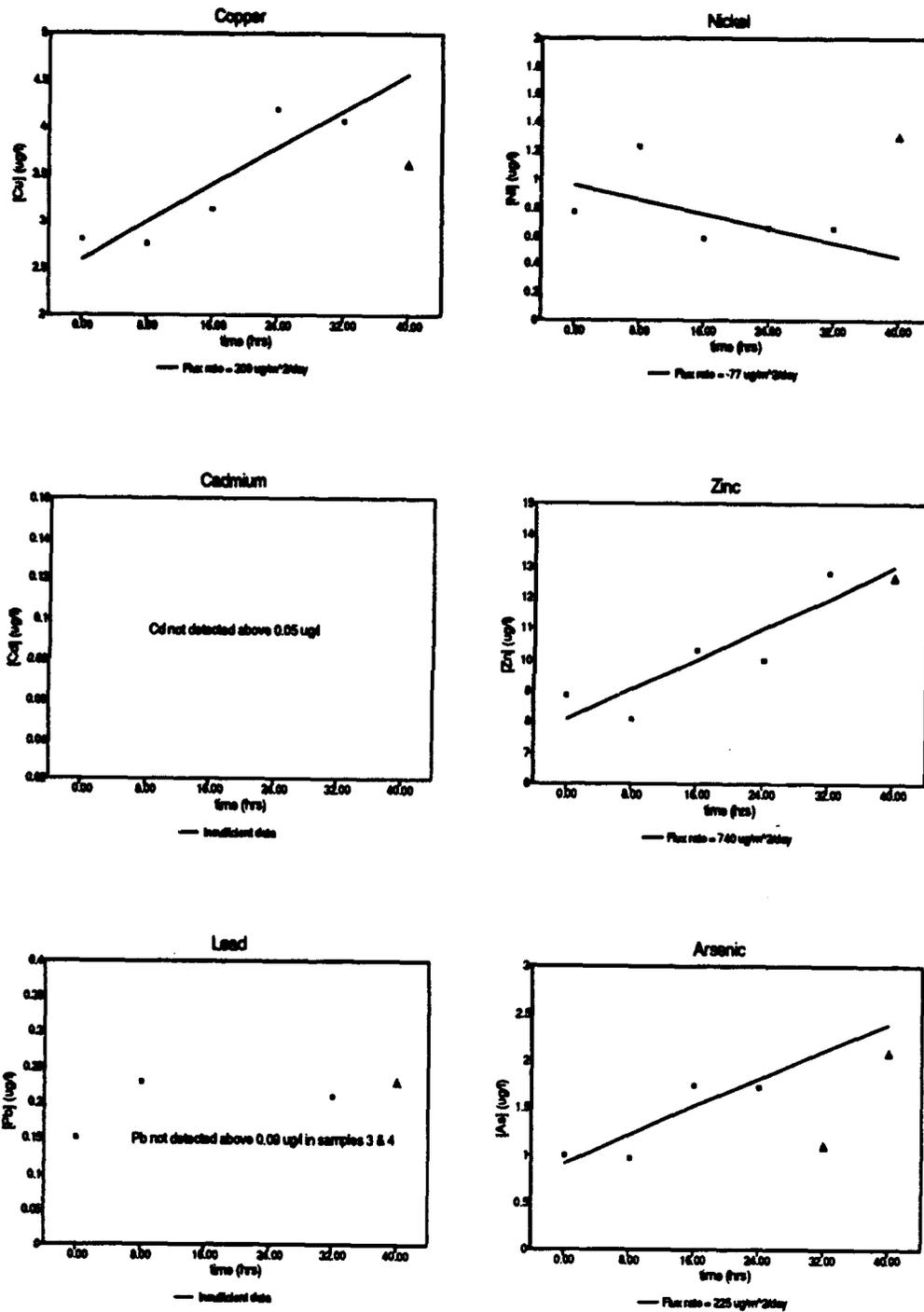


Figure 33. Time-series chamber samples and flux rates at site 3A based on a linear regression over the sampling period. Data not used in the regression are indicated by \blacktriangle (see table 4).

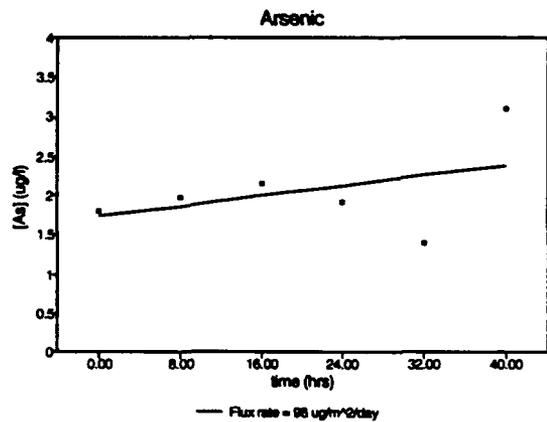
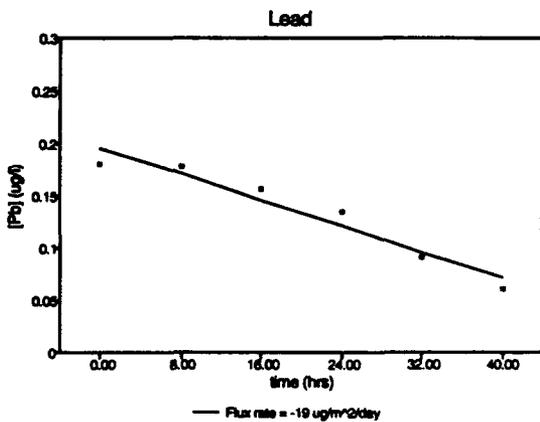
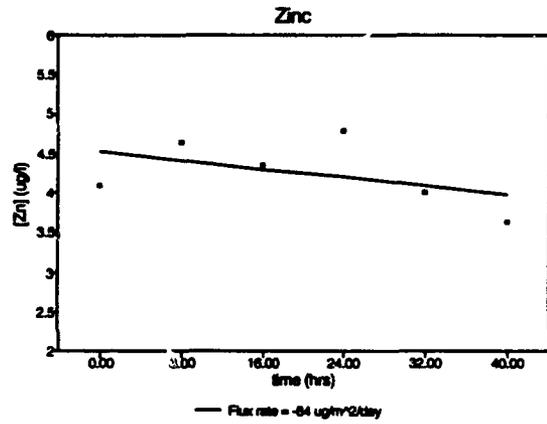
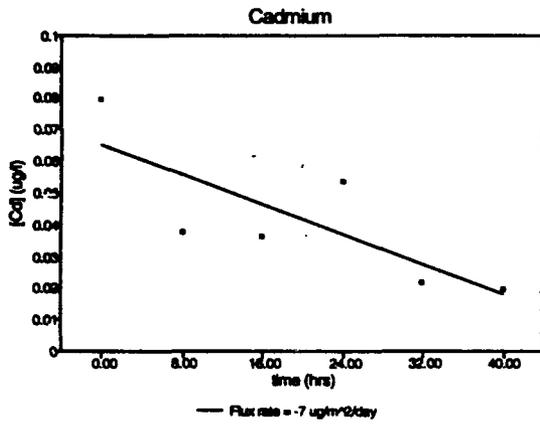
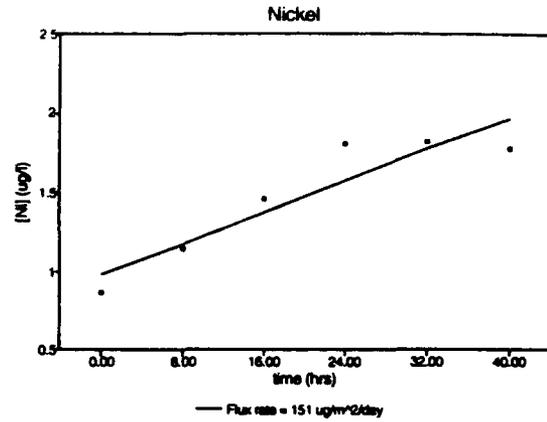
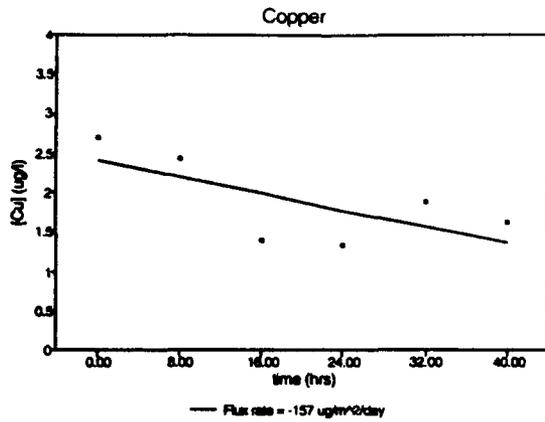


Figure 34. Time-series chamber samples and flux rates at site 3B based on a linear regression over the sampling period. Data not used in the regression are indicated by \blacktriangle (see table 4).

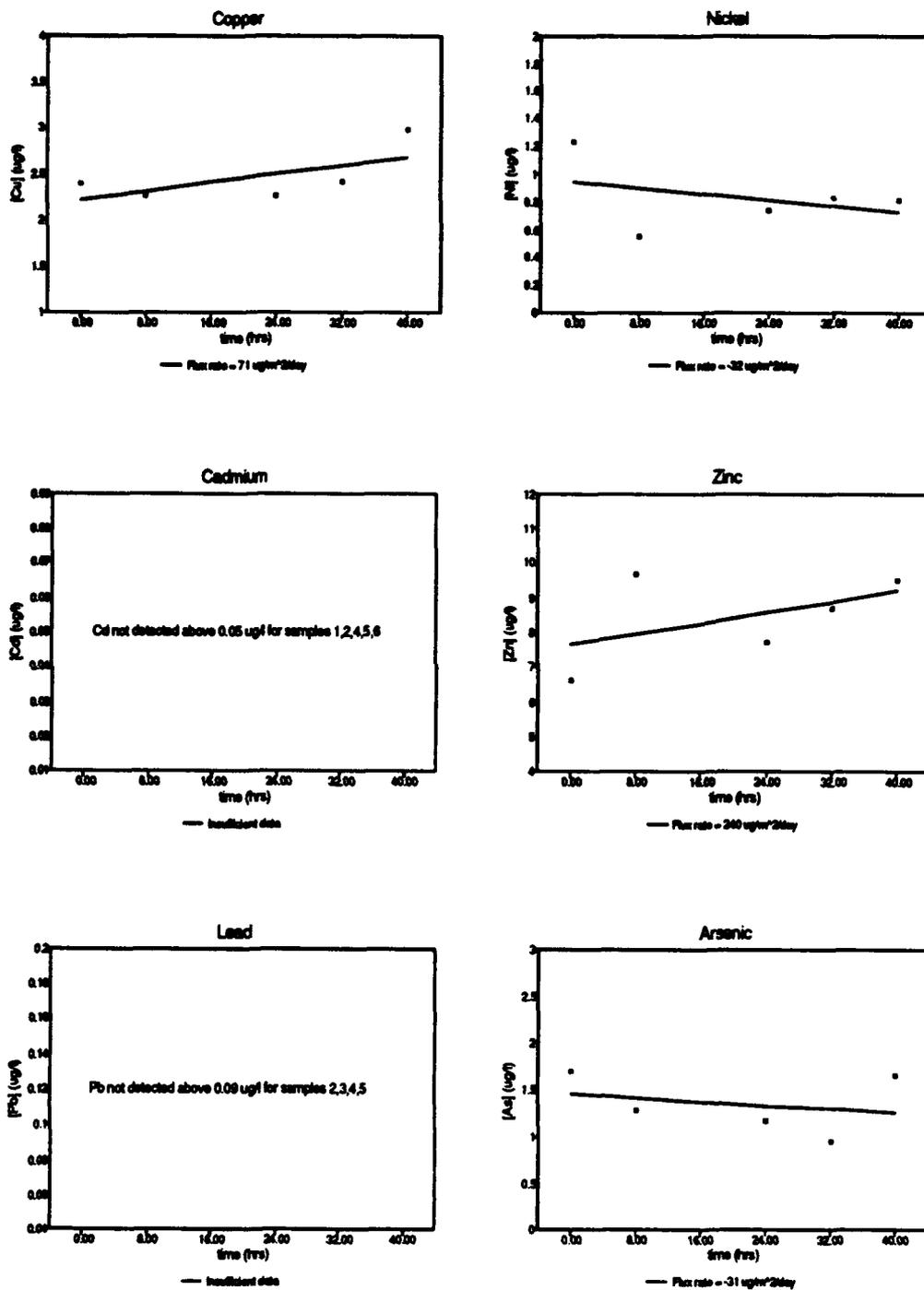


Figure 35. Time-series chamber samples and flux rates at site 4A based on a linear regression over the sampling period. Data not used in the regression are indicated by \blacktriangle (see table 4).

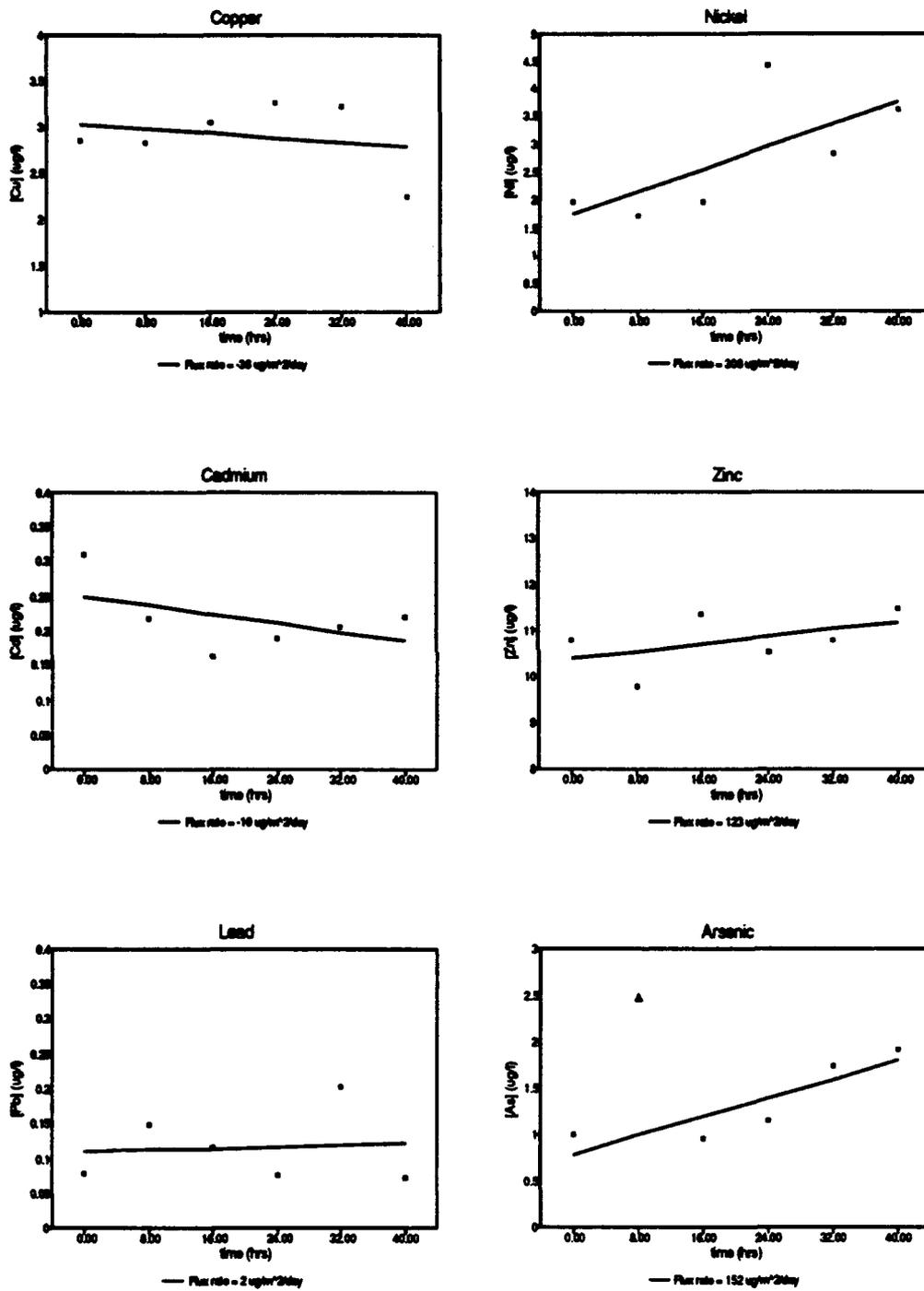


Figure 36. Time-series chamber samples and flux rates at site 4B based on a linear regression over the sampling period. Data not used in the regression are indicated by Δ (see table 4).

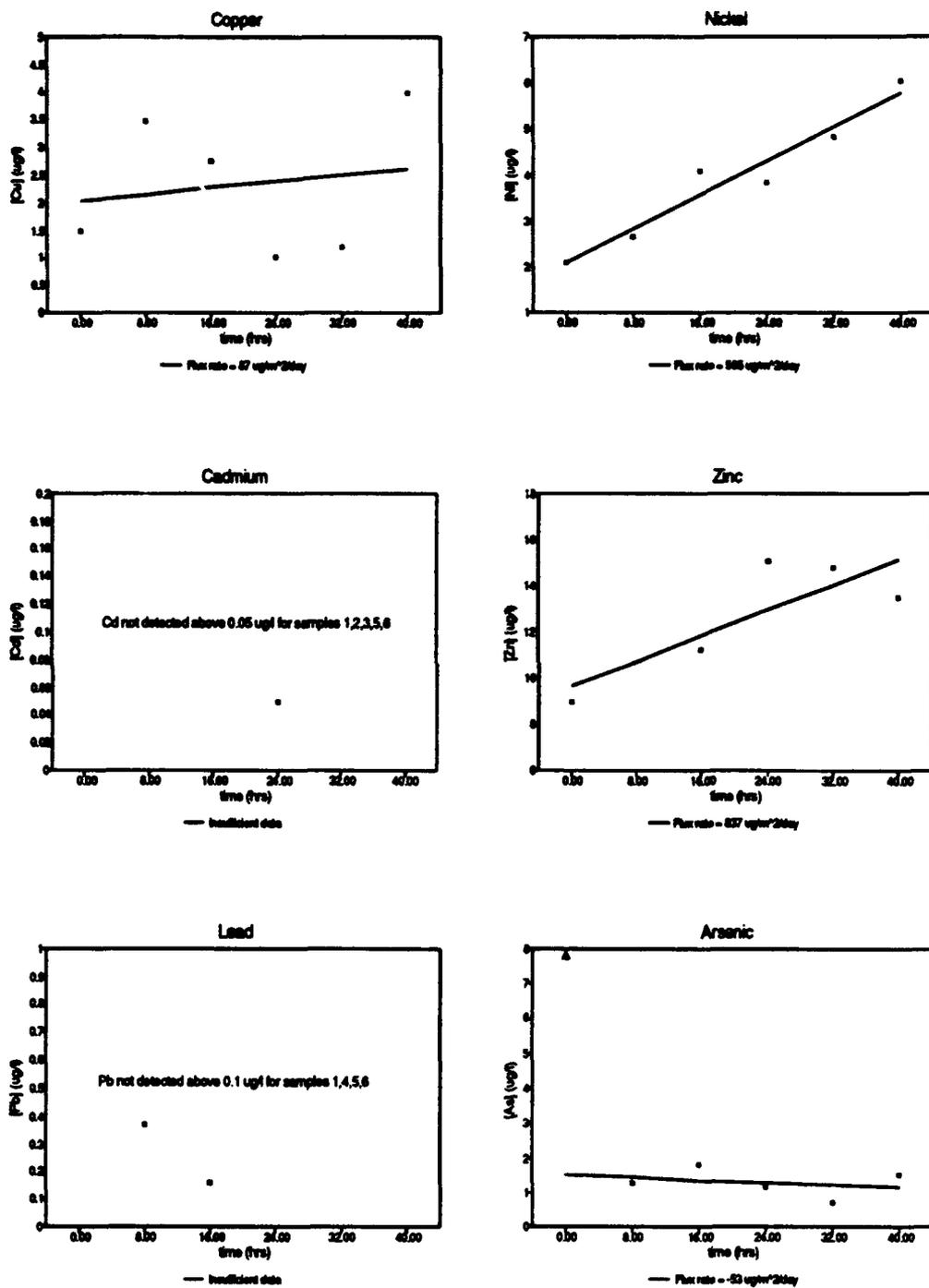


Figure 37. Time-series chamber samples and flux rates at site 5A based on a linear regression over the sampling period. Data not used in the regression are indicated by \blacktriangle (see table 4).

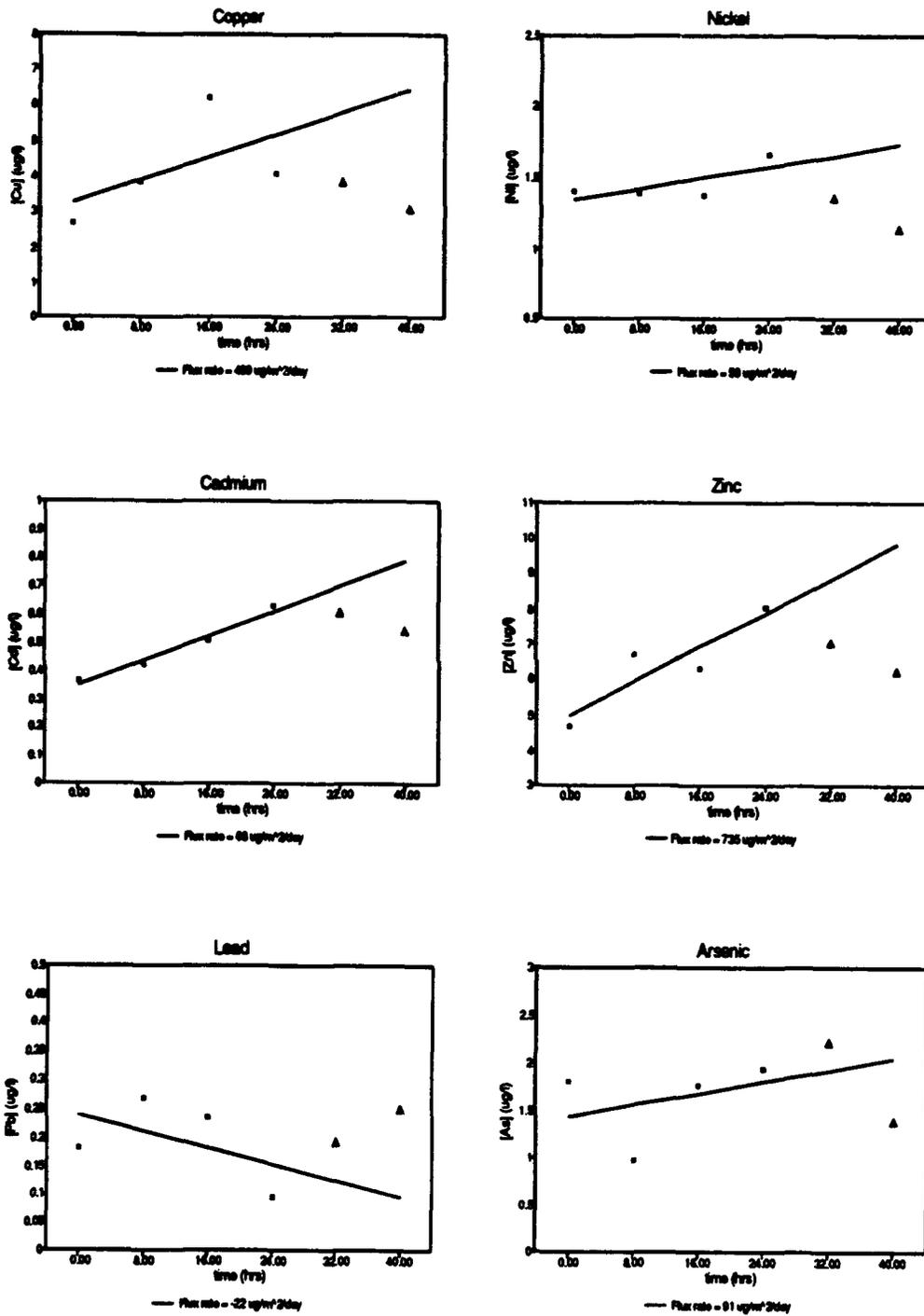


Figure 38. Time-series chamber samples and flux rates at site 5B based on a linear regression over the sampling period. Data not used in the regression are indicated by \blacktriangle (see table 4).

Table 5. Flux rates \pm 80% CI, and r^2 values for Cu, Cd, Pb, Ni, Zn, and As ($\mu\text{g}/\text{m}^2/\text{day}$). Missing values indicate insufficient data to calculate flux rate. Shaded cells indicate statistically significant release.

Site	Cu		Cd		Pb		Ni		Zn		As	
	flux	r^2	flux	r^2	flux	r^2	flux	r^2	flux	r^2	flux	r^2
1A	-176 \pm 88	0.70	4 \pm 2	0.58	-114 \pm 19	1.00	-21 \pm 28	0.33	-223 \pm 100	0.36	7 \pm 193	0.00
1B	140 \pm 826	0.21	10 \pm 88	0.11	--	--	24 \pm 94	0.37	762 \pm 1151	0.81	253 \pm 68	0.99
2A	-117 \pm 89	0.50	-10 \pm 8	0.48	-21 \pm 10	0.80	3 \pm 24	0.01	308 \pm 113	0.81	--	--
2B	-121 \pm 49	0.79	-15 \pm 4	0.84	--	--	307 \pm 106	0.83	-50 \pm 254	0.01	292 \pm 199	0.63
3A	300 \pm 133	0.82	--	--	--	--	-77 \pm 208	0.20	740 \pm 418	0.74	225 \pm 163	0.77
3B	-157 \pm 159	0.46	-7 \pm 5	0.62	-19 \pm 5	0.94	151 \pm 58	0.86	-84 \pm 143	0.23	98 \pm 1995	0.18
4A	71 \pm 78	0.42	--	--	--	--	-32 \pm 82	0.12	240 \pm 390	0.25	-31 \pm 106	0.07
4B	-36 \pm 114	0.06	10 \pm 13	0.23	2 \pm 16	0.01	308 \pm 241	0.49	123 \pm 167	0.24	152 \pm 82	0.76
5A	87 \pm 386	0.03	--	--	--	--	565 \pm 113	0.94	837 \pm 545	0.68	-53 \pm 178	0.07
5B	489 \pm 947	0.32	68 \pm 14	0.98	-22 \pm 52	0.24	59 \pm 75	0.53	735 \pm 462	0.72	91 \pm 319	0.13

BULK SEDIMENT TRACE METALS

Bulk sediment concentrations of trace metals measured during the BFSDD study are summarized in figure 39, along with the original Site Investigation (SI) data. Our data and the SI data are fairly consistent in magnitude except for Ni for which our concentrations were consistently higher (37–165 percent), and As for which our data were generally lower (200–3700 percent). These apparent biases may be attributed to differences in analytical methods (microwave digestion vs. acid digestion, GFAA analysis vs. ICP), while the more general variability is most likely related to spatial heterogeneity in the sediment distribution and sample collection for these elements.

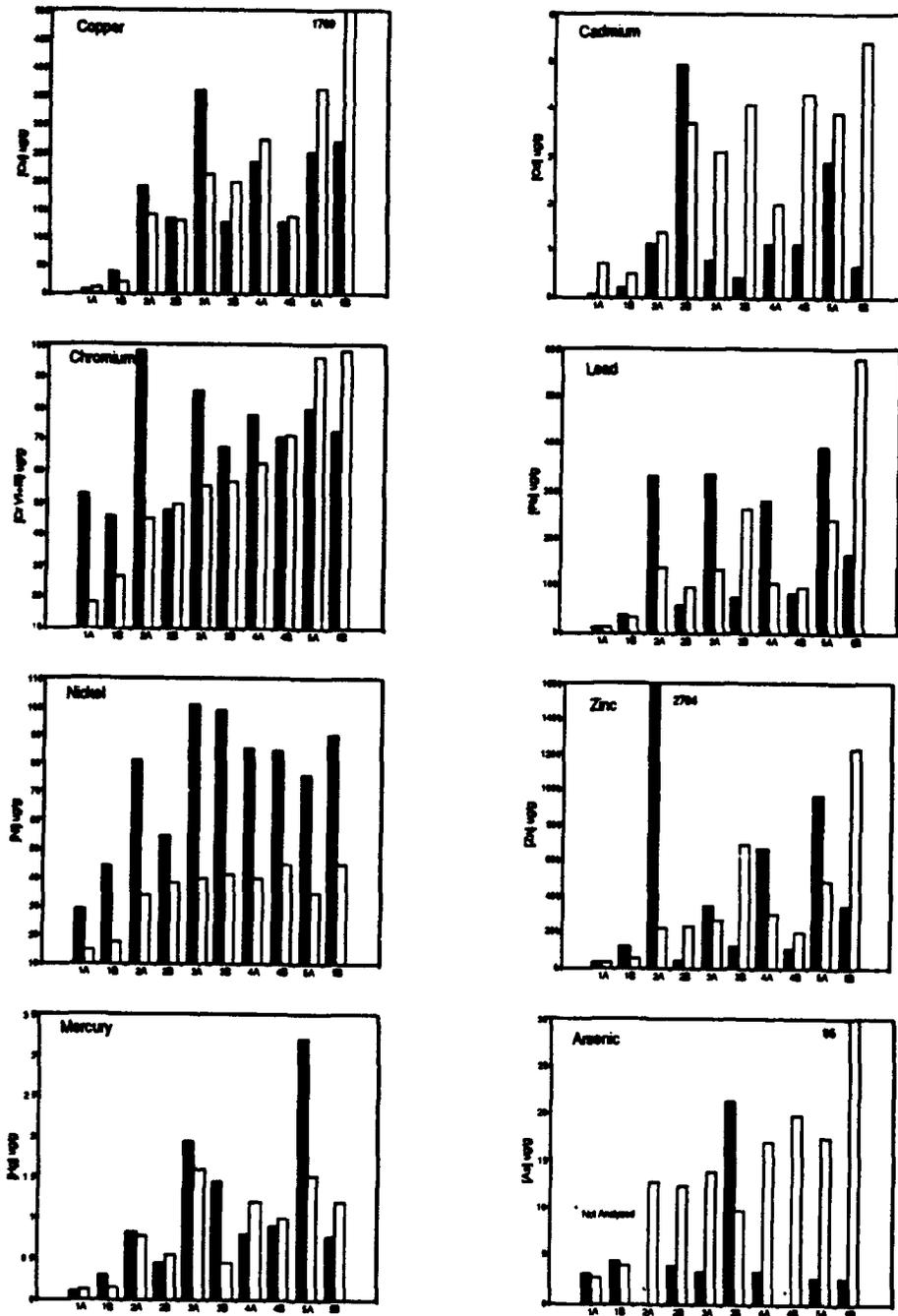


Figure 39. Bulk sediment trace metal concentrations at the 10 BFSD sites in Sinclair Inlet. The ■ indicates NRaD data and □ indicates SI data.

For Cu, Ni, Hg, Cd, Pb, and Zn, we generally found lowest bulk-sediment concentrations at the outer-inlet reference sites 1A and 1B, while the shipyard sites (2A,2B,3A,3B,4A,5A,5B) and the back inlet site (4B) were significantly higher. For Cr and As, this trend was weaker, and distributions appeared to be more uniform throughout the inlet. Cu concentrations ranged from a minimum of 4.9 $\mu\text{g/g}$ at the reference site (1A) to a maximum of 358 $\mu\text{g/g}$ at shipyard site 3B. Cr levels were more uniform through the inlet, with a low concentration of 46 $\mu\text{g/g}$ at site 1B near the ferry landing and a high of 98 $\mu\text{g/g}$ at shipyard site 2A. Ni was lowest at site 1A, with 28.9 $\mu\text{g/g}$; and highest at shipyard site 3A, with 101 $\mu\text{g/g}$. Hg levels ranged from 0.09 $\mu\text{g/g}$ at site 1A to a maximum of 2.7 $\mu\text{g/g}$ at shipyard site 5A. Reference site 1A was also lowest for Cd 0.08 $\mu\text{g/g}$, while the highest Cd concentration was found at shipyard site 2B (5.0 $\mu\text{g/g}$). Pb varied from a low of 10.9 $\mu\text{g/g}$ at site 1A to a maximum of 382 $\mu\text{g/g}$ at site 5A. Concentrations of Zn ranged from 26.1 (site 1A) to 2794 $\mu\text{g/g}$ (site 2A). The level at site 2A was considerably higher than any other site (factor of 2) and could have been associated with cable debris (galvanized steel) observed in the sediment at this site during BFSD deployments. Concentrations were more uniform through the inlet with lowest levels at shipyard site 5A and highest levels at shipyard site 3B. Bulk sediment concentrations are compared to recently published sediment-quality criteria (State of WA) in table 6.

Table 6. Bulk sediment concentrations and Washington State Criteria for trace metals at the 10 BFSD sites in Sinclair Inlet. All concentrations are in $\mu\text{g/g}$.

Site	Cu	Cd	Cr	Pb	Ni	Zn	Hg	As
1A	4.9	0.08	53	11	29	26	0.09	3.1
1B	38	0.22	46	38	44	124	0.29	4.5
2A	192	1.13	98	332	81	2794	0.81	---
2B	135	4.96	48	59	55	43	0.44	3.9
3A	358	0.82	85	338	101	353	1.93	3.4
3B	127	0.43	68	76	99	126	1.44	21.2
4A	235	1.12	78	279	85	668	0.80	3.3
4B	127	1.16	71	83	84	111	0.90	3.3
5A	257	3.71	61	382	66	916	2.71	2.7
5B	254	0.68	73	166	93	274	0.76	2.8
WA State Criteria	390	5.1	260	450	N/A	410	0.41	57

PAH/PCB FLUX RATES

Time-series BFSB samples were analyzed for a number of PAH compounds and PCB congeners (table 1) at 2 of the 10 sites (3B,5B). These results were evaluated using the same performance criteria as the trace-metals data, except that all six samples at site 3B were included in the calculations. This was based on the assumption (and observation) that anoxic conditions would not significantly affect the flux of these compounds. At site 5B, the same reduced sample set (1-4) was used as with the trace metals.

Results for the PAH fluxes are shown in figures 40-42 for site 3B and figures 43-45 for site 5B. At site 3B, release of several PAH compounds was observed, in particular for the more soluble, lower molecular weight PAHs such as naphthalene, acenaphthene, fluorene, and phenanthrene. Of the 24 PAH compounds measured, 11 showed a significant (80-percent CI) release, while the remainder had no detectable flux. The release rates for the compounds with detectable fluxes ranged from 28 ng/m²/day for Dibenzo[a,h]anthracene, to a maximum of 6600 ng/m²/day for C1-Naphthalene. At site 5B, PAH release was observed for 8 compounds predominantly of medium molecular weight (phenanthrene, fluoranthene, pyrene, and chrysene), while a small but statistically significant uptake was found for Benzo-b-fluoranthene, and no detectable flux was found for the remaining 15 compounds. Table 7 summarizes calculated release rates, 80-percent confidence intervals, and r² values from the regression for each of the PAH compounds at sites 3B and 5B.

Small sample volumes and low ambient-water concentrations limited our ability to measure flux rates of PCB congeners. Only PCB-110 could be quantified, and these values can only be interpreted as upper limits, since all but one of them lacked second-ion confirmation from the GC/MS analysis. Results for PCB-110 are shown in figure 46 for sites 3B and 5B. Equivalent concentrations of Aroclor 1254 from the PCB-110 data are given on a second y-scale based on comparison with a standard. No detectable flux was observed at either site, and PCB concentrations based on the Aroclor 1254 equivalents were generally below 1 ng/l.

BULK SEDIMENT PAH/PCB

A bulk sediment grab was collected, and a sample from the top 2 cm was analyzed for PAH/PCB at each of the 10 BFSB sites. Results for individual PAH compounds are shown in figures 47-48. Lowest levels were found at site 1A. Sites 1B, 2A, and 4B had moderate PAH concentrations, generally an order of magnitude higher than site 1A. Sites 2B, 3A, 3B, 4A, 5A, and 5B all had significantly higher concentrations with maximum levels at site 2B and 5A. The compositional distribution for PAHs was similar at most sites and generally showed maxima for fluoranthene, pyrene, and chrysene, except for reference site 1A. This site had proportionally higher levels of naphthalene than the other sites. PAH concentrations for individual and summed compounds normalized to total organic carbon (TOC) are summarized in table 8 and compared to Washington State Criteria.

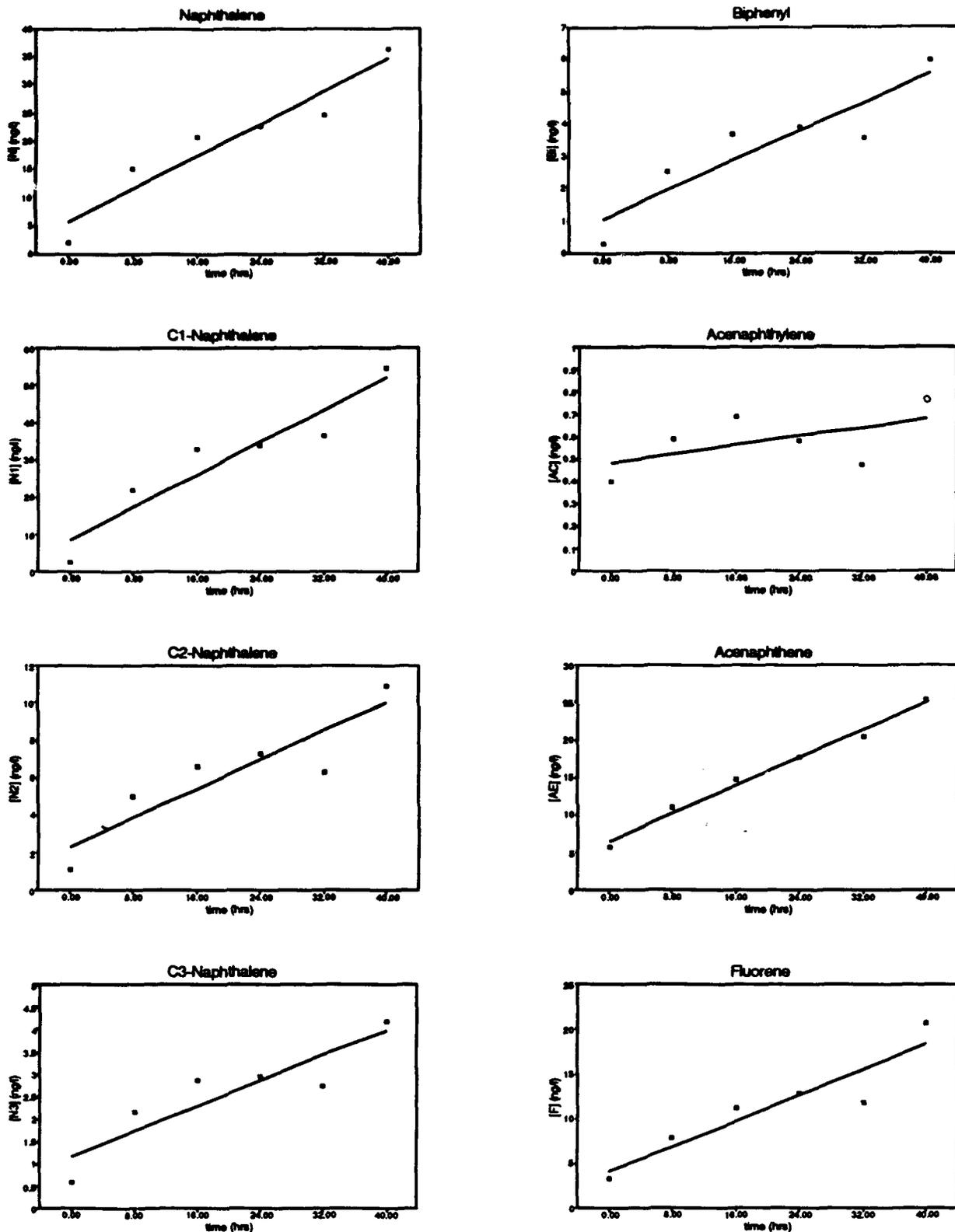


Figure 40. Time-series chamber samples and flux rates at site 3B based on a linear regression over the sampling period. \blacktriangle indicates data not used in regression (table 4), and \circ indicates sample lacked second-ion confirmation.

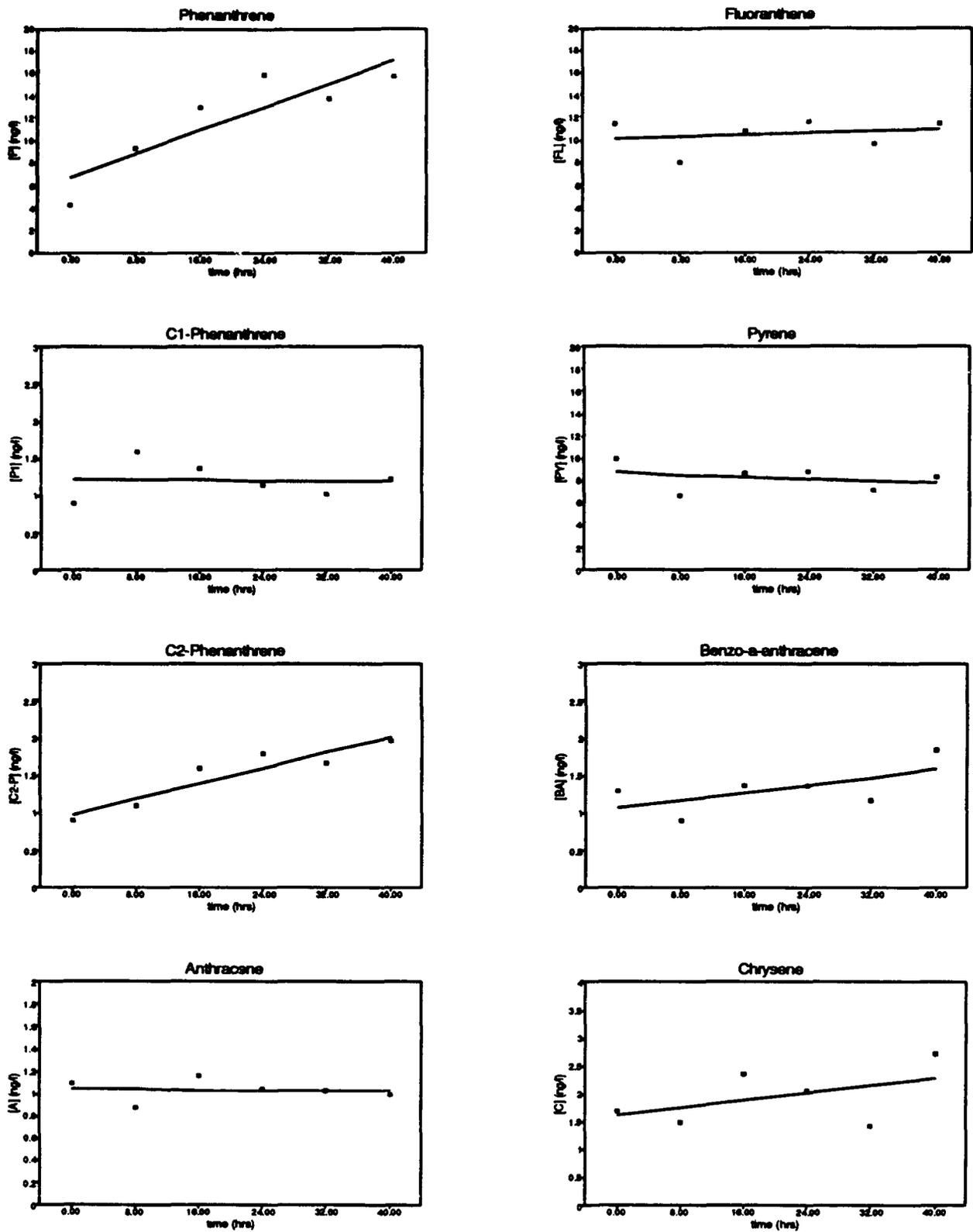


Figure 41. Time-series chamber samples and flux rates at site 3B based on a linear regression over the sampling period. ▲ indicates data not used in regression (table 4), and ○ indicates sample lacked second-ion confirmation.

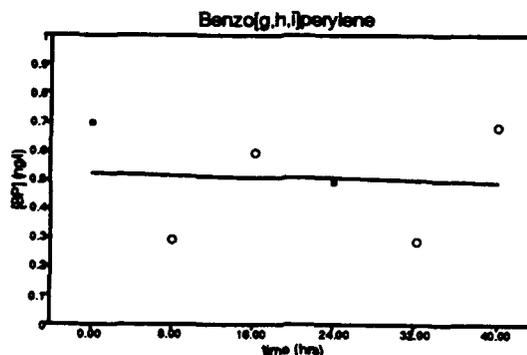
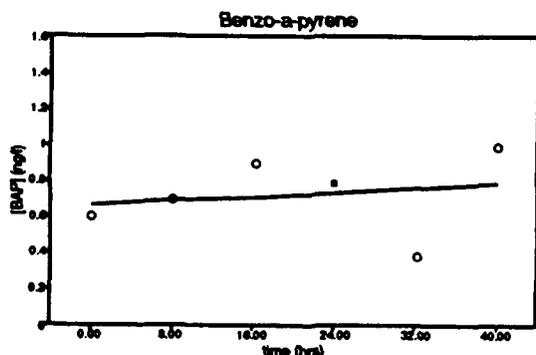
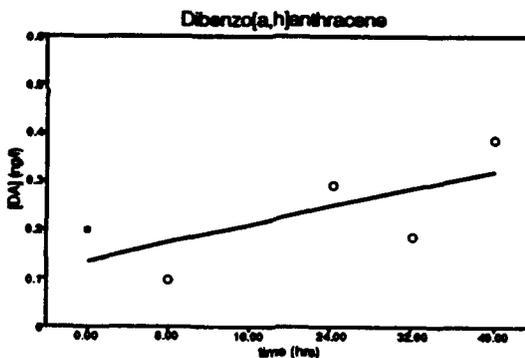
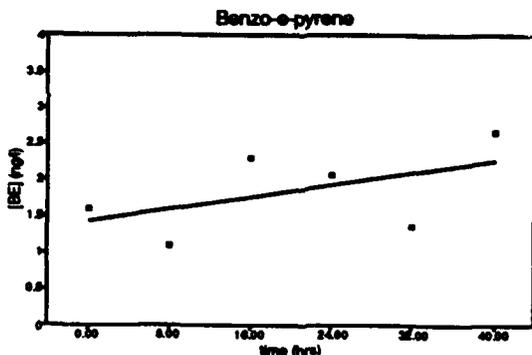
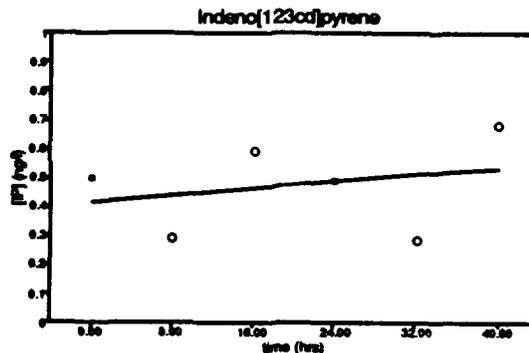
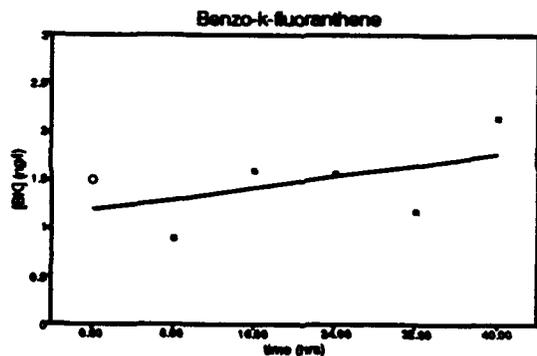
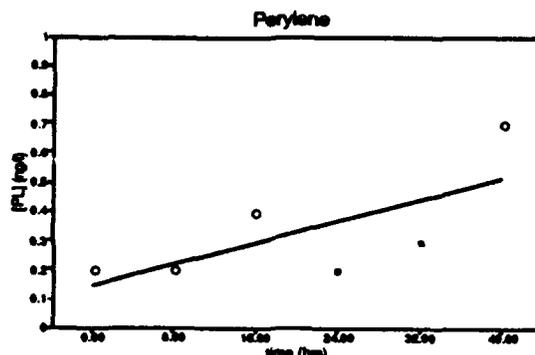
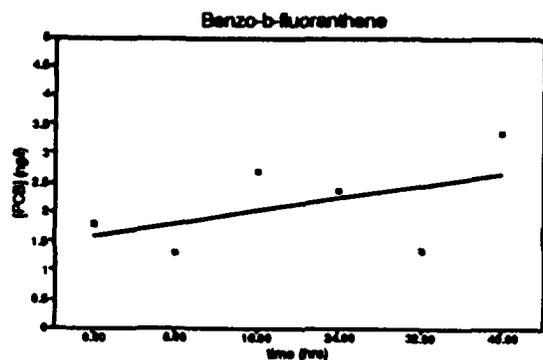


Figure 42. Time-series chamber samples and flux rates at site 3B based on a linear regression over the sampling period. ▲ indicates data not used in regression (table 4), and ○ indicates sample lacked second-ion confirmation.

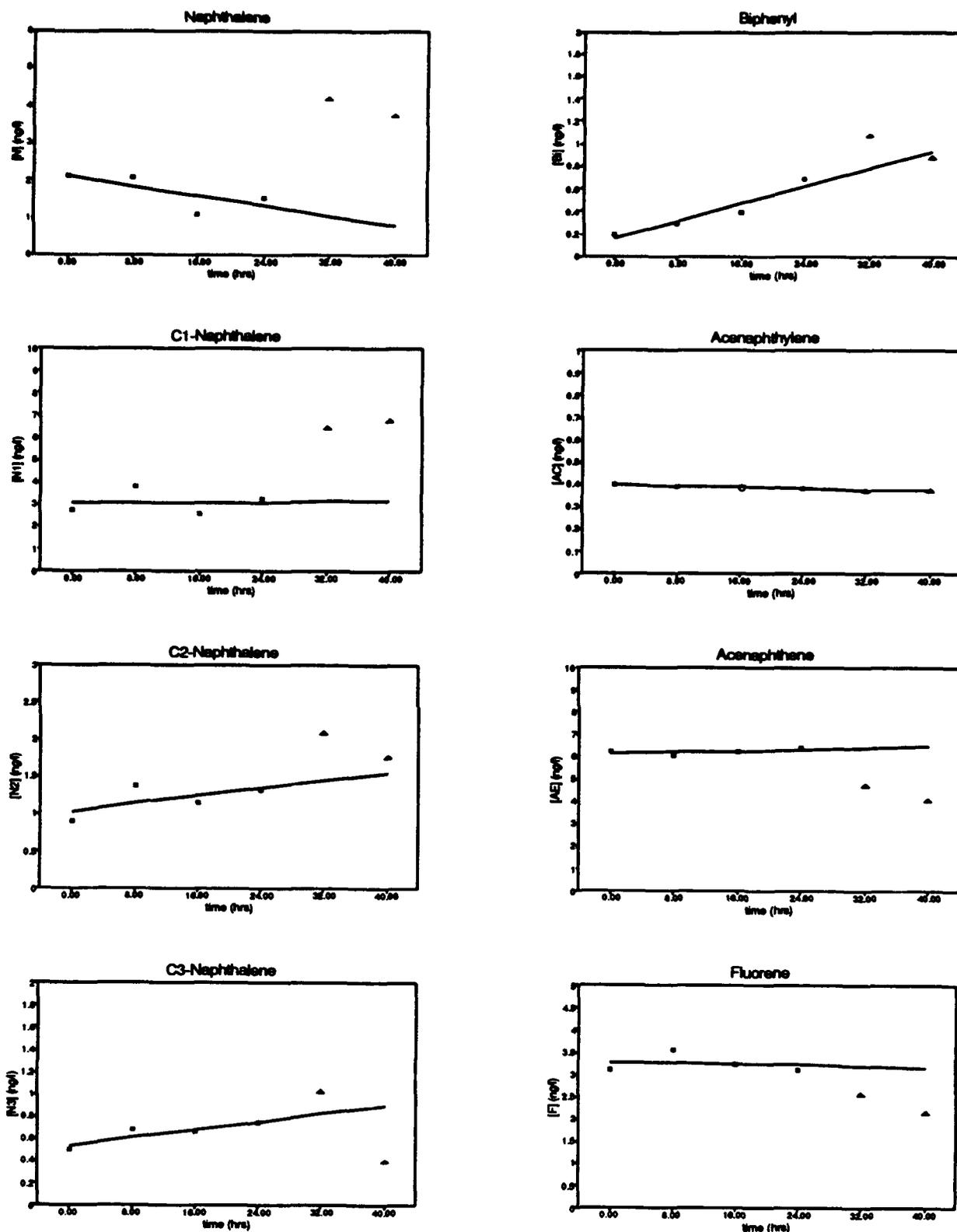


Figure 43. Time-series chamber samples and flux rates at site 5B based on a linear regression over the sampling period. ▲ indicates data not used in regression (table 4), and ○ indicates sample lacked second-ion confirmation.

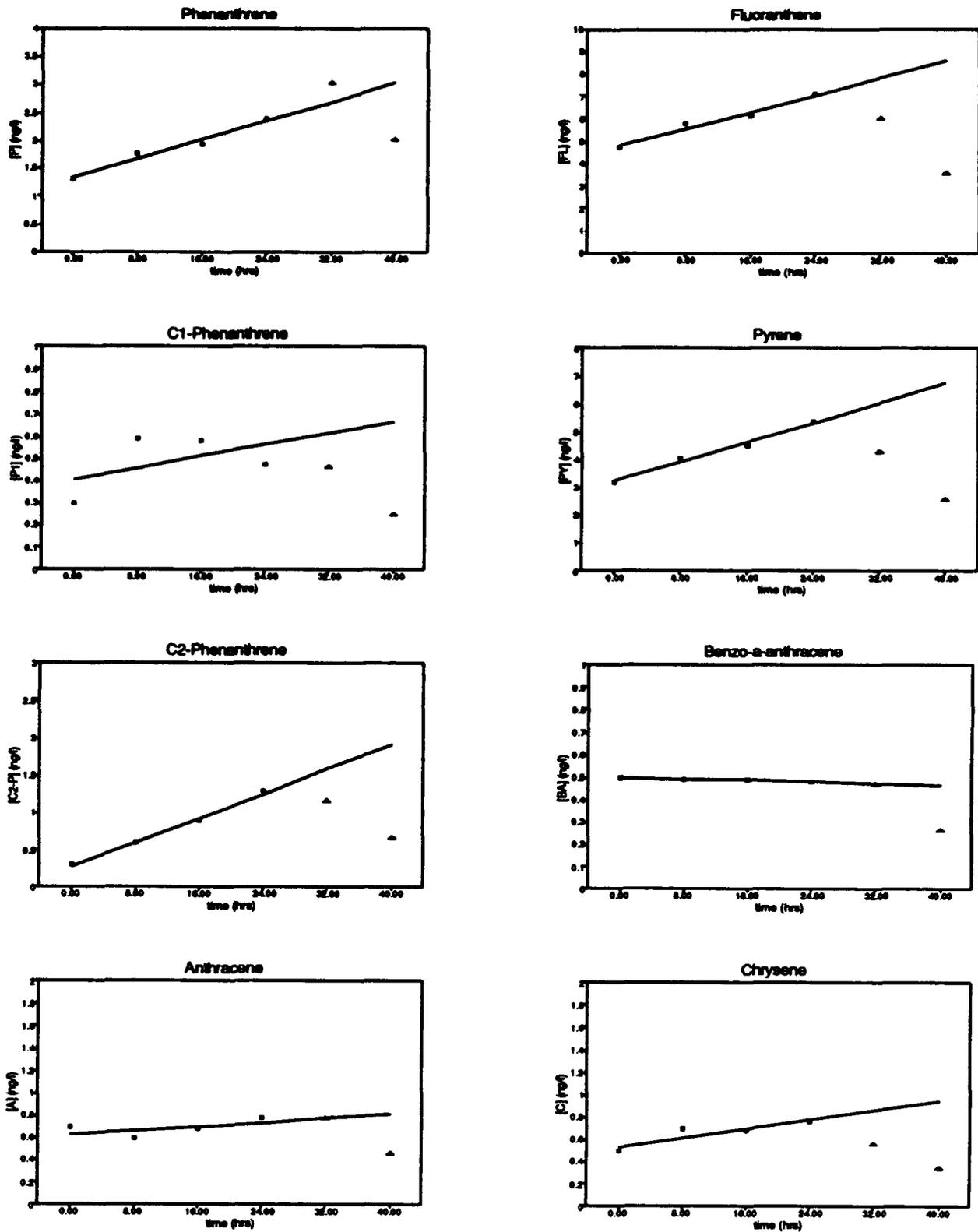


Figure 44. Time-series chamber samples and flux rates at site 5B based on a linear regression over the sampling period. ▲ indicates data not used in regression (table 4), and O indicates sample lacked second-ion confirmation.

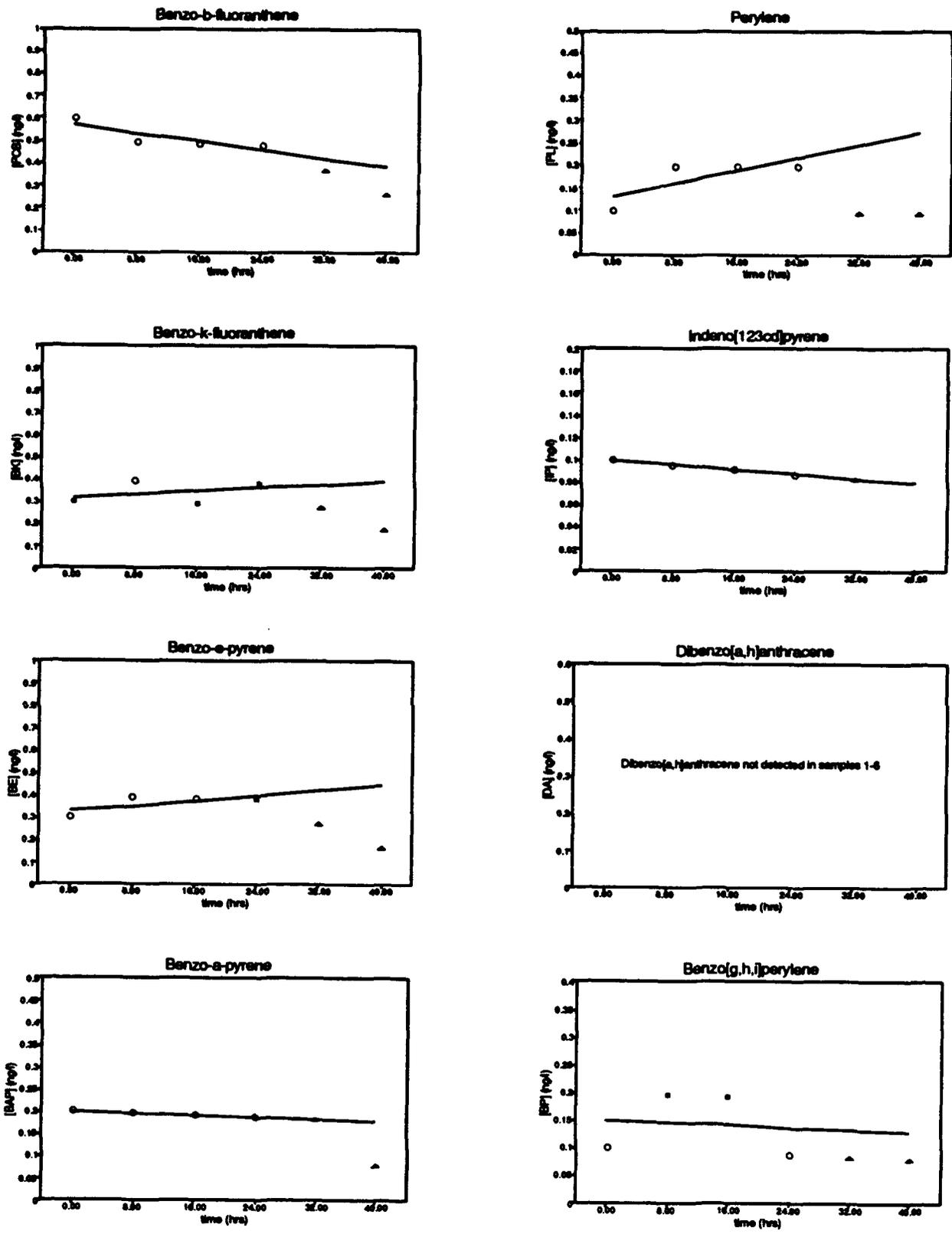


Figure 45. Time-series chamber samples and flux rates at site 5B based on a linear regression over the sampling period. ▲ indicates data not used in regression (table 4), and O indicates sample lacked second-ion confirmation.

Table 7. Flux \pm 80% confidence interval, and r^2 values for PAH compounds at the 10 sites in Sinclair Inlet. All flux rates in ng/m²/day.

PAH Compound	Site 3B		Site 5B	
	flux	r^2	flux	r^2
Naphthalene	4401 \pm 1083	0.91	-202 \pm 260	0.52
C1-Naphthalene	6611 \pm 1745	0.89	1 \pm 437	0.00
C2-Naphthalene	1179 \pm 437	0.81	81 \pm 130	0.40
C3-Naphthalene	429 \pm 164	0.80	54 \pm 38	0.78
Biphenyl	686 \pm 238	0.83	118 \pm 50	0.91
Acenaphthylene	30 \pm 35	0.30	-4 \pm 0	1.00
Acenaphthene	2821 \pm 223	0.99	56 \pm 75	0.50
Anthracene	-4 \pm 29	0.01	25 \pm 50	0.32
Fluorene	2186 \pm 672	0.86	-20 \pm 170	0.02
Phenanthrene	1594 \pm 661	0.77	260 \pm 149	0.97
C1-Phenanthrene	-6 \pm 76	0.00	39 \pm 93	0.23
C2-Phenanthrene	159 \pm 45	0.88	248 \pm 25	0.99
Fluoranthene	115 \pm 444	0.04	568 \pm 149	0.96
Pyrene	-143 \pm 356	0.09	534 \pm 66	0.99
Benzo (a) Anthracene	78 \pm 77	0.36	-5 \pm 0	1.00
Chrysene	103 \pm 140	0.24	61 \pm 31	0.82
Benzo (b) Fluoranthene	164 \pm 217	0.25	-29 \pm 25	0.71
Benzo (k) Fluoranthene	89 \pm 115	0.26	11 \pm 41	0.12
Benzo (e) Pyrene	128 \pm 157	0.28	18 \pm 25	0.47
Benzo (a) Pyrene	19 \pm 65	0.05	-3 \pm 0	1.00
Perylene	56 \pm 43	0.49	22 \pm 25	0.58
Indeno (123-cd) Pyrene	18 \pm 47	0.07	-3 \pm 0	1.00
Dibenzo (ah) Anthracene	28 \pm 26	0.48	----	----
Benzo (g,h,i) Perylene	-5 \pm 58	0.00	-3 \pm 46	0.01

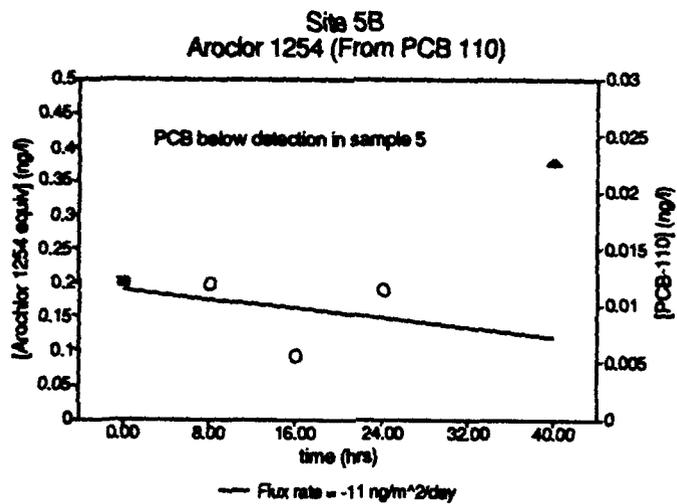
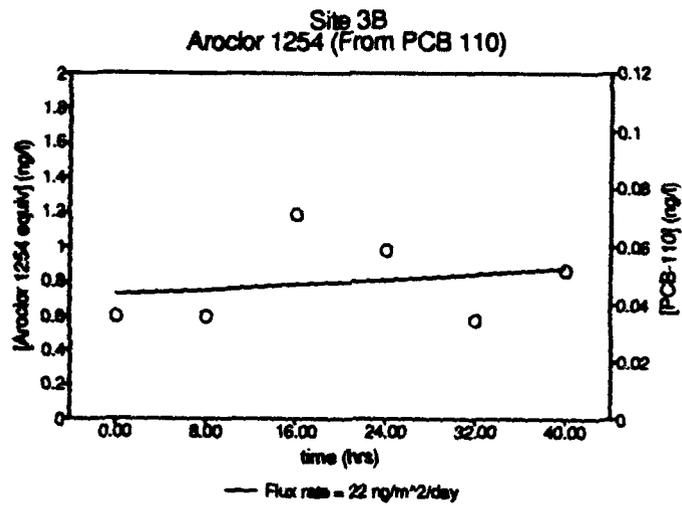


Figure 46. Time-series samples and flux rates for PCB-110 at sites 3B and 5B based on a linear regression. ▲ indicates data not used in regression (table 4), and ○ indicates sample lacked second-ion confirmation.

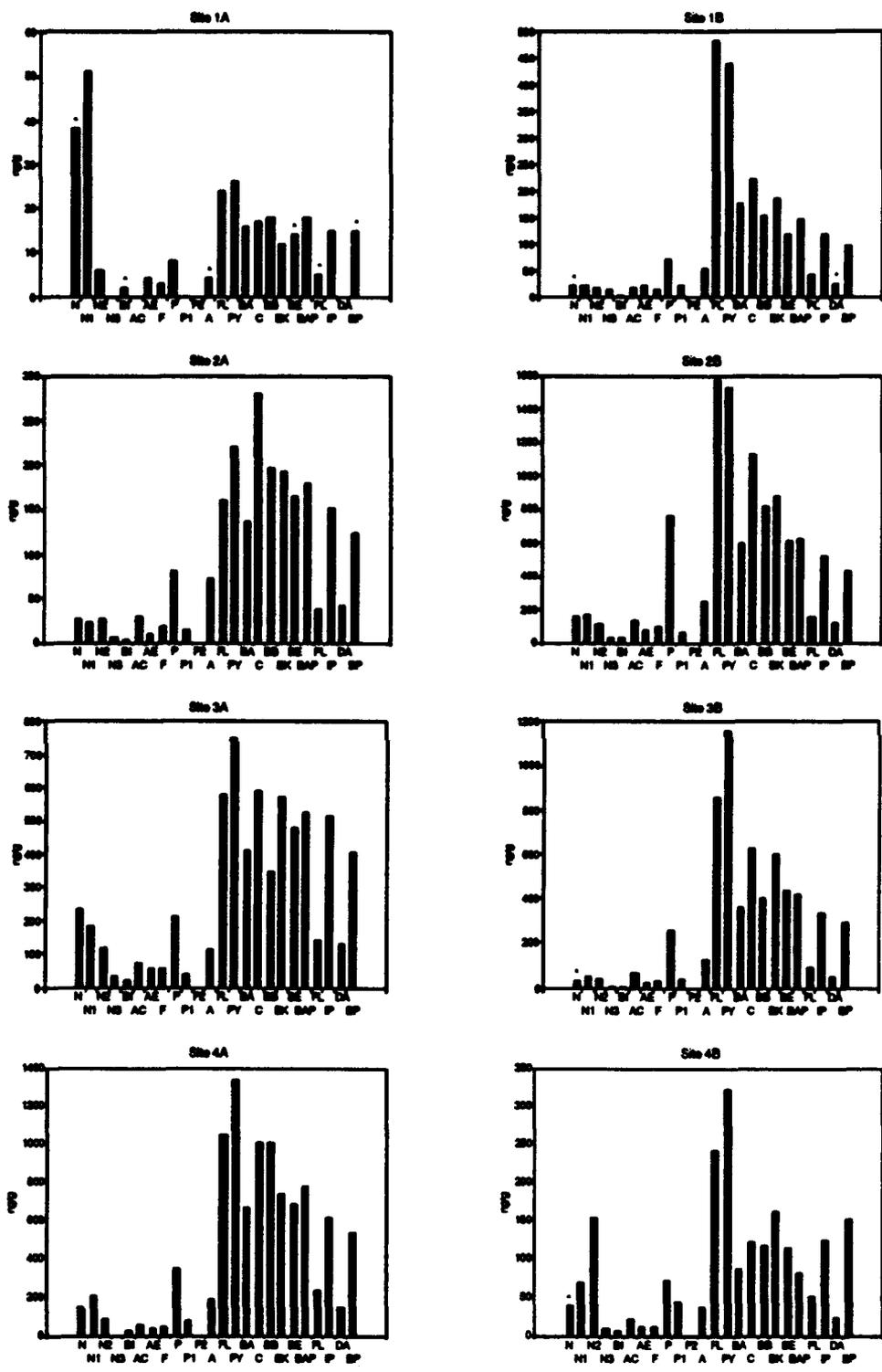


Figure 17. Bulk sediment: PAH concentrations at sites 1A-4B. Abbreviated compound names are explained in table 1. An * indicates data lacking second-ion confirmation.

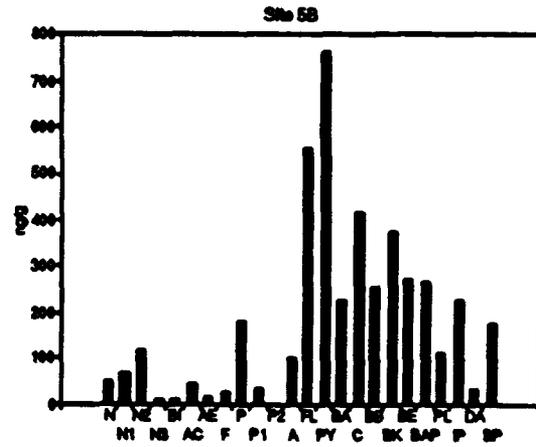
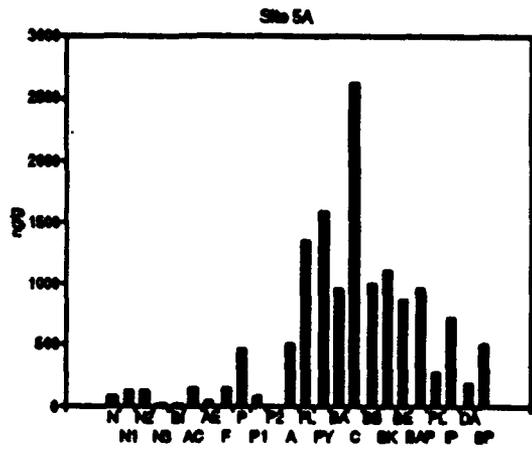


Figure 48. Bulk sediment PAH concentrations at sites 5A-5B. Abbreviated compound names are explained in table 1. An * indicates data lacked second-ion confirmation.

Table 8. TOC normalized bulk sediment concentrations and WA State Criteria for individual and summed PAHs in mg/(kg organic carbon). Σ LPAH and Σ HPAH are the summed concentrations of compounds listed above each sum in the table.

Chemical	1A	1B	2A	2B	3A	3B	4A	4B	5A	5B	Criteria
TOC(%)	0.3	1.1	1.6	3.7	3.1	2.2	3.7	5.6	5.1	2.4	
Naphthalene	14.5	1.9	1.7	4.0	7.7	1.5	4.0	0.7	1.4	1.9	99
2-Methylnaphthalene	2.3	1.4	1.6	2.9	3.9	1.7	2.3	2.7	2.4	4.9	38
Acenaphthylene	ND	1.4	1.7	3.5	2.4	2.8	1.5	0.4	2.7	1.7	66
Acenaphthene	1.5	2.0	0.6	2.2	1.7	0.9	0.9	0.2	0.7	0.6	16
Fluorene	1.1	1.0	1.2	2.6	1.9	1.5	1.2	0.2	2.8	1.2	23
Phenanthrene	3.0	6.8	5.0	21	6.8	11	9.3	1.3	9.1	7.7	100
Anthracene	1.5	5.0	4.4	6.5	3.7	5.7	4.9	0.7	10	4.2	220
Σ LPAH	24	20	16	43	28	25	24	6.2	29	22	370
Fluoranthene	9.1	45	9.9	43	19	39	28	4.3	26	23	160
Pyrene	9.9	41	14	41	25	53	36	5.8	31	32	1000
Benz(a)Anthracene	6.1	16	8.4	16	14	16	18	1.5	19	9.6	110
Chrysene	6.5	21	17	30	19	29	27	2.1	52	18	110
Σ Benzofluoranthenes	11	32	24	46	30	45	47	5.0	42	27	230
Benzo(a)Pyrene	6.9	14	11	17	17	19	21	1.4	19	11	99
Indeno(1,2,3-C,D) Pyrene	5.7	11	9.4	14	17	15	17	2.2	14	9.5	34
Dibenzo(a,h) Anthracene	ND	2.2	2.5	3.3	4.3	2.3	3.9	0.4	3.8	1.4	12
Benzo(g,h,i)Perylene	5.7	9.1	7.6	11	13	13	14	2.7	10	7.4	31
Σ HPAH	61	191	104	221	158	231	212	25	217	139	960

Results for bulk sediment analysis of individual PCB congeners and estimated total PCB as Aroclor 1254 are given in table 9. Of the 24 congeners measured, up to 22 were present at detectable levels at specific sites. No PCBs were found at site 1A, and only trace levels were present at sites 1B and 4B. The shipyard sites (2A,2B,3A,3B,4A,5A,5B) were generally higher, with sites 4A and 5B showing the highest levels. Estimated concentration of Aroclor 1254 ranged from below detection at site 1A to 965 ng/g at site 5B. Bulk and TOC normalized PCB concentrations are presented and compared to Washington State Criteria in figure 49.

SEDIMENT PORE-WATER MICROPFILES

In situ microprofiles of O₂, pH, and resistivity were measured successfully at four sites, 2B (replicate), 3B, 4A, and 5B. Sulfide and pCO₂ profiles were measured at site 2B only. Results from these measurements are shown in figures 50–53, and the complete report prepared by C. Reimers of Scripps Institution of Oceanography is included as Appendix 5. Based on visual inspection and the resistivity measurements, the sediments at the Sinclair Inlet sites were found to be primarily muddy sands, although some sites were littered with shell and/or shipyard debris (e.g., cables, welding rods). Resistivity measurements yielded formation factor ($F = R_{\text{sediment}}/R_{\text{water}}$) profiles that increased to F values of 2 to 2.5 in the first 6 cm, indicating a mixture of sand (typical F=2) and mud (typical F=2.5 to 3). At sites 4A and 2B, high-resistivity layers were encountered within the sediment profile suggesting sand deposition at a depth of about 2 cm.

Oxygen microprofiles for the four stations are shown in figure 51. The oxygen profiles illustrate that in Sinclair Inlet the sediments are a sink for dissolved oxygen. Oxygen was generally observed to be completely consumed in the first 0.5 cm of the sediment column and of the four sites, site 5B showed the steepest O₂ gradient with the anoxic boundary at a depth of about 0.1 cm.

Some problems were encountered with the pH microprofile measurements; these are discussed in detail in Appendix 5. In spite of these qualifications, the pH profiles (figure 52) do indicate that pore-water pH decreases abruptly in the first 0.5 cm of sediment. As with oxygen, the pH decrease is greatest at site 5B, and the level value reached at a depth of 6.2 is unusually low for marine systems.

Sulfide and pCO₂ electrodes are currently being tested on the microprofiler. A silver-silver sulfide electrode was successfully deployed at site 2B (figure 53). The electrode potential is ideally a direct function of the logarithm of the sulfide ion activity, however, some question remains about the calibration of the electrode (Appendix 5). Nonetheless, the profile at site 2B does give a relative indication of the sulfide distribution in the sediment. It shows a strong increase in the upper 0.5–1 cm, followed by a more gradual increase to a depth of 4 cm (note that lower EMF indicates higher sulfide activity). Below 4 cm, the electrode potential exceeded the input range of the instrument.

Table 9. Bulk sediment concentrations for PCB congeners, Σ PCB congeners, and Aroclor 1254. (All concentrations are in ng/g dry weight.) An * indicates data lacked second-ion confirmation.

PCB Congener	Site									
	1A	1B	2A	2B	3A	3B	4A	4B	5A	5B
018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
028+031	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
052	ND	ND	ND	ND	ND	4.9*	19.0*	ND	10.9	28.0
0.49	ND	ND	ND	ND	9.3*	7.4*	20.8*	ND	12.2	11.3*
044	ND	ND	ND	ND	2.8*	17.1*	ND	ND	5.5	10.9
074	ND	ND	ND	1.5*	ND	ND	11.7*	ND	5.0*	6.3*
070+076	ND	ND	ND	ND	ND	3.8*	33.9	3.0*	11.8	20.7
066	ND	ND	ND	ND	ND	1.8*	15.7*	2.0*	5.0*	4.3*
095	ND	ND	5.0	10.0*	10.2	8.2*	28.2	2.7*	25.3	47.6
101	ND	ND	8.1	15.6*	17.8	12.4*	67.5	7.7*	49.5	90.1
099	ND	ND	4.5	9.5*	9.6*	6.8*	27.5	ND	18.1	42.8
110	ND	ND	5.3	8.5	12.4	9.2*	44.2	3.9*	26.6	57.0
118	ND	ND	5.8	10.6*	11.6	8.0*	58.6	4.9*	30.5	74.2
105	ND	ND	3.7*	9.4*	11.9*	5.4*	45.2	ND	21.1	47.9
136	ND	ND	3.1*	4.8*	6.0*	5.8*	14.2*	ND	15.0	12.5
149	ND	ND	4.0	6.9*	14.2	9.2	29.7	5.4*	37.4	28.8
132+153	ND	3.3*	12.9	25.3	55.6	33.7	110	22.1	154	110
141	ND	ND	2.6*	ND	6.6*	3.6*	16.3*	ND	14.8	9.5
138	ND	ND	5.9	9.9	18.6	13.2	37.1	7.3	49.9	52.2
176	ND	ND	3.8	7.8	13.5	6.8*	ND	ND	2.9	10.1
183	ND	ND	ND	ND	8.0*	4.6	ND	ND	15.7	4.9
174	ND	ND	ND	ND	10.2	4.6*	11.9	ND	22.6	5.9
180	ND	ND	2.6	4.0	9.8	5.6	14.9	2.5	32.8	9.7
170+190	ND	ND	ND	ND	9.8*	5.0*	ND	1.7*	22.9	5.1
Σ PCB	ND	3	67	124	235	163	624	63	617	690
Aroc.1254	ND	ND	89	144	211	214	749	66	450	965

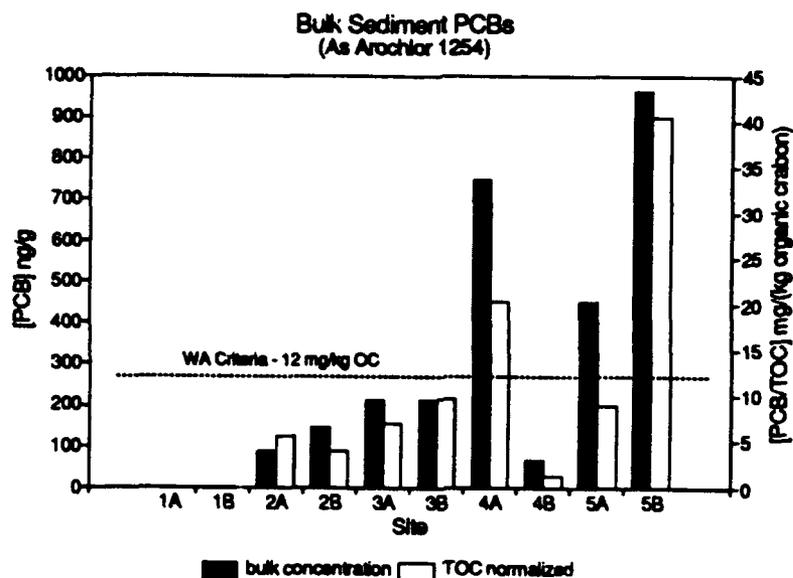


Figure 49. Bulk sediment PCB concentration as Arochlor 1254 at the 10 sites in Sinclair Inlet. Solid bars are bulk concentration, and open bars are organic-carbon normalized concentration.

Two $p\text{CO}_2$ profiles were measured during separate deployments at site 2B (figure 53). Combined with pH, these measurements form the basis for calculating concentrations for all the inorganic carbon species. The profiles measured indicated a similar gradient for $p\text{CO}_2$ in the upper layers from which a diffusive flux for ΣCO_2 of $0.3 \mu\text{mol}/\text{cm}^2/\text{day}$ was estimated. This value was considerably lower than the $10.6 \mu\text{mol}/\text{cm}^2/\text{day}$ flux determined from the BFSD pH and alkalinity measurements. This discrepancy could be due to calibration considerations for the $p\text{CO}_2$ electrode (Appendix 5), or inaccuracy of the BFSD pH electrode records used in calculating the BFSD flux.

ACID-VOLATILE SULFIDE

A sediment composite sample (0–10 cm) and three to five profile samples were analyzed for AVS at each of the 10 sites in Sinclair Inlet. A grab sample from Station 5A was also analyzed. Most cores had moderate AVS concentrations near the surface ($> 20 \mu\text{mol}/\text{g}$), increased AVS at intermediate depth (4–6 cm), and decreased AVS toward the bottom of the core (figure 55). These profiles are comparable to AVS core profiles

commonly measured from a variety of environments (W. Boothman, 1991, EPA ERLN)* and agree reasonably with the sulfide microprofile data at site 2B. Sites 2A, 5A, and 5B had the highest AVS measured (figure 54), and sites 1A and 1B had the lowest AVS. The low AVS at station 1A and 1B may be explained by the sandy and what appeared to be well-oxygenated sediments sampled at those locations. Those stations were located closer to the mouth of the inlet and were subject to more mixing (see hydrographic data). The high AVS measured at the other stations located around the shipyard showed that the majority of the sediment column was anoxic and that the formation of sulfides was favored at those stations. Station 3B was an anomaly. The low AVS measured from the cores collected at 3B could be attributed to increased bioturbation as reflected in the deeper oxygen penetration (figure 51) into the sediment column. A detailed account of this study can be found in Johnston, 1992.

* Personal communication via R. Johnston at the University of Rhode Island: "Acid-Volatile Sulfide Determination in Sediments using Sulfide-Specific Electrode Detection."

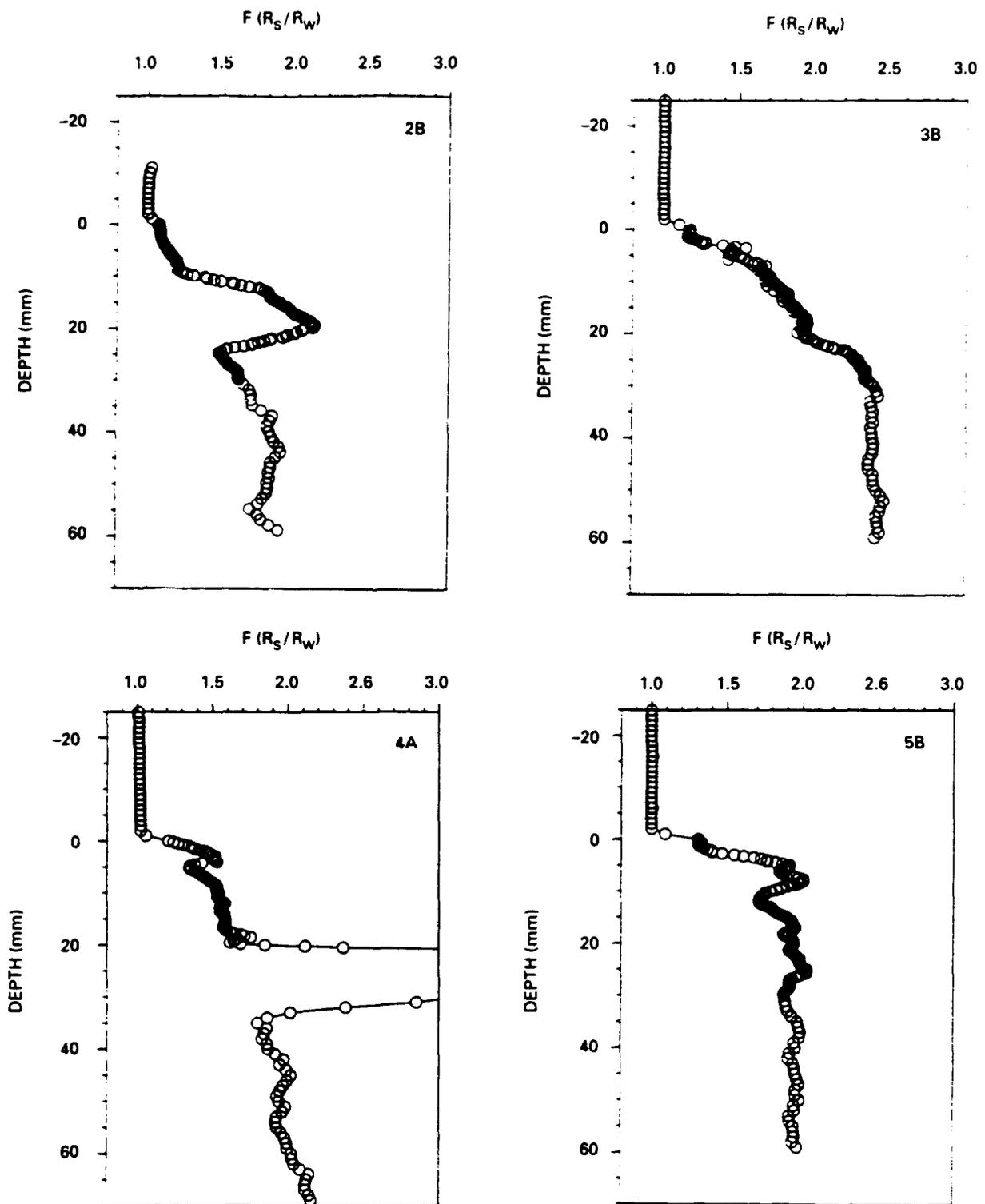


Figure 50. Formation-factor profiles from four sites (2B,3B,4A,5B) in Sinclair Inlet. Sites 2B and 4A show evidence of sand layering at about 20 mm.

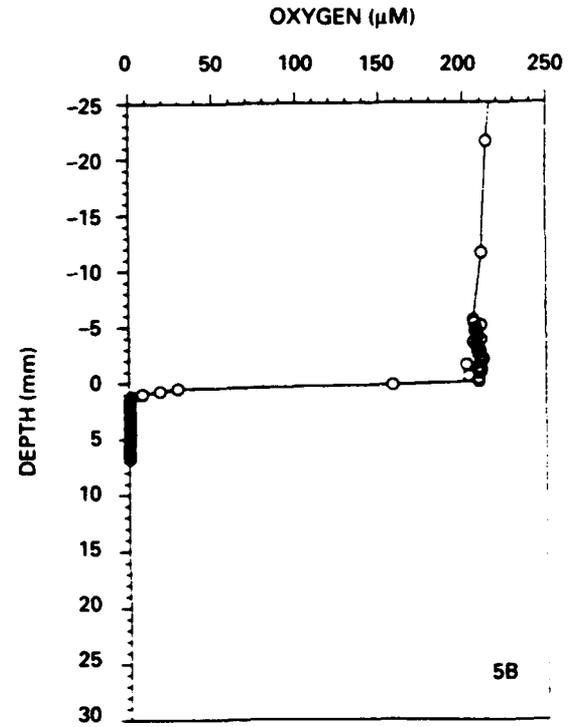
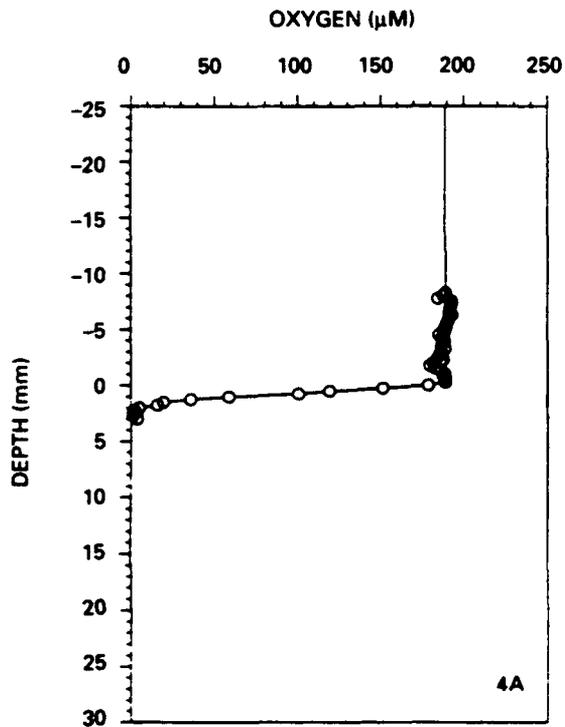
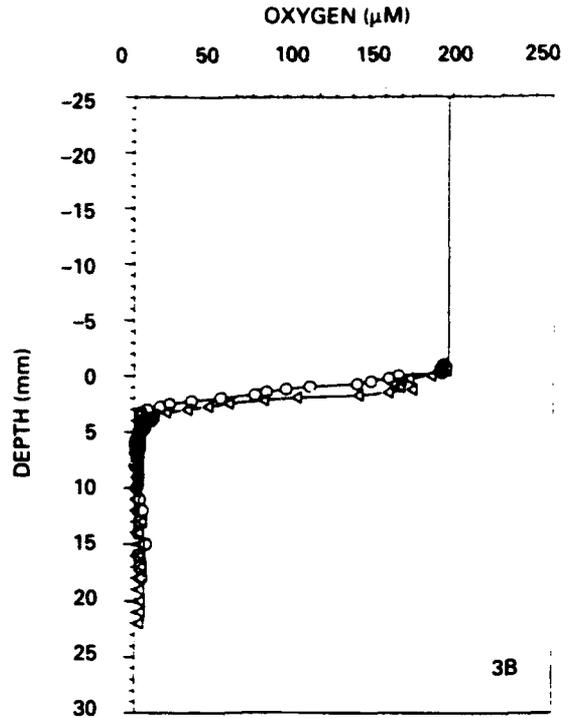
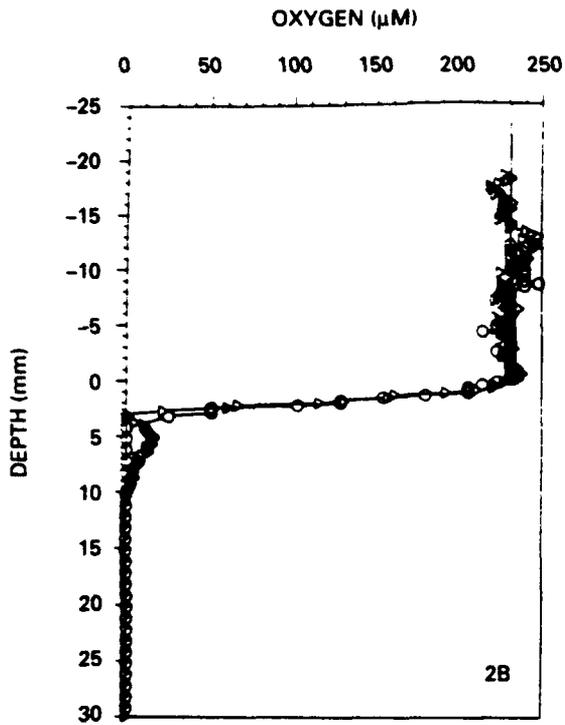


Figure 51. Oxygen microprofiles from four sites (2B,3B,4A,5B) in Sinclair Inlet. Many profiles do not extend very far into the sediment because the electrodes were broken by coarse sand and debris.

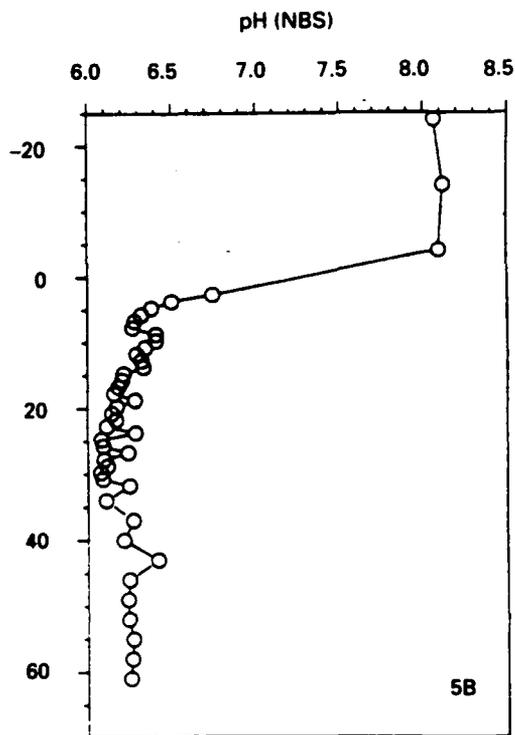
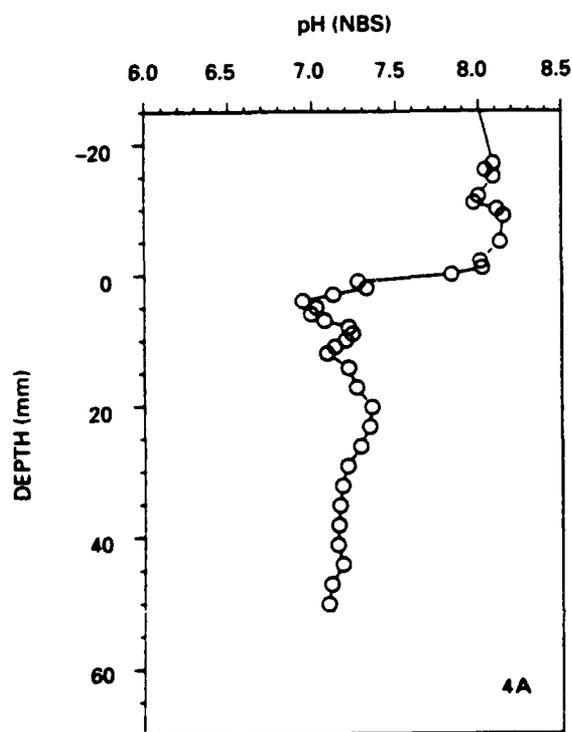
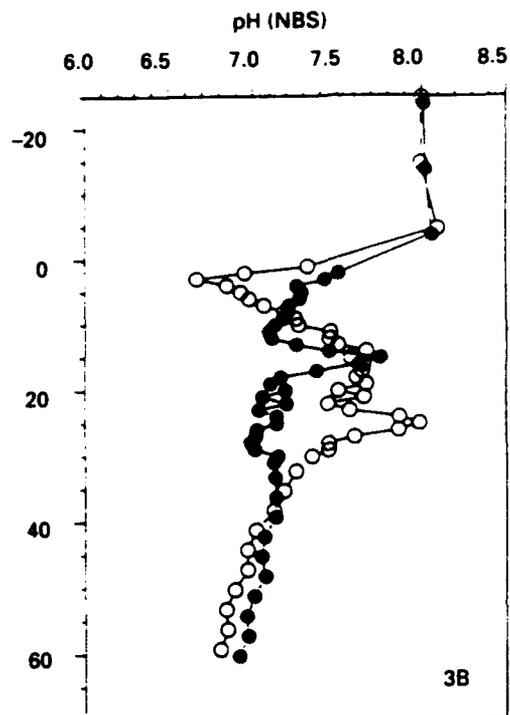
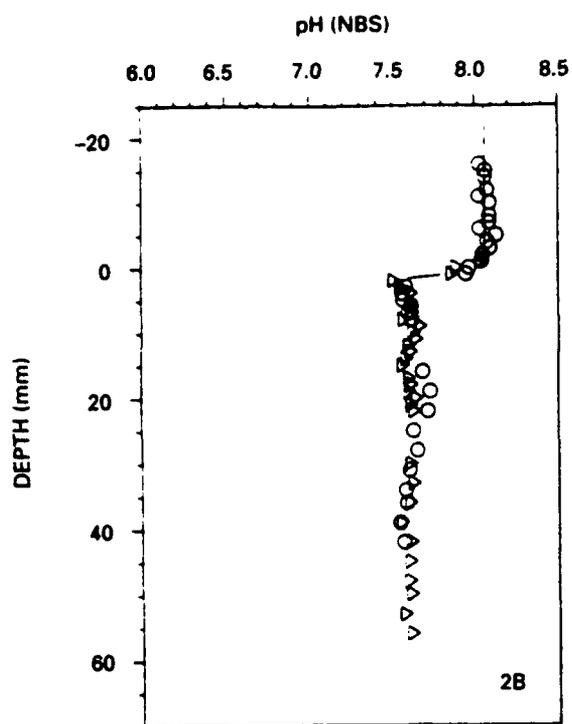


Figure 52. Profiles of pore-water pH at four sites (2B,3B,4A,5B) in Sinclair Inlet. Profiles indicate a sharp decrease in the first 0.5 cm of the sediment column.

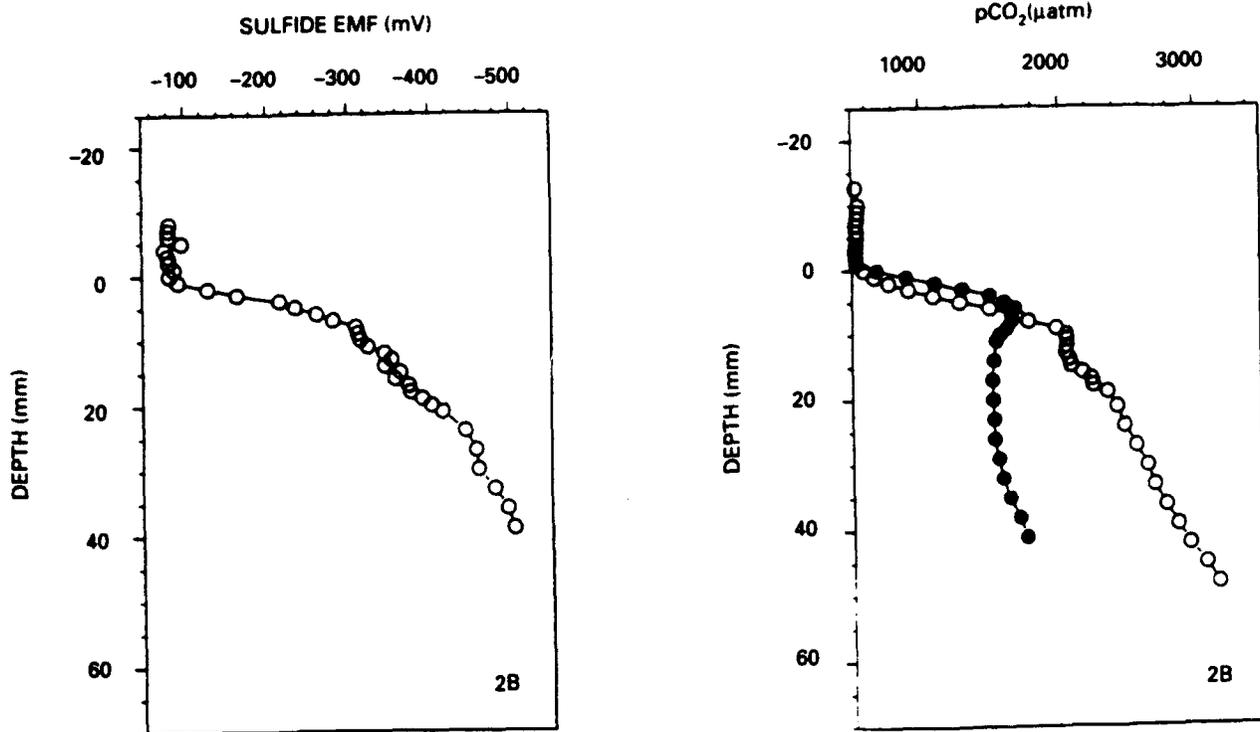


Figure 53. Microelectrode profiles of sulfide (EMF) and pCO₂ at site 2B. Calibration of these sensors was uncertain and requires further verification.

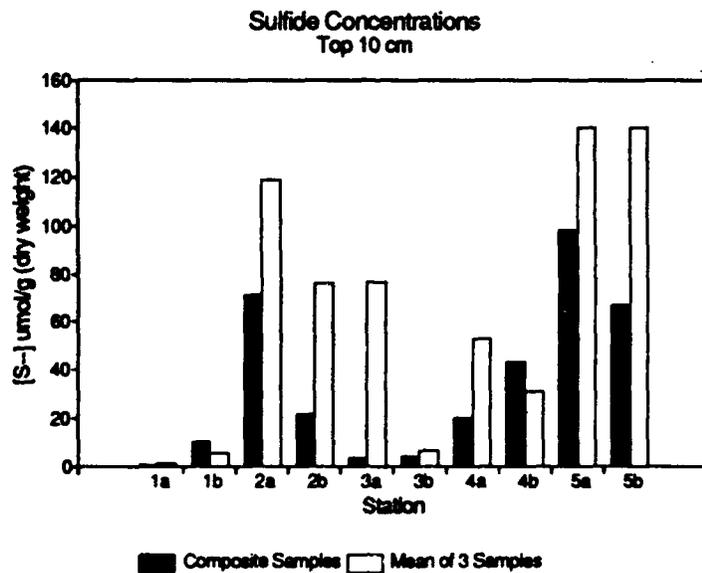


Figure 54. AVS concentrations in the top 10 cm of cores from the 10 sites in Sinclair Inlet—determined from composite samples and the mean of 3 vertical profile samples.

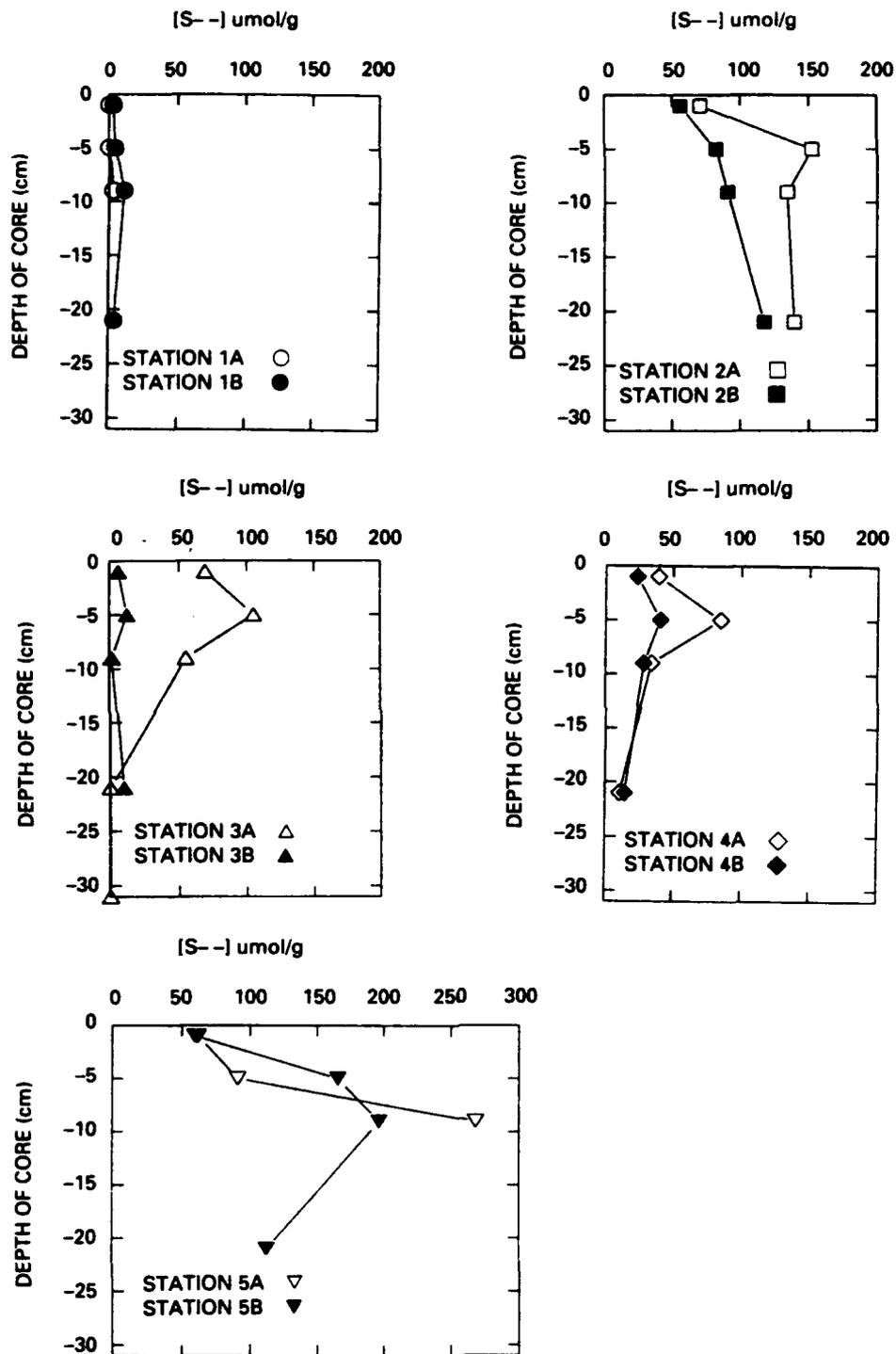


Figure 55. Vertical profiles of AVS determined in cores from the 10 sites in Sinclair Inlet.

DISCUSSION

TRACE METAL FLUXES

In assessing the flux rate measurements performed in Sinclair Inlet, the key issue we hoped to address was whether or not specific contaminants were being released from the sediments at significant rates. For the trace metals, we found that Ni, Zn, and As showed release at several sites, while Cu, Cd, and Pb showed little release; and Cr and Hg were generally below detection limits. Zn release was always associated with shipyard sites. However, Ni release was also found at site 4B in the western inlet, and As release was found at sites 4B and 1B, both of which are removed from the shipyard (1B to a lesser extent). While Zn is clearly a contaminant that would be associated with shipyard operations (anodes, paints, etc.), As and Ni are not as strongly linked and may have other significant sources in the inlet. This is reflected in the bulk sediment data for Ni (figures 3 and 39) and to some degree for As (figures 2 and 39). The highest release rates for Ni and Zn were measured at site 5A (565 and 837 $\mu\text{g}/\text{m}^2/\text{day}$ respectively), and for As, was found at site 2B (292 $\mu\text{g}/\text{m}^2/\text{day}$). For Ni and Zn, this site also showed elevated bottom-water concentrations based on the initial BFSB sample, while bottom-water concentrations of As were fairly uniform from site to site. Although sediment release could be driving this bottom-water elevation for Ni and Zn, in no case did the bottom-water concentrations exceed the EPA water-quality criterion of 7.1 $\mu\text{g}/\text{l}$ and 58 $\mu\text{g}/\text{l}$ respectively (EPA, 1986). For Cd and Pb, bottom-water concentrations were also well below EPA criteria. Although Cu release was only detected at one site (3A), bottom-water concentrations at most sites approached the EPA criterion of 2.9 $\mu\text{g}/\text{l}$. This may reflect the continued input of Cu to the inlet coming from antifouling coatings on Navy, commercial, and pleasure craft in the area, as well as other potential inputs from the shipyard, sewer outfall, and nonpoint sources.

Comparative data on trace metal fluxes are limited. Westerlund et al. (1986) performed benthic flux measurements in a fjord in western Sweden. They reported release rates for Cd, Cu, Ni, and Zn during a fall experiment as 0.6, 3.4, 5.8, and 42 $\mu\text{g}/\text{m}^2/\text{day}$ respectively, with no apparent release of Pb. These are roughly an order of magnitude lower than the rates we found in Sinclair Inlet and presumably are typical of background levels for a coastal environment. The short-term measurements we performed and the limitations of our analytical methods did not allow us to confidently detect flux rates at such low levels; however, such rates would probably have limited significance relative to other natural and anthropogenic sources. Hunt and Smith (1983) estimated release rates of Cu and Pb from contaminated sediment using a microcosm system and found rates of 67 $\mu\text{g}/\text{m}^2/\text{day}$ and 5 $\mu\text{g}/\text{m}^2/\text{day}$ respectively. These values are of similar magnitude as those reported here. Cu, Zn, Cd, and Pb flux rates were characterized at a marina site (Shelter Island) during the prototype testing of the BFSB. Flux rates for Cu and Zn (460 and 1860 $\mu\text{g}/\text{m}^2/\text{day}$) at this site were higher than the highest rates measured in Sinclair Inlet, while Pb and Cd showed little flux at either location. To our knowledge, no direct measurements of As fluxes have been made in the marine environment, although Bryan and Langston (1991) suggest that As mobility is favored by reducing conditions typical of

those present in Sinclair Inlet sediments. This, combined with the ubiquitous sources of As from inputs such as rock weathering, smelting, and metal-refining processes, may help to explain the more uniform nature of both the bulk sediment loadings and the observed release rates of As.

Several factors may be important in controlling or mediating the flux of contaminants from marine sediments. Westerlund et al. (1986) found that trace metal release was generally associated with oxidation phases as opposed to reduction as with manganese and iron. In laboratory studies, Lu and Chen (1977) found similar results with most trace metals being released under oxidizing conditions, while manganese and iron showed uptake, and the direction of the fluxes reversed under reducing conditions. The water- and sediment-oxygen data that we collected indicate that oxygen was present at all sites throughout the water column and typically penetrated from 1 to 5 mm into the sediment column. The sediment penetration of oxygen agrees well with data reported by Westerlund (1989) at the Swedish site and is thought to be typical of near-shore sediments. This means that the potential exists for the release of trace metals through oxidative reactions in the upper few millimeters of the sediment column. If the contamination is historical, it may be buried significantly below this depth. In this case, release could only occur through physical disturbance of the sediment (e.g., prop wash, dredging) or bioturbation by burrowing benthic organisms. Previous studies (Rutgers van der Loeff et al., 1984) demonstrated that, for nutrient fluxes, when anoxic conditions develop in the flux chamber, the biological component of the flux is lost, and only the diffusive component remains. At site 5B, the chamber went anoxic at hour 29, and a reversal in silica flux was observed (figure 18). This would indicate that bioturbation was of primary importance at that site.

Under reducing conditions, sulfide is thought to play a major role in immobilizing trace metals and mitigating bioavailability. In their analysis of geochemical partitioning of trace metals at the sediment surface, Lu and Chen (1977) found strong evidence that, under reducing conditions, metallic sulfide solids are the predominant species for Cd, Cu, Ni, Pb, and Zn. In more recent studies, Di Toro et al. (1990) found that toxicity of trace metals in marine sediment could be predicted well when the bulk-sediment concentration of the metal was normalized to the AVS content. The high AVS levels in the sediments around the shipyard suggest that the deeper sediments provide an effective sink for trace metals in Sinclair Inlet. Di Toro et al. (1990) demonstrated that Cd would form a metal-sulfide complex at the expense of iron and manganese monosulfides. Table 10 (from Di Toro et al., 1990) shows metal-sulfide solubility and activity ratios for several trace metals compared to manganese and iron. They predicted that metals below the dotted line would form solid sulfides at the expense of MnS and FeS. It is interesting to note that NiS and ZnS follow FeS based on solubility product $\log K_{sp}$. We speculate that since the release rates we observed were primarily for Ni and Zn, they may be dissolving during the formation of metallic sulfides of trace metals with smaller (more negative) solubility constants, especially if MnS and FeS have been exhausted. Although we were unable to detect Hg flux rates due to limited analytical sensitivity, this type of analysis would suggest that Hg would be preferentially bound as HgS and unlikely to flux. However, previous studies

(Jahnke et al., 1979) indicate that Hg release is not controlled by the low solubility of HgS and that release is generally favored by anoxic conditions. A detailed review of factors affecting sediment trace metal mobility and bioavailability is presented by Bryan and Langston (1991).

Table 10. Metal-sulfide solubilities (after DiToro, et al., 1990). Increasing solubility is indicated by less negative values of $\log K_{sp}$.

Metal Sulfide	$\log K_{sp,2}$	$\log K_{sp}$	$\log a$		$\log(aK_{sp})$ Average
			pH = 7.6	pH = 8.2	
MnS	-0.40	-19.15	0.13	0.13	-19.02
FeS(am)	-30.5	-21.80	0.10	0.12	-21.69
FeS	-3.64	-22.39	0.10	0.12	-22.28
NiS	-9.23	-27.98	0.11	0.17	-27.84
ZnS	-9.64	-28.39	0.12	0.14	-28.26
CdS	-14.10	-32.85	1.50	1.50	-31.35
PbS	-14.67	-33.42	1.12	1.32	-32.20
CuS	-22.19	-40.94	0.50	0.92	-40.23
HgS	-38.50	-57.25	15.10	15.10	-42.15

We were also interested in the relationship between trace metal flux rates and bulk sediment loadings. To address this, we calculated correlation coefficients for flux rate versus sediment concentration at the 10 sites (figure 56). For Cu, Zn, and As, we found significant ($p < 0.05$) positive correlation, while Cd, Ni, and Pb showed little or no relationship. Although the results for some metals suggest that bulk sediment concentration is one determining factor for mobility, the observed variability from site to site and the lack of correlation for several metals indicate that it is certainly not the only factor. Some portion of the variability observed could be attributed to differences in the sediment composition from which the flux was measured and those from which the bulk data were acquired.

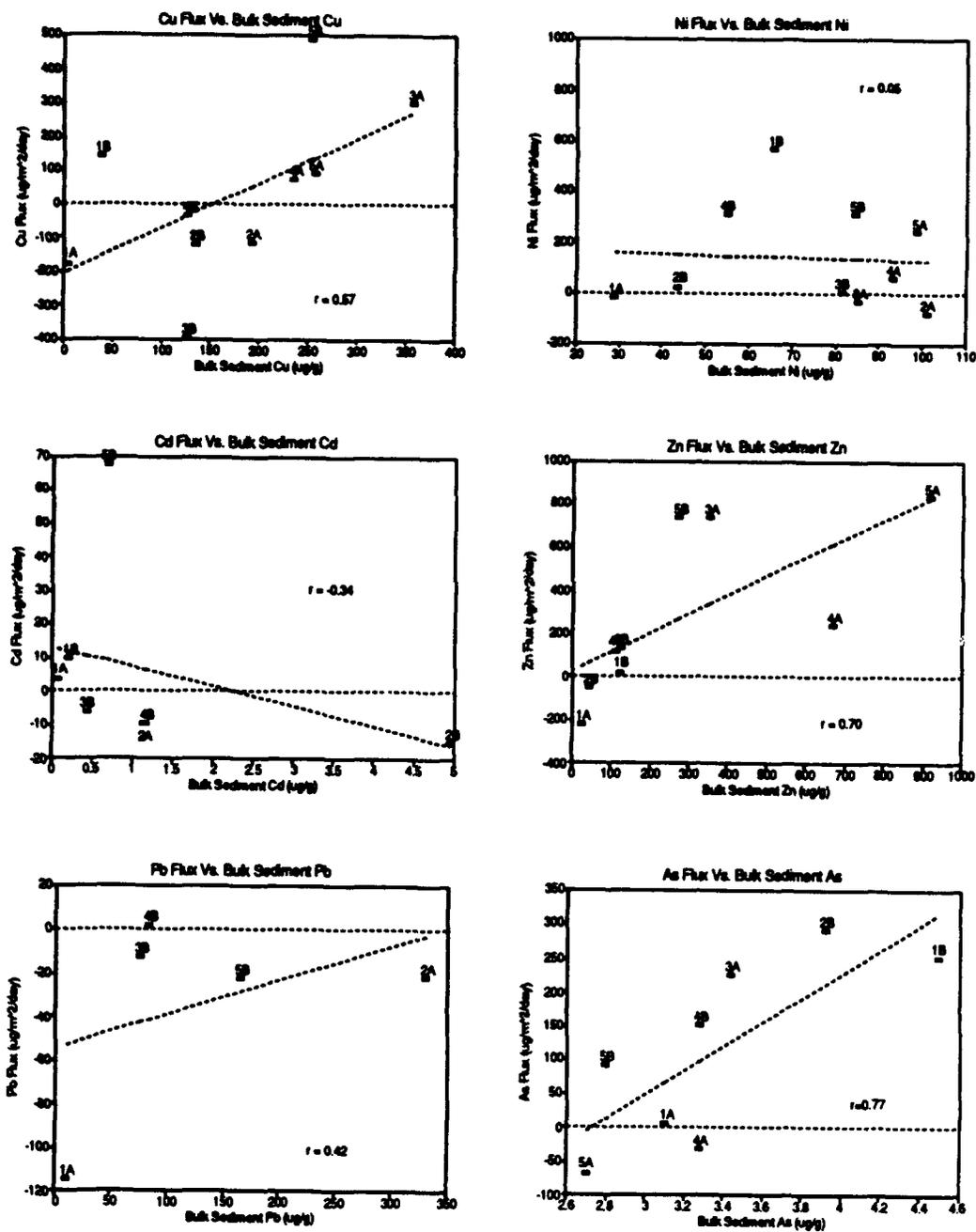


Figure 56. Correlations for trace metal flux rates and bulk sediment metal concentrations.

PAH/PCB FLUXES

Measurable release rates of several PAHs were detected at sites 3B and 5B. At 3B, release was most pronounced for the lower molecular weight PAHs, while at 5B, release was limited to a few of the more moderate weight PAHs. Very little information is available in the literature regarding flux rates of PAH compounds in the marine environment. Studies in freshwater sediments (Di Toro, 1989) suggest that dissolution and bioavailability of organic contaminants is controlled primarily by the mass fraction of organic carbon present and the hydrophobicity of the chemical. However, relating our measured flux rates to the bulk sediment concentrations is difficult. The organic carbon content was virtually the same at the two sites (2.2–2.4 percent), and the bulk sediment PAH concentrations were quite similar. High oxygen consumption, a steep oxygen gradient, and low pH in the sediment at site 5B are all indicators of active decomposition of organic matter. After the chamber became anoxic, the consistent reversal in flux rates of silica and several PAH compounds at site 5B suggest that the flux rates measured for these compounds may be primarily controlled by bioturbation.

In general, the bottom-water concentrations of PAH were quite low. To protect human health from potential carcinogenic effects of PAHs, the EPA has established a criterion of 31 ng/l for ambient seawater. The bottom-water concentrations at sites 3B and 5B of 22 and 12 ng/l total PAH did not exceed these levels. They were considerably lower than the 150 ng/l that we have typically measured off Naval Station, San Diego. When normalized for organic carbon, bulk sediment concentrations of PAH were well below criteria recently established by the State of Washington (State of WA, 1991). Thus, in spite of the release rates measured—in particular the relatively high rates at site 3B—bottom-water levels of PAH in the inlet do not appear to be significantly elevated. In addition, the oil-fluorescence mapping performed throughout the inlet indicated primary sources of PAHs along the southern shoreline, most likely associated with pleasure-boat operations and refueling. Although the PAH release does not represent a major source to the inlet, it may indicate a potential exposure source for benthic organisms.

No flux of PCB congeners was detected from the sediment at sites 3B and 5B. Bottom-water concentrations were very low at both sites, 0.6 and 0.1 ng/l respectively. The EPA criterion based on protection of human health is 0.079 ng/l based on a 10^{-6} risk level via consumption of aquatic organisms. Although the bottom-water levels appear to be exceeding this criterion at both sites, quantitation at these low levels is subject to considerable interpretation, and we found no evidence that these levels are being driven by release from sediments at the shipyard. Bulk sediment concentrations were generally low except at sites 4A and 5B, which, when quantified as Aroclor 1254 and normalized to organic carbon, yield values of 20 mg/kgOC and 41 mg/kgOC respectively. This is greater than the 12-mg/kgOC standard published by the State of Washington.

COMPARISON OF SEDIMENT FLUXES TO OTHER SOURCES

Remobilization of metals from the sediments of Sinclair Inlet represents a potential source that can be compared to other documented inputs in the region. To provide this

comparison, we gathered source data and estimated discharges from Navy ships, PSNS-permitted outfalls, the City of Bremerton municipal sewage outfall, and pleasure craft. Inputs from sediments were separated into fluxes from sediments associated with the shipyard and those remote from the shipyard. A mass loading from these two regions was calculated by averaging the statistically significant flux rates for the region and applying this average flux rate to the estimated sediment surface area in the region. Estimated inputs from Navy ships and pleasure boats were calculated for zinc and copper only. The input of zinc due to Navy ships was calculated by determining which ships at PSNS were using zinc cathodic protection, and the individual input from each of these ships, based on historical replacement rates. Zinc input from pleasure boats was estimated similarly from the total number of pleasure boats in the Inlet and an approximate anode replacement rate. Copper inputs from Navy ships and pleasure boats were calculated by estimating the total antifoulant surface area for each class and applying documented leach rates for typical copper antifouling coatings. Source loading from PSNS-permitted outfalls and the City of Bremerton municipal sewage outfall was determined from National Pollutant Discharge Elimination System (NPDES) monitoring data on concentration and flow rates. A detailed description of these calculations is included as Appendix 6.

The results of the budget analysis are shown in figure 57. Comparative data for all sources are only available for copper and zinc. The results indicate that the primary source of copper is from antifouling coatings on ships and pleasure boats in the Inlet. The average copper flux from sediments was negative in both the shipyard and Inlet-wide regions, and so no input is reported. Results for zinc indicate that ships, pleasure boats, and the PSNS-permitted outfalls all contribute significantly to the overall loading of the Inlet. Input of zinc from sediments is typically an order of magnitude less than those other sources. Sediment fluxes of nickel and arsenic may contribute a substantial fraction of the overall loading, however, insufficient data are available to compare these inputs to other potential sources. This analysis does not include several of the following potential sources: nonpoint source runoff, input from Gorst and Black Jack Creeks, uncontrolled shoreside and shipboard discharges, tidal transport into the Inlet, aerial fallout, and exchange from resuspended sediments.

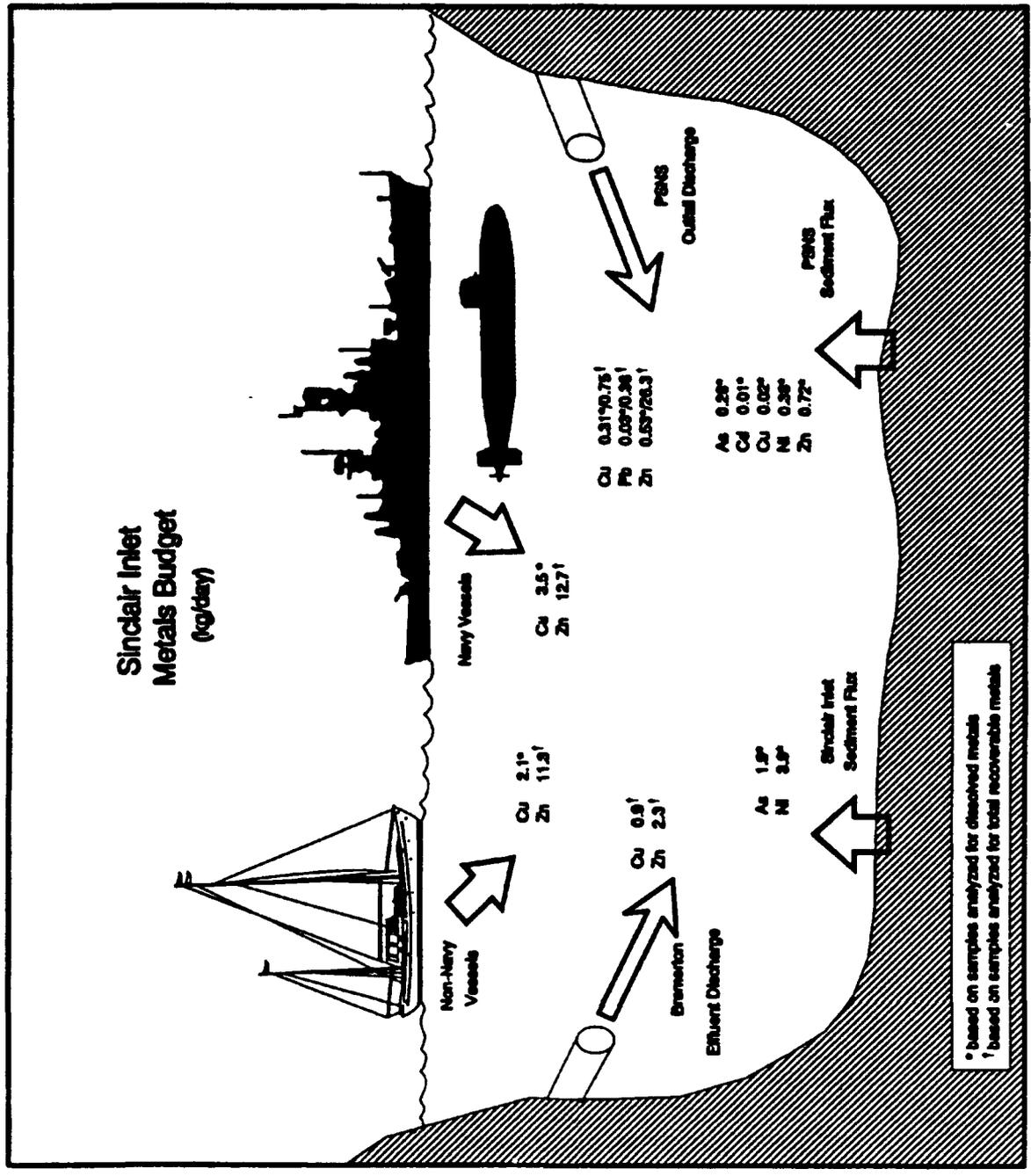


Figure 57. A source budget for metal inputs to Sinclair Inlet.

CONCLUSIONS

The objective of this project was to perform an on-site demonstration of the Benthic Flux Sampling Device (BFSD) to determine the mobility of contaminants in sediments off the Puget Sound Naval Shipyard in Sinclair Inlet, WA. Conclusions from the study fell into two categories: those relating to the results of the measurements performed and those related to the methods themselves. The measurement results suggest that for most of the contaminants we analyzed, little or no release is taking place. For the trace metals, this may be related to the strongly reducing characteristics of the sediments adjacent to the shipyard, as reflected in the shallow oxygen penetration, and the relatively high AVS and organic content. For Zn, Ni, and As, where measurable release was found, only Zn appeared to be strongly tied to shipyard sources, while Ni and As also exhibited release at sites removed from the shipyard. Bulk sediment results for the trace metals suggest that Zn and Hg at some sites are at elevated levels relative to published criteria, and release rates of Zn are positively correlated with the bulk levels.

These findings suggest that Zn loading may be a significant issue and that Hg probably warrants further investigation, especially for organic species. For PAHs and PCBs, the limited-release rates observed are probably attributable to low bulk levels, high organic loading, and the high particle affinity of many of these compounds. We attribute the release of lower molecular weight PAHs at shipyard site 3B to recent input, since these compounds are generally weathered or volatilized quickly in the marine environment. At site 5B, where the more moderate weight PAHs were released, the released compounds were more closely coupled with the bulk sediment loadings, and we believe bioturbation may have played a more active role. Where release of contaminants was found, the measured rates do not represent a significant source relative to other major inputs such as sewer discharges, nonpoint source runoff, and marinas. However, these contaminants may represent an exposure pathway for benthic biota with the potential for toxicological effects and/or bioaccumulation.

Regarding the sampling methodology, we concluded that on site, *in situ* measurements of contaminant release rates could be performed. We believe that these measurements could be enhanced by increasing the sampling period and collecting more samples to improve confidence levels for the flux rates. In-place filtration and preservation of samples should be incorporated to minimize the potential for adsorption, desorption, and degradation prior to retrieving the BFSD. We also have to improve sample collection and analytical methods for specific compounds such as Hg and Cr in order to detect the mobility of these contaminants. Analysis of PCB flux rates may require larger sample volumes. Future studies would be extremely useful that perform parallel, *in situ* biological studies such as shellfish bioaccumulation or amphipod bioassays to determine if a direct link exists between contaminant mobility and biological effects.

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LIST OF ACRONYMS AND ABBREVIATIONS

As	Arsenic
AVS	Acid-Volatile Sulfides
BFSD	Benthic Flux Sampling Device
Cd	Cadmium
CI	Confidence Interval
Cu	Copper
EFA	Engineering Field Activity (Naval Facilities Engineering Command)
EMF	Electromotive force
EPA-ERLN	Environmental Protection Agency, Environmental Research Laboratory at Newport
GC/MS	Gas Chromatography/Mass Spectrometry
GFAA	Graphite Furnace Atomic Absorption
Hg	Mercury
Ni	Nickel
PAH	Polynuclear Aromatic Hydrocarbons
Pb	Lead
PCB	Polychlorinated Biphenyls
PSEP	Puget Sound Estuary Program
PSNS	Puget Sound Naval Shipyard
QA/QC	Quality Assurance/Quality Control
SI	Site Investigation
SIO	Scripps Institute of Oceanography
TOC	Total Organic Carbon
URI	University of Rhode Island
Zn	Zinc

Appendix 1. Data Analysis

- 1. Statistical Analysis of Bulk Sediment Metal Concentrations to Determine Sampling Locations for the BFSD.**
- 2. Flux Rate Calculations for Silica, Trace Metals, PAHs, and PCBs.**

Initial Seeds

<u>Cluster</u>	<u>cumsum</u>
1	71.000
2	141.000
3	212.000
4	283.000
5	353.000

Cluster Statistics

<u>Cluster</u>	<u>Count</u>	<u>RMS Std Dev</u>
1	8	24.141
2	7	16.334
3	19	17.417
4	9	20.037
5	13	30.239

Variable Statistics

<u>Variable</u>	<u>Total Std</u>	<u>Within Std</u>	<u>R²</u>	<u>Ratio</u>
cumsum	105.789	22.284	.959	23.304
over-all	105.789	22.284	.959	23.304

Cluster Means

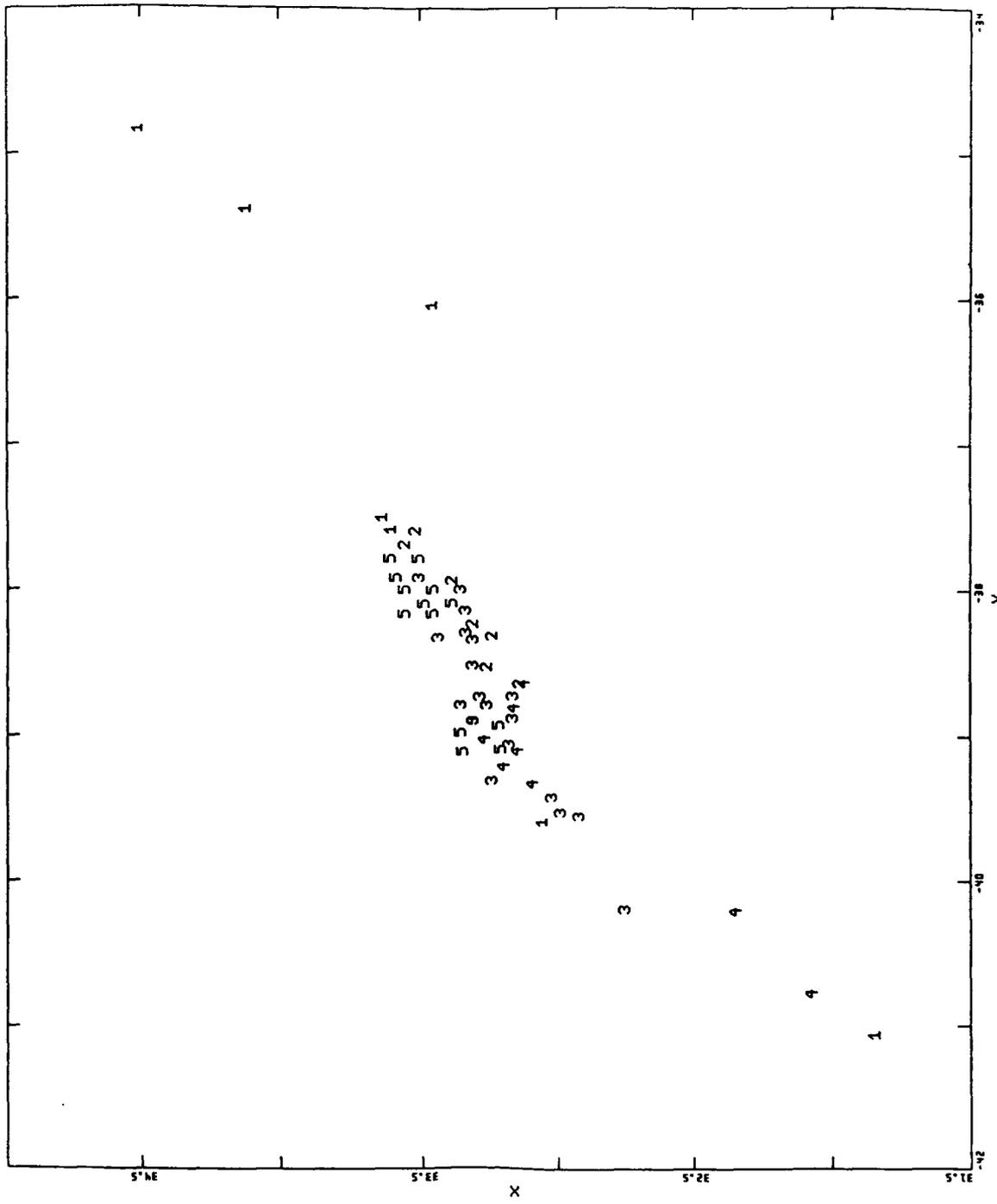
<u>Cluster</u>	<u>cumsum</u>
1	43.750
2	154.143
3	224.579
4	270.667
5	370.615

Cluster Standard Deviations

<u>Cluster</u>	<u>cumsum</u>
1	24.141
2	16.334
3	17.417
4	20.037
5	30.239

Cluster Mean Distances

<u>Cluster</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
1	0.000	110.393	180.829	226.917	326.865
2	110.392	3.04e+59	70.436	5.55e+29	216.472
3	180.829	70.436	0.000	46.087	146.036
4	226.917	5.55e+29	46.087	0.000	99.949
5	326.865	216.472	146.036	99.949	0.000



Variable	n	mean	std	stderr	min	max
Cluster=1						
As	8	5.513	4.790	1.694	2.300	16.900
Cd	8	1.250	0.558	0.197	0.490	2.200
Cr	8	23.750	5.653	1.999	17.300	32.800
Cu	8	27.613	24.935	8.816	5.400	78.200
Hg	8	0.205	0.100	0.036	0.120	0.350
Pb	8	30.388	21.603	7.638	9.000	65.100
Ni	8	20.663	5.0205	1.775	15.000	28.000
Zn	8	72.263	53.745	19.001	34.000	198.000
Cluster=2						
As	7	13.914	2.027	0.766	11.100	16.500
Cd	7	3.214	0.928	0.351	1.400	3.900
Cr	7	49.343	3.235	1.223	45.200	55.200
Cu	7	159.714	47.243	17.856	111.000	254.000
Hg	7	0.549	0.187	0.071	0.330	0.770
Pb	7	84.029	38.601	14.590	8.900	140.000
Ni	7	39.058	2.891	1.093	33.800	42.400
Zn	7	235.429	26.589	10.050	197.000	281.000
Cluster=3						
As	19	15.061	4.861	1.115	0.460	23.400
Cd	19	3.436	0.880	0.202	1.900	4.700
Cr	19	56.000	7.881	1.808	38.000	71.300
Cu	19	195.105	33.401	7.6636	132.000	242.000
Hg	19	0.931	0.463	0.106	0.410	2.300
Pb	19	126.100	43.792	10.046	90.900	264.000
Ni	19	39.405	7.491	1.719	10.600	45.100
Zn	19	308.421	135.583	31.105	220.000	694.000

Variable	n	mean	std	stderr	min	max
Cluster=4						
As	9	18.256	2.849	0.950	12.800	23.000
Cd	9	3.200	1.002	0.334	2.000	4.600
Cr	9	65.378	4.792	1.597	60.300	73.200
Cu	9	218.778	50.127	16.709	138.000	275.000
Hg	9	1.132	0.215	0.071	0.860	1.400
Pb	9	138.911	54.826	18.276	86.600	271.000
Ni	9	42.333	3.154	1.051	36.900	46.200
Zn	9	279.111	58.152	19.384	201.000	402.000
Cluster=5						
As	13	41.307	30.593	8.485	17.500	111.000
Cd	13	4.877	1.0353	0.287	3.000	6.500
Cr	13	90.162	31.315	8.685	62.800	168.000
Cu	13	517.769	414.917	115.077	242.000	1700.000
Hg	13	1.588	0.845	0.234	0.680	3.200
Pb	13	296.615	149.847	41.560	128.000	603.000
Ni	13	42.054	7.250	2.011	30.200	56.000
Zn	13	755.153	432.970	120.084	422.000	1950.000

Sinclair Inlet Contaminant Release Rate Study

Sta: 1B
Date: 7/10-7/28/01

Start time: 13:30:00 7/10/01
Interval: 08:00:00
End time: 08:30:00 7/29/01

GPS lat: 47 33.64 N
long: 122 37 46 W

Lat let: 47 33.80 N
long: 122 37 53 W
Depth: 12.4 m

lab data		BFSO data		outlier correct		dil. correction		born reg		Regressions		Flux rates	
sample id	[Conc] (ppb)	sample	elapsed time	[Conc] (ppb)	elapsed time	[Conc] (ppb)	[Conc] (ppb)	# of dilutions	[Conc] (ppb)				
Copper										Regression Output:			
SIN181-10	---	T0	---	---	---	---	---	---	---	Constant	0.70	Chamber Volume =	40.65 liters
SIN181-01	0.50	#1	0.00	0.50	0.00	0.50	0.50	0.00	0.70	Std Err of Y Est	0.50	Chamber Area =	1800.40 cm ²
SIN181-02	1.30	#2	8.00	1.30	8.00	1.30	1.29	1.00	0.89	R Squared	0.21		
SIN181-03	0.88	#3	16.00	0.88	16.00	0.88	0.87	2.00	1.07	No. of Observations	3.00	Flux rate =	140 ug/m ² /day
SIN181-04	0.88	#4	24.00	0.88	24.00	0.88	0.89	3.00	1.25	Degrees of Freedom	1.00		
SIN181-05	0.83	#5	32.00	0.83	32.00	0.83	0.83	4.00	1.44			80% CI (low) =	-866 ug/m ² /day
SIN181-06	1.20	#6	40.00	1.20	40.00	1.20	1.20	5.00	1.62	X Coefficient(s)	0.02	(high) =	966 ug/m ² /day
SIN181-01	37.80	SED		37.80						Std Err of Coef.	0.04		
Cadmium										Regression Output:			
SIN181-10	---	T0	---	---	---	---	---	---	---	Constant	0.17	Chamber Volume =	40.65 liters
SIN181-01	0.15	#1	0.00	0.15	0.00	0.15	0.15	0.00	0.17	Std Err of Y Est	0.05	Chamber Area =	1800.40 cm ²
SIN181-02	0.23	#2	8.00	0.23	8.00	0.23	0.23	1.00	0.18	R Squared	0.11		
SIN181-03	0.18	#3	16.00	0.18	16.00	0.18	0.18	2.00	0.20	No. of Observations	3.00	Flux rate =	10 ug/m ² /day
SIN181-04	0.20	#4	24.00	0.20	24.00	0.20	0.20	3.00	0.21	Degrees of Freedom	1.00		
SIN181-05	0.21	#5	32.00	0.21	32.00	0.21	0.21	4.00	0.22			80% CI (low) =	-78 ug/m ² /day
SIN181-06	0.19	#6	40.00	0.19	40.00	0.19	0.19	5.00	0.24	X Coefficient(s)	0.00	(high) =	98 ug/m ² /day
SIN181-01	0.22	SED		0.22						Std Err of Coef.	0.00		
Chromium VI										Regression Output:			
SIN181-10	---	T0	---	---	---	---	---	---	---	Constant	n/a	Chamber Volume =	40.65 liters
SIN181-01	-0.2	#1	0.00	-0.2	0.00	-0.2	0.00	0.00	0.00	Std Err of Y Est	n/a	Chamber Area =	1800.40 cm ²
SIN181-02	-0.2	#2	8.00	-0.2	8.00	-0.2	0.00	1.00	0.00	R Squared	n/a		
SIN181-03	-0.2	#3	16.00	-0.2	16.00	-0.2	0.00	2.00	0.00	No. of Observations	n/a	Flux rate =	0 ug/m ² /day
SIN181-04	-0.2	#4	24.00	-0.2	24.00	-0.2	0.00	3.00	0.00	Degrees of Freedom	n/a		
SIN181-05	-0.2	#5	32.00	-0.2	32.00	-0.2	0.00	4.00	0.00			80% CI (low) =	0 ug/m ² /day
SIN181-06	-0.2	#6	40.00	-0.2	40.00	-0.2	0.00	5.00	0.00	X Coefficient(s)	n/a	(high) =	0 ug/m ² /day
SIN181-01	45.30	SED		45.30						Std Err of Coef.	n/a		
Lead										Regression Output:			
SIN181-10	---	T0	---	---	---	---	---	---	---	Constant	n/a	Chamber Volume =	40.65 liters
SIN181-01	-0.08	#1	0.00	-0.08	0.00	-0.08	0.00	0.00	0.00	Std Err of Y Est	n/a	Chamber Area =	1800.40 cm ²
SIN181-02	0.08	#2	8.00	0.08	8.00	0.08	0.08	1.00	0.00	R Squared	n/a		
SIN181-03	0.15	#3	16.00	0.15	16.00	0.15	0.15	2.00	0.00	No. of Observations	n/a	Flux rate =	0 ug/m ² /day
SIN181-04	0.13	#4	24.00	0.13	24.00	0.13	0.13	3.00	0.00	Degrees of Freedom	n/a		
SIN181-05	0.09	#5	32.00	0.09	32.00	0.09	0.09	4.00	0.00			80% CI (low) =	0 ug/m ² /day
SIN181-06	0.16	#6	40.00	0.16	40.00	0.16	0.16	5.00	0.00	X Coefficient(s)	n/a	(high) =	0 ug/m ² /day
SIN181-01	38.40	SED		38.40						Std Err of Coef.	n/a		
Nickel										Regression Output:			
SIN181-10	---	T0	---	---	---	---	---	---	---	Constant	0.68	Chamber Volume =	40.65 liters
SIN181-01	0.68	#1	0.00	0.68	0.00	0.68	0.68	0.00	0.68	Std Err of Y Est	0.08	Chamber Area =	1800.40 cm ²
SIN181-02	0.77	#2	8.00	0.77	8.00	0.77	0.78	1.00	0.71	R Squared	0.37		
SIN181-03	0.74	#3	16.00	0.74	16.00	0.74	0.72	2.00	0.75	No. of Observations	3.00	Flux rate =	24 ug/m ² /day
SIN181-04	0.88	#4	24.00	0.88	24.00	0.88	0.88	3.00	0.78	Degrees of Freedom	1.00		
SIN181-05	0.91	#5	32.00	0.91	32.00	0.91	0.91	4.00	0.81			80% CI (low) =	-71 ug/m ² /day
SIN181-06	0.89	#6	40.00	0.89	40.00	0.89	0.89	5.00	0.84	X Coefficient(s)	0.00	(high) =	118 ug/m ² /day
SIN181-01	43.70	SED		43.70						Std Err of Coef.	0.01		
Zinc										Regression Output:			
SIN181-10	---	T0	---	---	---	---	---	---	---	Constant	3.42	Chamber Volume =	40.65 liters
SIN181-01	3.70	#1	0.00	3.70	0.00	3.70	3.70	0.00	3.42	Std Err of Y Est	0.89	Chamber Area =	1800.40 cm ²
SIN181-02	3.80	#2	8.00	3.80	8.00	3.80	3.85	1.00	4.42	R Squared	0.81		
SIN181-03	5.80	#3	16.00	5.80	16.00	5.80	5.70	2.00	5.42	No. of Observations	3.00	Flux rate =	762 ug/m ² /day
SIN181-04	5.80	#4	24.00	5.80	24.00	5.80	5.80	3.00	6.42	Degrees of Freedom	1.00		
SIN181-05	5.30	#5	32.00	5.30	32.00	5.30	5.30	4.00	7.42			80% CI (low) =	-389 ug/m ² /day
SIN181-06	5.30	#6	40.00	5.30	40.00	5.30	5.30	5.00	8.42	X Coefficient(s)	0.12	(high) =	1913 ug/m ² /day
SIN181-01	124.00	SED		124.00						Std Err of Coef.	0.06		
Mercury										Regression Output:			
SIN181-10	---	T0	---	---	---	---	---	---	---	Constant	n/a	Chamber Volume =	40.65 liters
SIN181-01	-0.2	#1	0.00	-0.2	0.00	-0.2	0.00	0.00	0.00	Std Err of Y Est	n/a	Chamber Area =	1800.40 cm ²
SIN181-02	-0.2	#2	8.00	-0.2	8.00	-0.2	0.00	1.00	0.00	R Squared	n/a		
SIN181-03	-0.2	#3	16.00	-0.2	16.00	-0.2	0.00	2.00	0.00	No. of Observations	n/a	Flux rate =	0 ug/m ² /day
SIN181-04	-0.2	#4	24.00	-0.2	24.00	-0.2	0.00	3.00	0.00	Degrees of Freedom	n/a		
SIN181-05	-0.2	#5	32.00	-0.2	32.00	-0.2	0.00	4.00	0.00			80% CI (low) =	0 ug/m ² /day
SIN181-06	-0.2	#6	40.00	-0.2	40.00	-0.2	0.00	5.00	0.00	X Coefficient(s)	n/a	(high) =	0 ug/m ² /day
SIN181-01	0.29	SED		0.29						Std Err of Coef.	n/a		
Arsenic										Regression Output:			
SIN181-10	---	T0	---	---	---	---	---	---	---	Constant	1.32	Chamber Volume =	40.65 liters
SIN181-01	1.30	#1	0.00	1.30	0.00	1.30	1.30	0.00	1.32	Std Err of Y Est	0.04	Chamber Area =	1800.40 cm ²
SIN181-02	1.70	#2	8.00	1.70	8.00	1.70	1.68	1.00	1.65	R Squared	0.98		
SIN181-03	2.00	#3	16.00	2.00	16.00	2.00	1.98	2.00	1.98	No. of Observations	3.00	Flux rate =	253 ug/m ² /day
SIN181-04	1.30	#4	24.00	1.30	24.00	1.30	1.30	3.00	2.31	Degrees of Freedom	1.00		
SIN181-05	2.00	#5	32.00	2.00	32.00	2.00	2.00	4.00	2.85			80% CI (low) =	186 ug/m ² /day
SIN181-06	1.20	#6	40.00	1.20	40.00	1.20	1.20	5.00	2.88	X Coefficient(s)	0.04	(high) =	321 ug/m ² /day
SIN181-01	4.48	SED		4.48						Std Err of Coef.	0.00		

Sindlar Inlet Contaminant Release Rate Study

Site 2A
Date 7/6-7/10/91

Start time: 13:10:00 7/6/91
Interval: 08:00:00
End time: 08:10:00 7/10/91

GPS lat: 47 33.56 N
long: 122 37.67 W

Loc lat: 47 33.52
long: 122 37.71
Depth: 12.8 m

lab data	BFSO data				outlier correct		dil. correction		from reg	Regressions	Flux rates
sample id	[Conc] (ppb)	sample	elapsed time	[Conc] (ppb)	elapsed time	[Conc] (ppb)	[Conc] (ppb)	# of dilutions	[Conc] (ppb)		
Copper									yes	Regression Output:	
SINQAI89-T0	3.10	T0		3.10		3.10				Constant	2.46 Chamber Volume = 40.65 Bars
SINQAI89-S1	2.20	S1	0.00	2.20	0.00	2.20	2.20	0.00	2.46	Std Err of Y Est	0.32 Chamber Area = 1600.40 cm ²
SINQAI89-S2	2.50	S2	8.00	2.50	8.00	2.50	2.46	1.00	2.31	R Squared	0.50
SINQAI89-S3	2.20	S3	16.00	2.20	16.00	2.20	2.12	2.00	2.16	No. of Observations	8.00 Flux rate = -117 ug/m ² /day
SINQAI89-S4	2.40	S4	24.00	2.40	24.00	2.40	2.27	3.00	2.00	Degrees of Freedom	4.00
SINQAI89-S5	2.30	S5	32.00	2.30	32.00	2.30	2.13	4.00	1.85		80% CI (low) = -205 ug/m ² /day
SINQAI89-S6	1.50	S6	40.00	1.50	40.00	1.50	1.29	5.00	1.70	X Coefficient(s)	-0.02 (high) = -27 ug/m ² /day
SINQAI89-S1	182.00	SED		182.00						Std Err of Coef.	0.01
Cadmium									yes	Regression Output:	
SINQAI89-T0	0.17	T0		0.17		0.17				Constant	0.18 Chamber Volume = 40.65 Bars
SINQAI89-S1	0.22	S1	0.00	0.22	0.00	0.22	0.22	0.00	0.16	Std Err of Y Est	0.03 Chamber Area = 1600.40 cm ²
SINQAI89-S2	0.14	S2	8.00	0.14	8.00	0.14	0.14	1.00	0.17	R Squared	0.46
SINQAI89-S3	0.14	S3	16.00	0.14	16.00	0.14	0.14	2.00	0.16	No. of Observations	6.00 Flux rate = -10 ug/m ² /day
SINQAI89-S4	0.14	S4	24.00	0.14	24.00	0.14	0.13	3.00	0.14	Degrees of Freedom	4.00
SINQAI89-S5	0.15	S5	32.00	0.15	32.00	0.15	0.14	4.00	0.13		80% CI (low) = -18 ug/m ² /day
SINQAI89-S6	0.14	S6	40.00	0.14	40.00	0.14	0.13	5.00	0.12	X Coefficient(s)	-0.00 (high) = -2 ug/m ² /day
SINQAI89-S1	1.13	SED		1.13						Std Err of Coef.	0.00
Chromium VI									no	Regression Output:	
SINQAI89-T0	<0.2	T0		<0.2		<0.2			0.00	Constant	n/a Chamber Volume = 40.65 Bars
SINQAI89-S1	<0.2	S1	0.00	<0.2	0.00	<0.2	0.00	0.00	0.00	Std Err of Y Est	n/a Chamber Area = 1600.40 cm ²
SINQAI89-S2	<0.2	S2	8.00	<0.2	8.00	<0.2	0.00	1.00	0.00	R Squared	n/a
SINQAI89-S3	<0.2	S3	16.00	<0.2	16.00	<0.2	0.00	2.00	0.00	No. of Observations	n/a Flux rate = 0 ug/m ² /day
SINQAI89-S4	<0.2	S4	24.00	<0.2	24.00	<0.2	0.00	3.00	0.00	Degrees of Freedom	n/a
SINQAI89-S5	<0.2	S5	32.00	<0.2	32.00	<0.2	0.00	4.00	0.00		80% CI (low) = 0 ug/m ² /day
SINQAI89-S6	<0.2	S6	40.00	<0.2	40.00	<0.2	0.00	5.00	0.00	X Coefficient(s)	n/a (high) = 0 ug/m ² /day
SINQAI89-S1	86.40	SED		86.40						Std Err of Coef.	n/a
Lead									yes	Regression Output:	
SINQAI89-T0	0.29	T0		0.29		0.29				Constant	0.14 Chamber Volume = 40.65 Bars
SINQAI89-S1	0.14	S1	0.00	0.14	0.00	0.14	0.14	0.00	0.14	Std Err of Y Est	0.03 Chamber Area = 1600.40 cm ²
SINQAI89-S2	0.14	S2	8.00	0.14	8.00	0.14	0.14	1.00	0.11	R Squared	0.80
SINQAI89-S3	0.08	S3	16.00	0.08	16.00	0.08	0.05	2.00	0.08	No. of Observations	5.00 Flux rate = -21 ug/m ² /day
SINQAI89-S4	0.08	S4	24.00	0.08	24.00	0.08	0.05	3.00	0.08	Degrees of Freedom	3.00
SINQAI89-S5	0.08	S5	32.00	0.08	32.00	0.08	0.04	4.00	0.03		80% CI (low) = -31 ug/m ² /day
SINQAI89-S6	<0.05	S6	40.00	<0.05	40.00	<0.05	0.00	5.00	0.00	X Coefficient(s)	-0.00 (high) = -11 ug/m ² /day
SINQAI89-S1	332.00	SED		332.00						Std Err of Coef.	0.00
Nickel									yes	Regression Output:	
SINQAI89-T0	3.02	T0		3.02		3.02				Constant	0.89 Chamber Volume = 40.65 Bars
SINQAI89-S1	0.80	S1	0.00	0.80	0.00	0.80	0.80	0.00	0.89	Std Err of Y Est	0.08 Chamber Area = 1600.40 cm ²
SINQAI89-S2	0.80	S2	8.00	0.80	8.00	0.80	0.86	1.00	0.89	R Squared	0.01
SINQAI89-S3	0.83	S3	16.00	0.83	16.00	0.83	0.85	2.00	0.80	No. of Observations	6.00 Flux rate = 3 ug/m ² /day
SINQAI89-S4	1.08	S4	24.00	1.08	24.00	1.08	0.96	3.00	0.80	Degrees of Freedom	4.00
SINQAI89-S5	1.18	S5	32.00	1.18	32.00	1.18	1.02	4.00	0.81		80% CI (low) = -20 ug/m ² /day
SINQAI89-S6	1.02	S6	40.00	1.02	40.00	1.02	0.82	5.00	0.81	X Coefficient(s)	0.00 (high) = 27 ug/m ² /day
SINQAI89-S1	81.30	SED		81.30						Std Err of Coef.	0.00
Zinc									yes	Regression Output:	
SINQAI89-T0	7.30	T0		7.30		7.30				Constant	3.14 Chamber Volume = 40.65 Bars
SINQAI89-S1	3.30	S1	0.00	3.30	0.00	3.30	3.30	0.00	3.14	Std Err of Y Est	0.40 Chamber Area = 1600.40 cm ²
SINQAI89-S2	3.40	S2	8.00	3.40	8.00	3.40	3.30	1.00	3.55	R Squared	0.81
SINQAI89-S3	3.80	S3	16.00	3.80	16.00	3.80	3.80	2.00	3.85	No. of Observations	6.00 Flux rate = 308 ug/m ² /day
SINQAI89-S4	5.10	S4	24.00	5.10	24.00	5.10	4.80	3.00	4.38	Degrees of Freedom	4.00
SINQAI89-S5	5.50	S5	32.00	5.50	32.00	5.50	5.10	4.00	4.78		80% CI (low) = 185 ug/m ² /day
SINQAI89-S6	5.30	S6	40.00	5.30	40.00	5.30	4.81	5.00	5.18	X Coefficient(s)	0.05 (high) = 421 ug/m ² /day
SINQAI89-S1	2784.00	SED		2784.00						Std Err of Coef.	0.01
Mercury									no	Regression Output:	
SINQAI89-T0	<0.2	T0		<0.2		<0.2			0.00	Constant	n/a Chamber Volume = 40.65 Bars
SINQAI89-S1	<0.2	S1	0.00	<0.2	0.00	<0.2	0.00	0.00	0.00	Std Err of Y Est	n/a Chamber Area = 1600.40 cm ²
SINQAI89-S2	<0.2	S2	8.00	<0.2	8.00	<0.2	0.00	1.00	0.00	R Squared	n/a
SINQAI89-S3	<0.2	S3	16.00	<0.2	16.00	<0.2	0.00	2.00	0.00	No. of Observations	n/a Flux rate = 0 ug/m ² /day
SINQAI89-S4	<0.2	S4	24.00	<0.2	24.00	<0.2	0.00	3.00	0.00	Degrees of Freedom	n/a
SINQAI89-S5	<0.2	S5	32.00	<0.2	32.00	<0.2	0.00	4.00	0.00		80% CI (low) = 0 ug/m ² /day
SINQAI89-S6	<0.2	S6	40.00	<0.2	40.00	<0.2	0.00	5.00	0.00	X Coefficient(s)	n/a (high) = 0 ug/m ² /day
SINQAI89-S1	0.81	SED		0.81						Std Err of Coef.	n/a
Arsenic									no	Regression Output:	
SINQAI89-T0	2.30	T0		2.30		2.30			0.00	Constant	n/a Chamber Volume = 40.65 Bars
SINQAI89-S1	<0.7	S1	0.00	<0.7	0.00	<0.7	0.00	0.00	0.00	Std Err of Y Est	n/a Chamber Area = 1600.40 cm ²
SINQAI89-S2	<0.7	S2	8.00	<0.7	8.00	<0.7	0.00	1.00	0.00	R Squared	n/a
SINQAI89-S3	<0.7	S3	16.00	<0.7	16.00	<0.7	0.00	2.00	0.00	No. of Observations	n/a Flux rate = 0 ug/m ² /day
SINQAI89-S4	<0.7	S4	24.00	<0.7	24.00	<0.7	0.00	3.00	0.00	Degrees of Freedom	n/a
SINQAI89-S5	<0.7	S5	32.00	<0.7	32.00	<0.7	0.00	4.00	0.00		80% CI (low) = 0 ug/m ² /day
SINQAI89-S6	<0.7	S6	40.00	<0.7	40.00	<0.7	0.00	5.00	0.00	X Coefficient(s)	n/a (high) = 0 ug/m ² /day
SINQAI89-S1		SED		0.00						Std Err of Coef.	n/a

Sindar Inlet Contaminant Release Rate Study

Site: 29
Date: 7/23-7/25/91

Start time: 15:15:00 7/23/91
Interval: 08:00:00
End time: 08:15:00 7/25/91

GPS lat: 47 33 43 N
long: 122 38 94 W

Loc lat: 47 33.39 N
long: 122 38.95 W
Depth: 14.2 m

lab data	BFSO data				outlier correct		dil. correction		tom reg	Regressors	Flux rates
sample id	[Conc] (ppb)	sample	elapsed time	[Conc] (ppb)	elapsed time	[Conc] (ppb)	[Conc] (ppb)	# of dilutions	[Conc] (ppb)		
Copper											
SN28204-T01	2.80	T0		2.80		2.80			yes	Regression Output	
SN28204-S1	2.10	#1	0.00	2.10	0.00	2.10	2.10	0.00	2.03	Constant	2.03 Chamber Volume = 40.65 Bars
SN28204-S2	1.80	#2	8.00	1.80	8.00	1.80	1.86	1.00	1.87	Std Err of Y Est	0.17 Chamber Area = 1800.40 cm ²
SN28204-S3	1.80	#3	16.00	1.80	16.00	1.80	1.52	2.00	1.71	R Squared	0.79
SN28204-S4	1.70	#4	24.00	1.70	24.00	1.70	1.58	3.00	1.56	No. of Observations	6.00 Flux rate = -121 ug/m ² /day
SN28204-S5	1.80	#5	32.00	1.80	32.00	1.80	1.84	4.00	1.40	Degrees of Freedom	4.00
SN28204-S6	1.30	#6	40.00	1.30	40.00	1.30	1.10	5.00	1.24	X Coefficient(s)	80% CI (low) = -170 ug/m ² /day
SN28204-S1	135.00	SED		135.00						Std Err of Coef.	(high) = -73 ug/m ² /day
Cadmium											
SN28204-T01	0.14	T0		0.14		0.14			yes	Regression Output	
SN28204-S1	0.14	#1	0.00	0.14	0.00	0.14	0.14	0.00	0.12	Constant	0.12 Chamber Volume = 40.65 Bars
SN28204-S2	0.08	#2	8.00	0.08	8.00	0.08	0.08	1.00	0.10	Std Err of Y Est	0.02 Chamber Area = 1800.40 cm ²
SN28204-S3	0.07	#3	16.00	0.07	16.00	0.07	0.07	2.00	0.08	R Squared	0.84
SN28204-S4	0.08	#4	24.00	0.08	24.00	0.08	0.05	3.00	0.08	No. of Observations	6.00 Flux rate = -15 ug/m ² /day
SN28204-S5	0.05	#5	32.00	0.05	32.00	0.05	0.04	4.00	0.04	Degrees of Freedom	4.00
SN28204-S6	0.04	#6	40.00	0.04	40.00	0.04	0.03	5.00	0.02	X Coefficient(s)	80% CI (low) = -19 ug/m ² /day
SN28204-S1	4.86	SED		4.86						Std Err of Coef.	(high) = -10 ug/m ² /day
Chromium VI											
SN28204-T01	<-0.2	T0		<-0.2		<-0.2			no	Regression Output	
SN28204-S1	<-0.2	#1	0.00	<-0.2	0.00	<-0.2	0.00	0.00	0.00	Constant	n/a Chamber Volume = 40.65 Bars
SN28204-S2	<-0.2	#2	8.00	<-0.2	8.00	<-0.2	0.00	1.00	0.00	Std Err of Y Est	n/a Chamber Area = 1800.40 cm ²
SN28204-S3	<-0.2	#3	16.00	<-0.2	16.00	<-0.2	0.00	2.00	0.00	R Squared	n/a
SN28204-S4	<-0.2	#4	24.00	<-0.2	24.00	<-0.2	0.00	3.00	0.00	No. of Observations	6.00 Flux rate = 0 ug/m ² /day
SN28204-S5	<-0.2	#5	32.00	<-0.2	32.00	<-0.2	0.00	4.00	0.00	Degrees of Freedom	n/a
SN28204-S6	<-0.2	#6	40.00	<-0.2	40.00	<-0.2	0.00	5.00	0.00	X Coefficient(s)	80% CI (low) = 0 ug/m ² /day
SN28204-S1	47.80	SED		47.80						Std Err of Coef.	(high) = 0 ug/m ² /day
Lead											
SN28204-T01	<-0.08	T0		<-0.08		<-0.08			no	Regression Output	
SN28204-S1	<-0.08	#1	0.00	<-0.08	0.00	<-0.08	0.00	0.00	0.00	Constant	n/a Chamber Volume = 40.65 Bars
SN28204-S2	<-0.08	#2	8.00	<-0.08	8.00	<-0.08	0.00	1.00	0.00	Std Err of Y Est	n/a Chamber Area = 1800.40 cm ²
SN28204-S3	<-0.08	#3	16.00	<-0.08	16.00	<-0.08	0.00	2.00	0.00	R Squared	n/a
SN28204-S4	0.12	#4	24.00	0.12	24.00	0.12	0.12	3.00	0.00	No. of Observations	6.00 Flux rate = 0 ug/m ² /day
SN28204-S5	<-0.08	#5	32.00	<-0.08	32.00	<-0.08	0.00	4.00	0.00	Degrees of Freedom	n/a
SN28204-S6	0.35	#6	40.00	0.35	40.00	0.35	0.35	5.00	0.00	X Coefficient(s)	80% CI (low) = 0 ug/m ² /day
SN28204-S1	58.00	SED		58.00						Std Err of Coef.	(high) = 0 ug/m ² /day
Nickel											
SN28204-T01	3.81	T0		3.81		3.81			yes	Regression Output	
SN28204-S1	0.89	#1	0.00	0.89	0.00	0.89	0.89	0.00	1.34	Constant	1.34 Chamber Volume = 40.65 Bars
SN28204-S2	1.84	#2	8.00	1.84	8.00	1.84	1.86	1.00	1.75	Std Err of Y Est	0.38 Chamber Area = 1800.40 cm ²
SN28204-S3	2.78	#3	16.00	2.78	16.00	2.78	2.86	2.00	2.15	R Squared	0.83
SN28204-S4	2.80	#4	24.00	2.80	24.00	2.80	2.85	3.00	2.55	No. of Observations	6.00 Flux rate = 307 ug/m ² /day
SN28204-S5	3.18	#5	32.00	3.18	32.00	3.18	2.95	4.00	2.95	Degrees of Freedom	4.00
SN28204-S6	3.33	#6	40.00	3.33	40.00	3.33	3.07	5.00	3.38	X Coefficient(s)	80% CI (low) = 201 ug/m ² /day
SN28204-S1	54.80	SED		54.80						Std Err of Coef.	(high) = 413 ug/m ² /day
Zinc											
SN28204-T01	4.20	T0		4.20		4.20			yes	Regression Output	
SN28204-S1	3.50	#1	0.00	3.50	0.00	3.50	3.50	0.00	4.34	Constant	4.34 Chamber Volume = 40.65 Bars
SN28204-S2	3.70	#2	8.00	3.70	8.00	3.70	3.64	1.00	4.27	Std Err of Y Est	1.23 Chamber Area = 1800.40 cm ²
SN28204-S3	6.20	#3	16.00	6.20	16.00	6.20	6.09	2.00	4.21	R Squared	0.01
SN28204-S4	4.70	#4	24.00	4.70	24.00	4.70	4.53	3.00	4.14	No. of Observations	6.00 Flux rate = -50 ug/m ² /day
SN28204-S5	4.80	#5	32.00	4.80	32.00	4.80	4.37	4.00	4.08	Degrees of Freedom	4.00
SN28204-S6	3.20	#6	40.00	3.20	40.00	3.20	2.82	5.00	4.01	X Coefficient(s)	80% CI (low) = -394 ug/m ² /day
SN28204-S1	42.80	SED		42.80						Std Err of Coef.	(high) = 294 ug/m ² /day
Mercury											
SN28204-T01	<-0.2	T0		<-0.2		<-0.2			no	Regression Output	
SN28204-S1	<-0.2	#1	0.00	<-0.2	0.00	<-0.2	0.00	0.00	0.00	Constant	n/a Chamber Volume = 40.65 Bars
SN28204-S2	<-0.2	#2	8.00	<-0.2	8.00	<-0.2	0.00	1.00	0.00	Std Err of Y Est	n/a Chamber Area = 1800.40 cm ²
SN28204-S3	<-0.2	#3	16.00	<-0.2	16.00	<-0.2	0.00	2.00	0.00	R Squared	n/a
SN28204-S4	<-0.2	#4	24.00	<-0.2	24.00	<-0.2	0.00	3.00	0.00	No. of Observations	6.00 Flux rate = 0 ug/m ² /day
SN28204-S5	<-0.2	#5	32.00	<-0.2	32.00	<-0.2	0.00	4.00	0.00	Degrees of Freedom	n/a
SN28204-S6	<-0.2	#6	40.00	<-0.2	40.00	<-0.2	0.00	5.00	0.00	X Coefficient(s)	80% CI (low) = 0 ug/m ² /day
SN28204-S1	0.44	SED		0.44						Std Err of Coef.	(high) = 0 ug/m ² /day
Arsenic											
SN28204-T01	1.20	T0		1.20		1.20			yes	Regression Output	
SN28204-S1	1.50	#1	0.00	1.50	0.00	1.50	1.50	0.00	1.22	Constant	1.22 Chamber Volume = 40.65 Bars
SN28204-S2	1.70	#2	8.00	1.70	8.00	1.70	1.66	1.00	1.80	Std Err of Y Est	0.54 Chamber Area = 1800.40 cm ²
SN28204-S3	1.20	#3	16.00	1.20	16.00	1.20	1.17	2.00	1.98	R Squared	0.83
SN28204-S4	2.70	#4	24.00	2.70	24.00	2.70	2.65	3.00	2.37	No. of Observations	5.00 Flux rate = 292 ug/m ² /day
SN28204-S5	3.00	#5	32.00	3.00	32.00	3.00	2.94	4.00	2.78	Degrees of Freedom	3.00
SN28204-S6	<-0.7	#6	40.00	<-0.7	40.00	<-0.7		5.00	3.14	X Coefficient(s)	80% CI (low) = 94 ug/m ² /day
SN28204-S1	3.82	SED		3.82						Std Err of Coef.	(high) = 481 ug/m ² /day

Sindair Inlet Contaminant Release Rate Study

Site: 3A
Date: 7/6-7/8/91

Start time: 12:25:00 7/6/91
Interval: 08:00:00
End time: 05:25:00 7/8/91

GPS lat: 47 33.26 N
long: 122 39.32 W

Loc lat: 47 33.24 N
long: 122 39.29 W
Depth: 8.0 m

lab data	BFSO data				outlier correct		dil. correction		from reg	Regressions	Flux rates
sample id	[Conc] (ppb)	sample	elapsed time	[Conc] (ppb)	elapsed time	[Conc] (ppb)	[Conc] (ppb)	# of dilutions	[Conc] (ppb)		
Copper											
SINDAI87-T0	2.70	T0		2.70		2.70			yes	Regression Output:	
SINDAI87-S1	2.80	#1	0.00	2.80	0.00	2.80	2.80	0.00	2.80	Constant	2.80 Chamber Volume = 40.65 Bars
SINDAI87-S2	2.80	#2	8.00	2.80	8.00	2.80	2.76	1.00	2.89	Std Err of Y Est	0.34 Chamber Area = 1800.40 cm ²
SINDAI87-S3	3.20	#3	16.00	3.20	16.00	3.20	3.13	2.00	3.39	R Squared	0.82
SINDAI87-S4	4.30	#4	24.00	4.30	24.00	4.30	4.18	3.00	3.78	No. of Observations	5.00 Flux rate = 300 ug/m ² /day
SINDAI87-S5	4.20	#5	32.00	4.20	32.00	4.20	4.05	4.00	4.17	Degrees of Freedom	3.00
SINDAI87-S6	3.80	#6	40.00	3.80	40.00	3.80		5.00	4.57		80% CI (low) = 188 ug/m ² /day
SINDAI87-S1	358.00	SED		358.00						X Coefficient(s)	0.05 (high) = 433 ug/m ² /day
										Std Err of Coef.	0.01
Cadmium											
SINDAI87-T0	<0.05	T0		<0.05		<0.05			no	Regression Output:	
SINDAI87-S1	<0.05	#1	0.00	<0.05	0.00	<0.05	0.00	0.00	0.00	Constant	n/a Chamber Volume = 40.65 Bars
SINDAI87-S2	<0.05	#2	8.00	<0.05	8.00	<0.05	0.00	1.00	0.00	Std Err of Y Est	n/a Chamber Area = 1800.40 cm ²
SINDAI87-S3	<0.05	#3	16.00	<0.05	16.00	<0.05	0.00	2.00	0.00	R Squared	n/a
SINDAI87-S4	<0.05	#4	24.00	<0.05	24.00	<0.05	0.00	3.00	0.00	No. of Observations	n/a Flux rate = 0 ug/m ² /day
SINDAI87-S5	<0.05	#5	32.00	<0.05	32.00	<0.05	0.00	4.00	0.00	Degrees of Freedom	n/a
SINDAI87-S6	<0.05	#6	40.00	<0.05	40.00	<0.05	0.00	5.00	0.00		80% CI (low) = 0 ug/m ² /day
SINDAI87-S1	0.82	SED		0.82						X Coefficient(s)	n/a (high) = 0 ug/m ² /day
										Std Err of Coef.	n/a
Chromium VI											
SINDAI87-T0	<0.2	T0		<0.2		<0.2			no	Regression Output:	
SINDAI87-S1	<0.2	#1	0.00	<0.2	0.00	<0.2	0.00	0.00	0.00	Constant	n/a Chamber Volume = 40.65 Bars
SINDAI87-S2	<0.2	#2	8.00	<0.2	8.00	<0.2	0.00	1.00	0.00	Std Err of Y Est	n/a Chamber Area = 1800.40 cm ²
SINDAI87-S3	<0.2	#3	16.00	<0.2	16.00	<0.2	0.00	2.00	0.00	R Squared	n/a
SINDAI87-S4	<0.2	#4	24.00	<0.2	24.00	<0.2	0.00	3.00	0.00	No. of Observations	n/a Flux rate = 0 ug/m ² /day
SINDAI87-S5	<0.2	#5	32.00	<0.2	32.00	<0.2	0.00	4.00	0.00	Degrees of Freedom	n/a
SINDAI87-S6	<0.2	#6	40.00	<0.2	40.00	<0.2	0.00	5.00	0.00		80% CI (low) = 0 ug/m ² /day
SINDAI87-S1	85.20	SED		85.20						X Coefficient(s)	n/a (high) = 0 ug/m ² /day
										Std Err of Coef.	n/a
Lead											
SINDAI87-T0	<0.09	T0		<0.09		<0.09			yes	Regression Output:	
SINDAI87-S1	0.15	#1	0.00	0.15	0.00	0.15	0.15	0.00	0.00	Constant	n/a Chamber Volume = 40.65 Bars
SINDAI87-S2	0.23	#2	8.00	0.23	8.00	0.23	0.23	1.00	0.00	Std Err of Y Est	n/a Chamber Area = 1800.40 cm ²
SINDAI87-S3	<0.09	#3	16.00	<0.09	16.00	<0.09	0.00	2.00	0.00	R Squared	n/a
SINDAI87-S4	<0.09	#4	24.00	<0.09	24.00	<0.09	0.00	3.00	0.00	No. of Observations	n/a Flux rate = 0 ug/m ² /day
SINDAI87-S5	0.21	#5	32.00	0.21	32.00	0.21	0.21	4.00	0.00	Degrees of Freedom	n/a
SINDAI87-S6	0.23	#6	40.00	0.23	40.00	0.23		5.00	0.00		80% CI (low) = 0 ug/m ² /day
SINDAI87-S1	338.00	SED		338.00						X Coefficient(s)	n/a (high) = 0 ug/m ² /day
										Std Err of Coef.	n/a
Nickel											
SINDAI87-T0	2.45	T0		2.45		2.45			yes	Regression Output:	
SINDAI87-S1	0.77	#1	0.00	0.77	0.00	0.77	0.77	0.00	0.95	Constant	0.95 Chamber Volume = 40.65 Bars
SINDAI87-S2	1.27	#2	8.00	1.27	8.00	1.27	1.24	1.00	0.88	Std Err of Y Est	0.32 Chamber Area = 1800.40 cm ²
SINDAI87-S3	0.85	#3	16.00	0.85	16.00	0.85	0.58	2.00	0.78	R Squared	0.20
SINDAI87-S4	0.75	#4	24.00	0.75	24.00	0.75	0.85	3.00	0.88	No. of Observations	4.00 Flux rate = -77 ug/m ² /day
SINDAI87-S5	0.79	#5	32.00	0.79	32.00	0.79	0.86	4.00	0.56	Degrees of Freedom	2.00
SINDAI87-S6	1.47	#6	40.00	1.47	40.00	1.47		5.00	0.46		80% CI (low) = -285 ug/m ² /day
SINDAI87-S1	101.00	SED		101.00						X Coefficient(s)	-0.01 (high) = 129 ug/m ² /day
										Std Err of Coef.	0.02
Zinc											
SINDAI87-T0	8.50	T0		8.50		8.50			yes	Regression Output:	
SINDAI87-S1	8.80	#1	0.00	8.80	0.00	8.80	8.80	0.00	8.08	Constant	8.08 Chamber Volume = 40.65 Bars
SINDAI87-S2	8.20	#2	8.00	8.20	8.00	8.20	8.07	1.00	8.05	Std Err of Y Est	1.08 Chamber Area = 1800.40 cm ²
SINDAI87-S3	10.80	#3	16.00	10.80	16.00	10.80	10.34	2.00	10.02	R Squared	0.74
SINDAI87-S4	10.40	#4	24.00	10.40	24.00	10.40	10.01	3.00	10.99	No. of Observations	5.00 Flux rate = 740 ug/m ² /day
SINDAI87-S5	13.30	#5	32.00	13.30	32.00	13.30	12.79	4.00	11.87	Degrees of Freedom	3.00
SINDAI87-S6	13.30	#6	40.00	13.30	40.00	13.30		5.00	12.84		80% CI (low) = 322 ug/m ² /day
SINDAI87-S1	353.00	SED		353.00						X Coefficient(s)	0.12 (high) = 1158 ug/m ² /day
										Std Err of Coef.	0.04
Mercury											
SINDAI87-T0	<0.2	T0		<0.2		<0.2			no	Regression Output:	
SINDAI87-S1	<0.2	#1	0.00	<0.2	0.00	<0.2	0.00	0.00	0.00	Constant	n/a Chamber Volume = 40.65 Bars
SINDAI87-S2	<0.2	#2	8.00	<0.2	8.00	<0.2	0.00	1.00	0.00	Std Err of Y Est	n/a Chamber Area = 1800.40 cm ²
SINDAI87-S3	<0.2	#3	16.00	<0.2	16.00	<0.2	0.00	2.00	0.00	R Squared	n/a
SINDAI87-S4	<0.2	#4	24.00	<0.2	24.00	<0.2	0.00	3.00	0.00	No. of Observations	n/a Flux rate = 0 ug/m ² /day
SINDAI87-S5	<0.2	#5	32.00	<0.2	32.00	<0.2	0.00	4.00	0.00	Degrees of Freedom	n/a
SINDAI87-S6	<0.2	#6	40.00	<0.2	40.00	<0.2	0.00	5.00	0.00		80% CI (low) = 0 ug/m ² /day
SINDAI87-S1	1.83	SED		1.83						X Coefficient(s)	n/a (high) = 0 ug/m ² /day
										Std Err of Coef.	n/a
Arsenic											
SINDAI87-T0	1.80	T0		1.80		1.80			yes	Regression Output:	
SINDAI87-S1	1.00	#1	0.00	1.00	0.00	1.00	1.00	0.00	0.92	Constant	0.92 Chamber Volume = 40.65 Bars
SINDAI87-S2	1.00	#2	8.00	1.00	8.00	1.00	0.98	1.00	1.22	Std Err of Y Est	0.25 Chamber Area = 1800.40 cm ²
SINDAI87-S3	1.80	#3	16.00	1.80	16.00	1.80	1.75	2.00	1.51	R Squared	0.77
SINDAI87-S4	1.80	#4	24.00	1.80	24.00	1.80	1.73	3.00	1.81	No. of Observations	4.00 Flux rate = 225 ug/m ² /day
SINDAI87-S5	1.20	#5	32.00	1.20	32.00	1.20		4.00	2.10	Degrees of Freedom	2.00
SINDAI87-S6	2.20	#6	40.00	2.20	40.00	2.20		5.00	2.40		80% CI (low) = 83 ug/m ² /day
SINDAI87-S1	3.44	SED		3.44						X Coefficient(s)	0.04 (high) = 368 ug/m ² /day
										Std Err of Coef.	0.01

Sindair Inlet Contaminant Release Rate Study

Site 38
Date: 7/21-7/23/81

Start time: 14:00:00 7/21/81
Interval: 08:00:00
End time: 07:15:00 7/23/81

GPS lat: 47 33.28 N
long: 122 38.74 W

Loc lat: 47 33.28 N
long: 122 38.76 W
Depth: 18.5 m

lab data		GFSD data		outlier correct		dil. correction		from reg		Regressors		Flux rates	
sample id	[Conc] (ppb)	sample	elapsed time	[Conc] (ppb)	elapsed time	[Conc] (ppb)	[Conc] (ppb)	# of dilutions	[Conc] (ppb)				
Copper													
SIN08202-T01	4.20	T0		4.20		4.20			yes	Regression Output:			
SIN08202-S1	2.70	#1	0.00	2.70	0.00	2.70	2.70	0.00	2.74	Constant	2.74	Chamber Volume =	40.85 Bars
SIN08202-S2	2.50	#2	8.00	2.50	8.00	2.50	2.44	1.00	2.22	Std Err of Y Est	0.29	Chamber Area =	1800.40 cm ²
SIN08202-S3	1.50	#3	16.00	1.50	16.00	1.50	1.38	2.00	1.71	R Squared	0.88		
SIN08202-S4	1.50	#4	24.00	1.50	24.00	1.50	1.33	3.00	1.18	No. of Observations	4.00	Flux rate =	-394 ug/m ² /day
SIN08202-S5	2.10	#5	32.00	2.10	32.00	2.10		4.00	0.87	Degrees of Freedom	2.00		
SIN08202-S6	1.80	#6	40.00	1.80	40.00	1.80		5.00	0.16	X Coefficient(s)	-0.0548	80% CI (low) =	-682 ug/m ² /day
SIN08202-S1	127.00	SED		127.00						Std Err of Coef.	0.0164	(high) =	-305 ug/m ² /day
Cadmium													
SIN08202-T01	0.15	T0		0.15		0.15			yes	Regression Output:			
SIN08202-S1	0.08	#1	0.00	0.08	0.00	0.08	0.08	0.00	0.08	Constant	0.08	Chamber Volume =	40.85 Bars
SIN08202-S2	0.04	#2	8.00	0.04	8.00	0.04	0.04	1.00	0.08	Std Err of Y Est	0.02	Chamber Area =	1800.40 cm ²
SIN08202-S3	0.04	#3	16.00	0.04	16.00	0.04	0.04	2.00	0.05	R Squared	0.28		
SIN08202-S4	0.08	#4	24.00	0.08	24.00	0.08	0.05	3.00	0.04	No. of Observations	4.00	Flux rate =	-6 ug/m ² /day
SIN08202-S5	0.03	#5	32.00	0.03	32.00	0.03		4.00	0.03	Degrees of Freedom	2.00		
SIN08202-S6	0.03	#6	40.00	0.03	40.00	0.03		5.00	0.02	X Coefficient(s)	-0.0010	80% CI (low) =	-20 ug/m ² /day
SIN08202-S1	0.43	SED		0.43						Std Err of Coef.	0.0012	(high) =	8 ug/m ² /day
Chromium VI													
SIN08202-T01	<0.2	T0		<0.2		<0.2			no	Regression Output:			
SIN08202-S1	<0.2	#1	0.00	<0.2	0.00	<0.2	0.00	0.00	0.00	Constant	n/a	Chamber Volume =	40.85 Bars
SIN08202-S2	<0.2	#2	8.00	<0.2	8.00	<0.2	0.00	1.00	0.00	Std Err of Y Est	n/a	Chamber Area =	1800.40 cm ²
SIN08202-S3	<0.2	#3	16.00	<0.2	16.00	<0.2	0.00	2.00	0.00	R Squared	n/a		
SIN08202-S4	<0.2	#4	24.00	<0.2	24.00	<0.2	0.00	3.00	0.00	No. of Observations	n/a	Flux rate =	0 ug/m ² /day
SIN08202-S5	<0.2	#5	32.00	<0.2	32.00	<0.2	0.00	4.00	0.00	Degrees of Freedom	n/a		
SIN08202-S6	<0.2	#6	40.00	<0.2	40.00	<0.2	0.00	5.00	0.00	X Coefficient(s)	n/a	80% CI (low) =	0 ug/m ² /day
SIN08202-S1	67.80	SED		67.80						Std Err of Coef.	n/a	(high) =	0 ug/m ² /day
Lead													
SIN08202-T01	0.13	T0		0.13		0.13			yes	Regression Output:			
SIN08202-S1	0.18	#1	0.00	0.18	0.00	0.18	0.18	0.00	0.19	Constant	0.19	Chamber Volume =	40.85 Bars
SIN08202-S2	0.18	#2	8.00	0.18	8.00	0.18	0.18	1.00	0.17	Std Err of Y Est	0.01	Chamber Area =	1800.40 cm ²
SIN08202-S3	0.18	#3	16.00	0.18	16.00	0.18	0.18	2.00	0.15	R Squared	0.81		
SIN08202-S4	0.14	#4	24.00	0.14	24.00	0.14	0.13	3.00	0.14	No. of Observations	4.00	Flux rate =	-12 ug/m ² /day
SIN08202-S5	0.10	#5	32.00	0.10	32.00	0.10		4.00	0.12	Degrees of Freedom	2.00		
SIN08202-S6	0.07	#6	40.00	0.07	40.00	0.07		5.00	0.11	X Coefficient(s)	-0.0020	80% CI (low) =	-17 ug/m ² /day
SIN08202-S1	75.80	SED		75.80						Std Err of Coef.	0.0004	(high) =	-7 ug/m ² /day
Nickel													
SIN08202-T01	4.00	T0		4.00		4.00			yes	Regression Output:			
SIN08202-S1	0.88	#1	0.00	0.88	0.00	0.88	0.88	0.00	0.84	Constant	0.84	Chamber Volume =	40.85 Bars
SIN08202-S2	1.18	#2	8.00	1.18	8.00	1.18	1.14	1.00	1.15	Std Err of Y Est	0.02	Chamber Area =	1800.40 cm ²
SIN08202-S3	1.58	#3	16.00	1.58	16.00	1.58	1.45	2.00	1.47	R Squared	1.00		
SIN08202-S4	1.88	#4	24.00	1.88	24.00	1.88	1.80	3.00	1.78	No. of Observations	4.00	Flux rate =	238 ug/m ² /day
SIN08202-S5	2.03	#5	32.00	2.03	32.00	2.03		4.00	2.09	Degrees of Freedom	2.00		
SIN08202-S6	2.04	#6	40.00	2.04	40.00	2.04		5.00	2.41	X Coefficient(s)	0.0381	80% CI (low) =	222 ug/m ² /day
SIN08202-S1	98.80	SED		98.80						Std Err of Coef.	0.0014	(high) =	254 ug/m ² /day
Zinc													
SIN08202-T01	5.80	T0		5.80		5.80			yes	Regression Output:			
SIN08202-S1	4.10	#1	0.00	4.10	0.00	4.10	4.10	0.00	4.20	Constant	4.20	Chamber Volume =	40.85 Bars
SIN08202-S2	4.70	#2	8.00	4.70	8.00	4.70	4.62	1.00	4.37	Std Err of Y Est	0.24	Chamber Area =	1800.40 cm ²
SIN08202-S3	4.50	#3	16.00	4.50	16.00	4.50	4.35	2.00	4.55	R Squared	0.57		
SIN08202-S4	5.00	#4	24.00	5.00	24.00	5.00	4.77	3.00	4.72	No. of Observations	4.00	Flux rate =	133 ug/m ² /day
SIN08202-S5	4.30	#5	32.00	4.30	32.00	4.30		4.00	4.80	Degrees of Freedom	2.00		
SIN08202-S6	4.00	#6	40.00	4.00	40.00	4.00		5.00	5.07	X Coefficient(s)	0.0218	80% CI (low) =	-21 ug/m ² /day
SIN08202-S1	128.00	SED		128.00						Std Err of Coef.	0.0134	(high) =	287 ug/m ² /day
Mercury													
SIN08202-T01	<0.2	T0		<0.2		<0.2			no	Regression Output:			
SIN08202-S1	<0.2	#1	0.00	<0.2	0.00	<0.2	0.00	0.00	0.00	Constant	n/a	Chamber Volume =	40.85 Bars
SIN08202-S2	<0.2	#2	8.00	<0.2	8.00	<0.2	0.00	1.00	0.00	Std Err of Y Est	n/a	Chamber Area =	1800.40 cm ²
SIN08202-S3	<0.2	#3	16.00	<0.2	16.00	<0.2	0.00	2.00	0.00	R Squared	n/a		
SIN08202-S4	<0.2	#4	24.00	<0.2	24.00	<0.2	0.00	3.00	0.00	No. of Observations	n/a	Flux rate =	0 ug/m ² /day
SIN08202-S5	<0.2	#5	32.00	<0.2	32.00	<0.2	0.00	4.00	0.00	Degrees of Freedom	n/a		
SIN08202-S6	<0.2	#6	40.00	<0.2	40.00	<0.2	0.00	5.00	0.00	X Coefficient(s)	n/a	80% CI (low) =	0 ug/m ² /day
SIN08202-S1	1.44	SED		1.44						Std Err of Coef.	n/a	(high) =	0 ug/m ² /day
Arsenic													
SIN08202-T01	1.70	T0		1.70		1.70			yes	Regression Output:			
SIN08202-S1	1.80	#1	0.00	1.80	0.00	1.80	1.80	0.00	1.88	Constant	1.88	Chamber Volume =	40.85 Bars
SIN08202-S2	2.00	#2	8.00	2.00	8.00	2.00	1.86	1.00	1.84	Std Err of Y Est	0.15	Chamber Area =	1800.40 cm ²
SIN08202-S3	2.20	#3	16.00	2.20	16.00	2.20	2.15	2.00	1.89	R Squared	0.25		
SIN08202-S4	2.00	#4	24.00	2.00	24.00	2.00	1.83	3.00	2.05	No. of Observations	4.00	Flux rate =	43 ug/m ² /day
SIN08202-S5	1.50	#5	32.00	1.50	32.00	1.50		4.00	2.11	Degrees of Freedom	2.00		
SIN08202-S6	3.20	#6	40.00	3.20	40.00	3.20		5.00	2.18	X Coefficient(s)	0.0071	80% CI (low) =	-56 ug/m ² /day
SIN08202-S1	21.20	SED		21.20						Std Err of Coef.	0.0087	(high) =	143 ug/m ² /day

Sindair Inlet Contaminant Release Rate Study

Site 4A
Date: 7/3-7/5/91

Start time 12:45:00 7/3/91
Interval 08:00:00
End time: 08:45:00 7/5/91

GPS lat: 47.3320 N
long 122.3811 W

Loc lat: 47.3319 N
long 122.3803 W
Depth: 14.4 m

lab data	BFSO data		outlier correct	dil. correction		from sig	Regressions		Flux rates		
sample id	[Conc] (ppb)	sample	elapsed time	[Conc] (ppb)	elapsed time	[Conc] (ppb)	[Conc] (ppb)	# of dilutions	[Conc] (ppb)		
Copper									yes	Regression Output	
SNIA184-T0	3.30	T0		3.30		3.30				Constant	2.22
SNIA184-S1	2.40	F1		2.40	0.00	2.40	2.40	0.00	2.22	Std Err of Y Est	0.28
SNIA184-S2	2.30	F2	8.00	2.30	8.00	2.30	2.26	1.00	2.32	R Squared	0.42
SNIA184-S3	—	F3	16.00	—	16.00	—	—	2.00	2.41	No. of Observations	5.00
SNIA184-S4	2.40	F4	24.00	2.40	24.00	2.40	2.27	3.00	2.50	Degrees of Freedom	3.00
SNIA184-S5	2.80	F5	32.00	2.80	32.00	2.80	2.42	4.00	2.58		
SNIA184-S6	3.20	F6	40.00	3.20	40.00	3.20	2.88	5.00	2.88	X Coefficient(s)	0.0116
SNIA184-S1	235.00	SED		235.00						Std Err of Coef.	0.0078
											80% CI (low) = -8 ug/m ² /day (high) = 148 ug/m ² /day
Cadmium									no	Regression Output	
SNIA184-T0	<0.05	T0		<0.05		<0.05				Constant	n/a
SNIA184-S1	<0.05	F1	0.00	<0.05	0.00	<0.05	0.00	0.00	0.00	Std Err of Y Est	n/a
SNIA184-S2	<0.05	F2	8.00	<0.05	8.00	<0.05	0.00	1.00	0.00	R Squared	n/a
SNIA184-S3	0.04	F3	16.00	0.04	16.00	0.04	0.04	2.00	0.00	No. of Observations	n/a
SNIA184-S4	<0.05	F4	24.00	<0.05	24.00	<0.05	0.00	3.00	0.00	Degrees of Freedom	n/a
SNIA184-S5	<0.05	F5	32.00	<0.05	32.00	<0.05	0.00	4.00	0.00		
SNIA184-S6	<0.05	F6	40.00	<0.05	40.00	<0.05	0.00	5.00	0.00	X Coefficient(s)	n/a
SNIA184-S1	1.12	SED		1.12						Std Err of Coef.	n/a
											80% CI (low) = 0 ug/m ² /day (high) = 0 ug/m ² /day
Chromium VI									no	Regression Output	
SNIA184-T0	<0.2	T0		<0.2		<0.2				Constant	n/a
SNIA184-S1	<0.2	F1	0.00	<0.2	0.00	<0.2	0.00	0.00	0.00	Std Err of Y Est	n/a
SNIA184-S2	<0.2	F2	8.00	<0.2	8.00	<0.2	0.00	1.00	0.00	R Squared	n/a
SNIA184-S3	<0.2	F3	16.00	<0.2	16.00	<0.2	0.00	2.00	0.00	No. of Observations	n/a
SNIA184-S4	<0.2	F4	24.00	<0.2	24.00	<0.2	0.00	3.00	0.00	Degrees of Freedom	n/a
SNIA184-S5	<0.2	F5	32.00	<0.2	32.00	<0.2	0.00	4.00	0.00		
SNIA184-S6	<0.2	F6	40.00	<0.2	40.00	<0.2	0.00	5.00	0.00	X Coefficient(s)	n/a
SNIA184-S1	77.80	SED		77.80						Std Err of Coef.	n/a
											80% CI (low) = 0 ug/m ² /day (high) = 0 ug/m ² /day
Lead									no	Regression Output	
SNIA184-T0	1.00	T0		1.00		1.00				Constant	n/a
SNIA184-S1	0.21	F1	0.00	0.21	0.00	0.21	0.21	0.00	0.00	Std Err of Y Est	n/a
SNIA184-S2	<0.09	F2	8.00	<0.09	8.00	<0.09	0.00	1.00	0.00	R Squared	n/a
SNIA184-S3	—	F3	16.00	—	16.00	—	—	2.00	0.00	No. of Observations	n/a
SNIA184-S4	<0.09	F4	24.00	<0.09	24.00	<0.09	0.00	3.00	0.00	Degrees of Freedom	n/a
SNIA184-S5	<0.09	F5	32.00	<0.09	32.00	<0.09	0.00	4.00	0.00		
SNIA184-S6	0.15	F6	40.00	0.15	40.00	0.15	0.08	5.00	0.00	X Coefficient(s)	n/a
SNIA184-S1	278.00	SED		278.00						Std Err of Coef.	n/a
											80% CI (low) = 0 ug/m ² /day (high) = 0 ug/m ² /day
Nickel									yes	Regression Output	
SNIA184-T0	0.56	T0		0.56		0.56				Constant	0.84
SNIA184-S1	1.24	F1	0.00	1.24	0.00	1.24	1.24	0.00	0.84	Std Err of Y Est	0.27
SNIA184-S2	0.56	F2	8.00	0.56	8.00	0.56	0.55	1.00	0.80	R Squared	0.12
SNIA184-S3	—	F3	16.00	—	16.00	—	—	2.00	0.88	No. of Observations	5.00
SNIA184-S4	0.78	F4	24.00	0.78	24.00	0.78	0.74	3.00	0.82	Degrees of Freedom	3.00
SNIA184-S5	0.85	F5	32.00	0.85	32.00	0.85	0.82	4.00	0.77		
SNIA184-S6	0.85	F6	40.00	0.85	40.00	0.85	0.81	5.00	0.73	X Coefficient(s)	-0.0052
SNIA184-S1	85.20	SED		85.20						Std Err of Coef.	0.0082
											80% CI (low) = -114 ug/m ² /day (high) = 51 ug/m ² /day
Zinc									yes	Regression Output	
SNIA184-T0	7.20	T0		7.20		7.20				Constant	7.83
SNIA184-S1	6.80	F1	0.00	6.80	0.00	6.80	6.80	0.00	7.83	Std Err of Y Est	1.29
SNIA184-S2	8.80	F2	8.00	8.80	8.00	8.80	8.70	1.00	7.84	R Squared	0.25
SNIA184-S3	—	F3	16.00	—	16.00	—	—	2.00	8.26	No. of Observations	5.00
SNIA184-S4	8.00	F4	24.00	8.00	24.00	8.00	7.71	3.00	8.57	Degrees of Freedom	3.00
SNIA184-S5	8.10	F5	32.00	8.10	32.00	8.10	8.71	4.00	8.88		
SNIA184-S6	10.00	F6	40.00	10.00	40.00	10.00	8.51	5.00	8.20	X Coefficient(s)	0.0384
SNIA184-S1	688.00	SED		688.00						Std Err of Coef.	0.0380
											80% CI (low) = -148 ug/m ² /day (high) = 830 ug/m ² /day
Mercury									no	Regression Output	
SNIA184-T0	<0.2	T0		<0.2		<0.2				Constant	n/a
SNIA184-S1	<0.2	F1	0.00	<0.2	0.00	<0.2	0.00	0.00	0.00	Std Err of Y Est	n/a
SNIA184-S2	<0.2	F2	8.00	<0.2	8.00	<0.2	0.00	1.00	0.00	R Squared	n/a
SNIA184-S3	—	F3	16.00	—	16.00	—	—	2.00	0.00	No. of Observations	n/a
SNIA184-S4	<0.2	F4	24.00	<0.2	24.00	<0.2	0.00	3.00	0.00	Degrees of Freedom	n/a
SNIA184-S5	<0.2	F5	32.00	<0.2	32.00	<0.2	0.00	4.00	0.00		
SNIA184-S6	<0.2	F6	40.00	<0.2	40.00	<0.2	0.00	5.00	0.00	X Coefficient(s)	n/a
SNIA184-S1	0.80	SED		0.80						Std Err of Coef.	n/a
											80% CI (low) = 0 ug/m ² /day (high) = 0 ug/m ² /day
Arsenic									yes	Regression Output	
SNIA184-T0	0.70	T0		0.70		0.70				Constant	1.46
SNIA184-S1	1.70	F1	0.00	1.70	0.00	1.70	1.70	0.00	1.46	Std Err of Y Est	0.35
SNIA184-S2	1.30	F2	8.00	1.30	8.00	1.30	1.29	1.00	1.42	R Squared	0.07
SNIA184-S3	—	F3	16.00	—	16.00	—	—	2.00	1.38	No. of Observations	5.00
SNIA184-S4	1.20	F4	24.00	1.20	24.00	1.20	1.17	3.00	1.34	Degrees of Freedom	3.00
SNIA184-S5	1.00	F5	32.00	1.00	32.00	1.00	0.96	4.00	1.30		
SNIA184-S6	1.70	F6	40.00	1.70	40.00	1.70	1.85	5.00	1.26	X Coefficient(s)	-0.0051
SNIA184-S1	3.28	SED		3.28						Std Err of Coef.	0.0105
											80% CI (low) = -137 ug/m ² /day (high) = 75 ug/m ² /day

Sinclair Inlet Contaminant Release Rate Study

Site: 4B
Date: 7/6-7/8/91

Start time: 162000 7/6/91
Interval: 0800.00
End time: 082000 7/8/91

GPS lat: 47 32.08 N
long: 122 40.76 W

Loc lat: 47 32.08 N
long: 122 40.66 W
Depth: 6.7 m

lab data		BPBD data		outlier correct		dl. correction		from reg		Regression		Flux rates	
sample id	[Conc] (ppb)	sample	elapsed time	[Conc] (ppb)	elapsed time	[Conc] (ppb)	[Conc] (ppb)	# of dilutions	[Conc] (ppb)				
Copper													
SN48197-T0	3.80	T0		3.80		3.80			yes	Regression Output:			
SN48197-S1	2.85	#1	0.00	2.85	0.00	2.85	2.85	0.00	3.02	Constant	3.02	Chamber Volume =	40.65 ltr
SN48197-S2	2.87	#2	8.00	2.87	8.00	2.87	2.82	1.00	2.97	Std Err of Y Est	0.41	Chamber Area =	1800.40 cm ²
SN48197-S3	3.14	#3	16.00	3.14	16.00	3.14	3.04	2.00	2.83	R Squared	0.08		
SN48197-S4	3.42	#4	24.00	3.42	24.00	3.42	3.27	3.00	2.88	No. of Observations	8.00	Flux rate =	-36 ug/m ² /day
SN48197-S5	3.42	#5	32.00	3.42	32.00	3.42	3.21	4.00	2.88	Degrees of Freedom	4.00		
SN48197-S6	2.48	#6	40.00	2.48	40.00	2.48	2.23	5.00	2.78	X Coefficient(s)	-0.0080	80% CI (low) =	-150 ug/m ² /day
SN48197-S1	127.00	SED		127.00						Std Err of Coef.	0.0122	(high) =	76 ug/m ² /day
Cadmium													
SN48197-T0	0.27	T0		0.27		0.27			yes	Regression Output:			
SN48197-S1	0.31	#1	0.00	0.31	0.00	0.31	0.31	0.00	0.25	Constant	0.25	Chamber Volume =	40.65 ltr
SN48197-S2	0.22	#2	8.00	0.22	8.00	0.22	0.22	1.00	0.24	Std Err of Y Est	0.05	Chamber Area =	1800.40 cm ²
SN48197-S3	0.17	#3	16.00	0.17	16.00	0.17	0.16	2.00	0.22	R Squared	0.23		
SN48197-S4	0.20	#4	24.00	0.20	24.00	0.20	0.19	3.00	0.21	No. of Observations	6.00	Flux rate =	-1 ug/m ² /day
SN48197-S5	0.22	#5	32.00	0.22	32.00	0.22	0.21	4.00	0.20	Degrees of Freedom	4.00		
SN48197-S6	0.24	#6	40.00	0.24	40.00	0.24	0.22	5.00	0.18	X Coefficient(s)	-0.0016	80% CI (low) =	-23 ug/m ² /day
SN48197-S1	1.16	SED		1.16						Std Err of Coef.	0.0015	(high) =	4 ug/m ² /day
Chromium VI													
SN48197-T0	<0.2	T0		<0.2		<0.2			no	Regression Output:			
SN48197-S1	<0.2	#1	0.00	<0.2	0.00	<0.2	0.00	0.00	0.00	Constant	n/a	Chamber Volume =	40.65 ltr
SN48197-S2	<0.2	#2	8.00	<0.2	8.00	<0.2	0.00	1.00	0.00	Std Err of Y Est	n/a	Chamber Area =	1800.40 cm ²
SN48197-S3	<0.2	#3	16.00	<0.2	16.00	<0.2	0.00	2.00	0.00	R Squared	n/a		
SN48197-S4	<0.2	#4	24.00	<0.2	24.00	<0.2	0.00	3.00	0.00	No. of Observations	n/a	Flux rate =	0 ug/m ² /day
SN48197-S5	<0.2	#5	32.00	<0.2	32.00	<0.2	0.00	4.00	0.00	Degrees of Freedom	n/a		
SN48197-S6	<0.2	#6	40.00	<0.2	40.00	<0.2	0.00	5.00	0.00	X Coefficient(s)	n/a	80% CI (low) =	0 ug/m ² /day
SN48197-S1	70.50	SED		70.50						Std Err of Coef.	n/a	(high) =	0 ug/m ² /day
Lead													
SN48197-T0	0.11	T0		0.11		0.11			yes	Regression Output:			
SN48197-S1	0.08	#1	0.00	0.08	0.00	0.08	0.08	0.00	0.11	Constant	0.11	Chamber Volume =	40.65 ltr
SN48197-S2	0.15	#2	8.00	0.15	8.00	0.15	0.15	1.00	0.11	Std Err of Y Est	0.08	Chamber Area =	1800.40 cm ²
SN48197-S3	0.12	#3	16.00	0.12	16.00	0.12	0.12	2.00	0.12	R Squared	0.01		
SN48197-S4	0.08	#4	24.00	0.08	24.00	0.08	0.08	3.00	0.12	No. of Observations	8.00	Flux rate =	2 ug/m ² /day
SN48197-S5	0.21	#5	32.00	0.21	32.00	0.21	0.20	4.00	0.12	Degrees of Freedom	4.00		
SN48197-S6	0.08	#6	40.00	0.08	40.00	0.08	0.07	5.00	0.12	X Coefficient(s)	0.0003	80% CI (low) =	-14 ug/m ² /day
SN48197-S1	83.20	SED		83.20						Std Err of Coef.	0.0017	(high) =	18 ug/m ² /day
Nickel													
SN48197-T0	6.81	T0		6.81		6.81			yes	Regression Output:			
SN48197-S1	1.88	#1	0.00	1.88	0.00	1.88	1.88	0.00	1.74	Constant	1.74	Chamber Volume =	40.65 ltr
SN48197-S2	1.79	#2	8.00	1.79	8.00	1.79	1.70	1.00	2.15	Std Err of Y Est	0.88	Chamber Area =	1800.40 cm ²
SN48197-S3	2.16	#3	16.00	2.16	16.00	2.16	1.88	2.00	2.55	R Squared	0.48		
SN48197-S4	4.88	#4	24.00	4.88	24.00	4.88	4.41	3.00	2.85	No. of Observations	6.00	Flux rate =	308 ug/m ² /day
SN48197-S5	3.19	#5	32.00	3.19	32.00	3.19	2.83	4.00	3.38	Degrees of Freedom	4.00		
SN48197-S6	4.07	#6	40.00	4.07	40.00	4.07	3.82	5.00	3.78	X Coefficient(s)	0.0505	80% CI (low) =	86 ug/m ² /day
SN48197-S1	84.30	SED		84.30						Std Err of Coef.	0.0258	(high) =	548 ug/m ² /day
Zinc													
SN48197-T0	8.20	T0		8.20		8.20			yes	Regression Output:			
SN48197-S1	10.80	#1	0.00	10.80	0.00	10.80	10.80	0.00	10.39	Constant	10.39	Chamber Volume =	40.65 ltr
SN48197-S2	8.80	#2	8.00	8.80	8.00	8.80	8.78	1.00	10.95	Std Err of Y Est	0.80	Chamber Area =	1800.40 cm ²
SN48197-S3	11.80	#3	16.00	11.80	16.00	11.80	11.35	2.00	10.71	R Squared	0.24		
SN48197-S4	10.80	#4	24.00	10.80	24.00	10.80	10.53	3.00	10.87	No. of Observations	6.00	Flux rate =	123 ug/m ² /day
SN48197-S5	11.30	#5	32.00	11.30	32.00	11.30	10.80	4.00	11.03	Degrees of Freedom	4.00		
SN48197-S6	12.10	#6	40.00	12.10	40.00	12.10	11.48	5.00	11.18	X Coefficient(s)	0.0202	80% CI (low) =	-44 ug/m ² /day
SN48197-S1	111.00	SED		111.00						Std Err of Coef.	0.0178	(high) =	290 ug/m ² /day
Mercury													
SN48197-T0	<0.2	T0		<0.2		<0.2			no	Regression Output:			
SN48197-S1	<0.2	#1	0.00	<0.2	0.00	<0.2	0.00	0.00	0.00	Constant	n/a	Chamber Volume =	40.65 ltr
SN48197-S2	<0.2	#2	8.00	<0.2	8.00	<0.2	0.00	1.00	0.00	Std Err of Y Est	n/a	Chamber Area =	1800.40 cm ²
SN48197-S3	<0.2	#3	16.00	<0.2	16.00	<0.2	0.00	2.00	0.00	R Squared	n/a		
SN48197-S4	<0.2	#4	24.00	<0.2	24.00	<0.2	0.00	3.00	0.00	No. of Observations	n/a	Flux rate =	0 ug/m ² /day
SN48197-S5	<0.2	#5	32.00	<0.2	32.00	<0.2	0.00	4.00	0.00	Degrees of Freedom	n/a		
SN48197-S6	<0.2	#6	40.00	<0.2	40.00	<0.2	0.00	5.00	0.00	X Coefficient(s)	n/a	80% CI (low) =	0 ug/m ² /day
SN48197-S1	0.80	SED		0.80						Std Err of Coef.	n/a	(high) =	0 ug/m ² /day
Arsenic													
SN48197-T0	1.20	T0		1.20		1.20			yes	Regression Output:			
SN48197-S1	1.00	#1	0.00	1.00	0.00	1.00	1.00	0.00	0.78	Constant	0.78	Chamber Volume =	40.65 ltr
SN48197-S2	2.50	#2	8.00	2.50	8.00	2.50	2.50	1.00	0.89	Std Err of Y Est	0.25	Chamber Area =	1800.40 cm ²
SN48197-S3	1.00	#3	16.00	1.00	16.00	1.00	0.97	2.00	1.19	R Squared	0.78		
SN48197-S4	1.20	#4	24.00	1.20	24.00	1.20	1.15	3.00	1.39	No. of Observations	5.00	Flux rate =	152 ug/m ² /day
SN48197-S5	1.80	#5	32.00	1.80	32.00	1.80	1.74	4.00	1.59	Degrees of Freedom	3.00		
SN48197-S6	2.00	#6	40.00	2.00	40.00	2.00	1.92	5.00	1.79	X Coefficient(s)	0.0250	80% CI (low) =	71 ug/m ² /day
SN48197-S1	3.28	SED		3.28						Std Err of Coef.	0.0081	(high) =	234 ug/m ² /day

Sindair Inlet Contaminant Release Rate Study

Site: SA
Date: 6/30-7/2/01

Start time: 13:55:00 6/30/01
Interval: 08:00:00
End time: 07:55:00 7/2/01

GPS lat: 47 33.36 N
long: 122 38.96 W

Lor lat: 47 33.36 N
long: 122 38.85 W
Depth: 4.7 m

lab data	BFSO data				outlier correct		dil. correction		from reg	Regressions	Flux rates
sample id	[Conc] (ppb)	sample	elapsed time	[Conc] (ppb)	elapsed time	[Conc] (ppb)	[Conc] (ppb)	# of dilutions	[Conc] (ppb)		
Copper											
SPNSA101-T0	1.50	T0		1.50		1.50			yes	Regression Output:	
SPNSA101-S1	1.50	F1	0.00	1.50	0.00	1.50	1.50	0.00	2.05	Constant	2.05 Chamber Volume = 40.85 Bars
SPNSA101-S2	3.50	F2	8.00	3.50	8.00	3.50	3.48	1.00	2.16	Std Err of Y Est	1.38 Chamber Area = 1800.40 cm ²
SPNSA101-S3	2.80	F3	16.00	2.80	16.00	2.80	2.76	2.00	2.28	R Squared	0.00
SPNSA101-S4	1.10	F4	24.00	1.10	24.00	1.10	1.04	3.00	2.38	No. of Observations	6.00 Flux rate = 87 ug/m ² /day
SPNSA101-S5	1.30	F5	32.00	1.30	32.00	1.30	1.22	4.00	2.50	Degress of Freedom	4.00
SPNSA101-S6	4.10	F6	40.00	4.10	40.00	4.10	4.00	5.00	2.62	X Coefficient(s)	0.0142 80% CI (low) = 288 ug/m ² /day
SPNSA101-S1	257.00	SED		257.00						Std Err of Coef.	0.0413 (high) = 473 ug/m ² /day
Cadmium											
SPNSA101-T0	<0.05	T0		<0.05		<0.05			no	Regression Output:	
SPNSA101-S1	<0.05	F1	0.00	<0.05	0.00	<0.05		0.00	0.00	Constant	n/a Chamber Volume = 40.85 Bars
SPNSA101-S2	<0.05	F2	8.00	<0.05	8.00	<0.05		1.00	0.00	Std Err of Y Est	n/a Chamber Area = 1800.40 cm ²
SPNSA101-S3	<0.05	F3	16.00	<0.05	16.00	<0.05		2.00	0.00	R Squared	n/a
SPNSA101-S4	0.05	F4	24.00	0.05	24.00	0.05	0.05	3.00	0.00	No. of Observations	n/a Flux rate = 0 ug/m ² /day
SPNSA101-S5	<0.05	F5	32.00	<0.05	32.00	<0.05		4.00	0.00	Degress of Freedom	n/a
SPNSA101-S6	<0.05	F6	40.00	<0.05	40.00	<0.05		5.00	0.00	X Coefficient(s)	n/a 80% CI (low) = 0 ug/m ² /day
SPNSA101-S1	3.71	SED		3.71						Std Err of Coef.	n/a (high) = 0 ug/m ² /day
Chromium VI											
SPNSA101-T0	<0.2	T0		<0.2		<0.2			no	Regression Output:	
SPNSA101-S1	<0.2	F1	0.00	<0.2	0.00	<0.2	0.00	0.00	0.00	Constant	n/a Chamber Volume = 40.85 Bars
SPNSA101-S2	<0.2	F2	8.00	<0.2	8.00	<0.2	0.00	1.00	0.00	Std Err of Y Est	n/a Chamber Area = 1800.40 cm ²
SPNSA101-S3	<0.2	F3	16.00	<0.2	16.00	<0.2	0.00	2.00	0.00	R Squared	n/a
SPNSA101-S4	<0.2	F4	24.00	<0.2	24.00	<0.2	0.00	3.00	0.00	No. of Observations	n/a Flux rate = 0 ug/m ² /day
SPNSA101-S5	<0.2	F5	32.00	<0.2	32.00	<0.2	0.00	4.00	0.00	Degress of Freedom	n/a
SPNSA101-S6	<0.2	F6	40.00	<0.2	40.00	<0.2	0.00	5.00	0.00	X Coefficient(s)	n/a 80% CI (low) = 0 ug/m ² /day
SPNSA101-S1	80.70	SED		80.70						Std Err of Coef.	n/a (high) = 0 ug/m ² /day
Lead											
SPNSA101-T0	<0.10	T0		<0.10		<0.10			no	Regression Output:	
SPNSA101-S1	<0.10	F1	0.00	<0.10	0.00	<0.10		0.00	0.00	Constant	n/a Chamber Volume = 40.85 Bars
SPNSA101-S2	0.37	F2	8.00	0.37	8.00	0.37	0.37	1.00	0.00	Std Err of Y Est	n/a Chamber Area = 1800.40 cm ²
SPNSA101-S3	0.16	F3	16.00	0.16	16.00	0.16	0.16	2.00	0.00	R Squared	n/a
SPNSA101-S4	<0.10	F4	24.00	<0.10	24.00	<0.10		3.00	0.00	No. of Observations	n/a Flux rate = 0 ug/m ² /day
SPNSA101-S5	<0.10	F5	32.00	<0.10	32.00	<0.10		4.00	0.00	Degress of Freedom	n/a
SPNSA101-S6	<0.10	F6	40.00	<0.10	40.00	<0.10		5.00	0.00	X Coefficient(s)	n/a 80% CI (low) = 0 ug/m ² /day
SPNSA101-S1	382.00	SED		382.00						Std Err of Coef.	n/a (high) = 0 ug/m ² /day
Nickel											
SPNSA101-T0	7.48	T0		7.48		7.48			yes	Regression Output:	
SPNSA101-S1	2.10	F1	0.00	2.10	0.00	2.10	2.10	0.00	2.08	Constant	2.08 Chamber Volume = 40.85 Bars
SPNSA101-S2	2.78	F2	8.00	2.78	8.00	2.78	2.88	1.00	2.82	Std Err of Y Est	0.40 Chamber Area = 1800.40 cm ²
SPNSA101-S3	4.30	F3	16.00	4.30	16.00	4.30	4.10	2.00	3.55	R Squared	0.94
SPNSA101-S4	4.13	F4	24.00	4.13	24.00	4.13	3.83	3.00	4.30	No. of Observations	6.00 Flux rate = 585 ug/m ² /day
SPNSA101-S5	5.23	F5	32.00	5.23	32.00	5.23	4.82	4.00	5.04	Degress of Freedom	4.00
SPNSA101-S6	6.58	F6	40.00	6.58	40.00	6.58	6.05	5.00	5.78	X Coefficient(s)	0.0828 80% CI (low) = 452 ug/m ² /day
SPNSA101-S1	65.80	SED		65.80						Std Err of Coef.	0.0121 (high) = 676 ug/m ² /day
Zinc											
SPNSA101-T0	--	T0		--		--			yes	Regression Output:	
SPNSA101-S1	8.00	F1	0.00	8.00	0.00	8.00	8.00	0.00	8.84	Constant	8.84 Chamber Volume = 40.85 Bars
SPNSA101-S2	--	F2	8.00	--	8.00	--	--	1.00	10.74	Std Err of Y Est	1.88 Chamber Area = 1800.40 cm ²
SPNSA101-S3	11.80	F3	16.00	11.80	16.00	11.80	11.28	2.00	11.84	R Squared	0.98
SPNSA101-S4	15.40	F4	24.00	15.40	24.00	15.40	15.03	3.00	12.94	No. of Observations	5.00 Flux rate = 837 ug/m ² /day
SPNSA101-S5	15.30	F5	32.00	15.30	32.00	15.30	14.81	4.00	14.04	Degress of Freedom	3.00
SPNSA101-S6	14.10	F6	40.00	14.10	40.00	14.10	13.42	5.00	15.14	X Coefficient(s)	0.1373 80% CI (low) = 282 ug/m ² /day
SPNSA101-S1	816.00	SED		816.00						Std Err of Coef.	0.0545 (high) = 1382 ug/m ² /day
Mercury											
SPNSA101-T0	<0.2	T0		<0.2		<0.2			no	Regression Output:	
SPNSA101-S1	<0.2	F1	0.00	<0.2	0.00	<0.2	0.00	0.00	0.00	Constant	n/a Chamber Volume = 40.85 Bars
SPNSA101-S2	<0.2	F2	8.00	<0.2	8.00	<0.2	0.00	1.00	0.00	Std Err of Y Est	n/a Chamber Area = 1800.40 cm ²
SPNSA101-S3	<0.2	F3	16.00	<0.2	16.00	<0.2	0.00	2.00	0.00	R Squared	n/a
SPNSA101-S4	<0.2	F4	24.00	<0.2	24.00	<0.2	0.00	3.00	0.00	No. of Observations	n/a Flux rate = 0 ug/m ² /day
SPNSA101-S5	<0.2	F5	32.00	<0.2	32.00	<0.2	0.00	4.00	0.00	Degress of Freedom	n/a
SPNSA101-S6	<0.2	F6	40.00	<0.2	40.00	<0.2	0.00	5.00	0.00	X Coefficient(s)	n/a 80% CI (low) = 0 ug/m ² /day
SPNSA101-S1	2.71	SED		2.71						Std Err of Coef.	n/a (high) = 0 ug/m ² /day
Arsenic											
SPNSA101-T0	<0.7	T0		<0.7		<0.7			yes	Regression Output:	
SPNSA101-S1	7.80	F1	0.00	7.80	0.00	7.80		0.00	1.51	Constant	1.51 Chamber Volume = 40.85 Bars
SPNSA101-S2	1.30	F2	8.00	1.30	8.00	1.30	1.30	1.00	1.44	Std Err of Y Est	0.45 Chamber Area = 1800.40 cm ²
SPNSA101-S3	1.80	F3	16.00	1.80	16.00	1.80	1.80	2.00	1.37	R Squared	0.07
SPNSA101-S4	1.20	F4	24.00	1.20	24.00	1.20	1.20	3.00	1.30	No. of Observations	5.00 Flux rate = -53 ug/m ² /day
SPNSA101-S5	0.70	F5	32.00	0.70	32.00	0.70	0.70	4.00	1.23	Degress of Freedom	3.00
SPNSA101-S6	1.50	F6	40.00	1.50	40.00	1.50	1.50	5.00	1.16	X Coefficient(s)	-0.0087 80% CI (low) = -231 ug/m ² /day
SPNSA101-S1	2.70	SED		2.70						Std Err of Coef.	0.0178 (high) = 125 ug/m ² /day

Sinclair Inlet Contaminant Release Rate Study

Sta: SB
Date: 7/19-7/21/81

Start time: 12:45.00 7/19/81
Interval: 08:00:00
End time: 05:45.00 7/21/81

GPS lat: 47 33.45 N
long: 122 38.16 W

Loc lat: 47 33.43 N
long: 122 38.18 W
Depth: 17.1 m

lab data		BFSO data		outlier correct		dl. correction		from log		Regressions		Flux rates	
sample id	[Conc] (ppb)	sample	elapsed time	[Conc] (ppb)	elapsed time	[Conc] (ppb)	[Conc] (ppb)	# of dilutions	[Conc] (ppb)				
Copper													
SN8200-T01	3.80	T0		3.80		3.80				yes	Regression Output		
SN8200-S1	254.00	SED		254.00							Constant	3.24	Chamber Volume = 40.65 liters
SN8200-S1	254.00	SED		254.00							Std Err of Y Est	1.47	Chamber Area = 1800.40 cm ²
SN8200-S1	254.00	SED		254.00							R Squared	0.32	
SN8200-S1	254.00	SED		254.00							No. of Observations	4.00	Flux rate = 489 ug/m ² /day
SN8200-S1	254.00	SED		254.00							Degrees of Freedom	2.00	
SN8200-S1	254.00	SED		254.00							X Coefficient(s)	0.0802	80% CI (low) = -458 ug/m ² /day
SN8200-S1	254.00	SED		254.00							Std Err of Coef.	0.0824	(high) = 1438 ug/m ² /day
Cadmium													
SN8200-T01	0.53	T0		0.53		0.53				yes	Regression Output		
SN8200-S1	0.68	SED		0.68							Constant	0.35	Chamber Volume = 40.65 liters
SN8200-S1	0.68	SED		0.68							Std Err of Y Est	0.02	Chamber Area = 1800.40 cm ²
SN8200-S1	0.68	SED		0.68							R Squared	0.98	
SN8200-S1	0.68	SED		0.68							No. of Observations	4.00	Flux rate = 66 ug/m ² /day
SN8200-S1	0.68	SED		0.68							Degrees of Freedom	2.00	
SN8200-S1	0.68	SED		0.68							X Coefficient(s)	0.0111	80% CI (low) = 54 ug/m ² /day
SN8200-S1	0.68	SED		0.68							Std Err of Coef.	0.0012	(high) = 81 ug/m ² /day
Chromium VI													
SN8200-T01	<0.2	T0		<0.2		<0.2				no	Regression Output		
SN8200-S1	73.00	SED		73.00							Constant	n/a	Chamber Volume = 40.65 liters
SN8200-S1	73.00	SED		73.00							Std Err of Y Est	n/a	Chamber Area = 1800.40 cm ²
SN8200-S1	73.00	SED		73.00							R Squared	n/a	
SN8200-S1	73.00	SED		73.00							No. of Observations	n/a	Flux rate = 0 ug/m ² /day
SN8200-S1	73.00	SED		73.00							Degrees of Freedom	n/a	
SN8200-S1	73.00	SED		73.00							X Coefficient(s)	n/a	80% CI (low) = 0 ug/m ² /day
SN8200-S1	73.00	SED		73.00							Std Err of Coef.	n/a	(high) = 0 ug/m ² /day
Lead													
SN8200-T01	0.14	T0		0.14		0.14				yes	Regression Output		
SN8200-S1	168.00	SED		168.00							Constant	0.24	Chamber Volume = 40.65 liters
SN8200-S1	168.00	SED		168.00							Std Err of Y Est	0.08	Chamber Area = 1800.40 cm ²
SN8200-S1	168.00	SED		168.00							R Squared	0.24	
SN8200-S1	168.00	SED		168.00							No. of Observations	4.00	Flux rate = -22 ug/m ² /day
SN8200-S1	168.00	SED		168.00							Degrees of Freedom	2.00	
SN8200-S1	168.00	SED		168.00							X Coefficient(s)	-0.0038	80% CI (low) = -74 ug/m ² /day
SN8200-S1	168.00	SED		168.00							Std Err of Coef.	0.0045	(high) = 30 ug/m ² /day
Nickel													
SN8200-T01	8.30	T0		8.30		8.30				yes	Regression Output		
SN8200-S1	83.00	SED		83.00							Constant	1.34	Chamber Volume = 40.65 liters
SN8200-S1	83.00	SED		83.00							Std Err of Y Est	0.12	Chamber Area = 1800.40 cm ²
SN8200-S1	83.00	SED		83.00							R Squared	0.53	
SN8200-S1	83.00	SED		83.00							No. of Observations	4.00	Flux rate = 59 ug/m ² /day
SN8200-S1	83.00	SED		83.00							Degrees of Freedom	2.00	
SN8200-S1	83.00	SED		83.00							X Coefficient(s)	0.0067	80% CI (low) = -15 ug/m ² /day
SN8200-S1	83.00	SED		83.00							Std Err of Coef.	0.0065	(high) = 134 ug/m ² /day
Zinc													
SN8200-T01	8.30	T0		8.30		8.30				yes	Regression Output		
SN8200-S1	274.00	SED		274.00							Constant	5.00	Chamber Volume = 40.65 liters
SN8200-S1	274.00	SED		274.00							Std Err of Y Est	0.72	Chamber Area = 1800.40 cm ²
SN8200-S1	274.00	SED		274.00							R Squared	0.82	
SN8200-S1	274.00	SED		274.00							No. of Observations	4.00	Flux rate = 735 ug/m ² /day
SN8200-S1	274.00	SED		274.00							Degrees of Freedom	2.00	
SN8200-S1	274.00	SED		274.00							X Coefficient(s)	0.1205	80% CI (low) = 273 ug/m ² /day
SN8200-S1	274.00	SED		274.00							Std Err of Coef.	0.0402	(high) = 1197 ug/m ² /day
Mercury													
SN8200-T01	<0.2	T0		<0.2		<0.2				no	Regression Output		
SN8200-S1	0.78	SED		0.78							Constant	n/a	Chamber Volume = 40.65 liters
SN8200-S1	0.78	SED		0.78							Std Err of Y Est	n/a	Chamber Area = 1800.40 cm ²
SN8200-S1	0.78	SED		0.78							R Squared	n/a	
SN8200-S1	0.78	SED		0.78							No. of Observations	n/a	Flux rate = 0 ug/m ² /day
SN8200-S1	0.78	SED		0.78							Degrees of Freedom	n/a	
SN8200-S1	0.78	SED		0.78							X Coefficient(s)	n/a	80% CI (low) = 0 ug/m ² /day
SN8200-S1	0.78	SED		0.78							Std Err of Coef.	n/a	(high) = 0 ug/m ² /day
Arsenic													
SN8200-T01	1.50	T0		1.50		1.50				yes	Regression Output		
SN8200-S1	2.80	SED		2.80							Constant	1.44	Chamber Volume = 40.65 liters
SN8200-S1	2.80	SED		2.80							Std Err of Y Est	0.50	Chamber Area = 1800.40 cm ²
SN8200-S1	2.80	SED		2.80							R Squared	0.13	
SN8200-S1	2.80	SED		2.80							No. of Observations	4.00	Flux rate = 91 ug/m ² /day
SN8200-S1	2.80	SED		2.80							Degrees of Freedom	2.00	
SN8200-S1	2.80	SED		2.80							X Coefficient(s)	0.0150	80% CI (low) = -228 ug/m ² /day
SN8200-S1	2.80	SED		2.80							Std Err of Coef.	0.0277	(high) = 410 ug/m ² /day

Sinclair Inlet Contaminant Release Rate Study

Site: 38
Date: 7/10-7/21/01

Start time: 12:45:00 7/10/01
Interval: 05:00:00
End time: 05:45:00 7/21/01

GPS lat: 47 33.46 N
long: 122 38.16 W

Lat lat: 47 33.43 N
long: 122 38.19 W
Depth: 17.1 m

lab data		SPED data		outlet correct		dl. correction		trans reg	Regression	Flux rates	
sample id	[Conc] (Amol/m3)	sample	elapsed time	[Conc] (Amol/m3)	elapsed time	[Conc] (Amol/m3)	[Conc] (Amol/m3)	# of Observ	[Conc] (Amol/m3)		
1A								yes	Regression Output		
SP08200-T01	21.70	T0		21.70		21.70			Constant	29.80	Chamber Volume = 40.85 liters
SP08200-B1	22.10	F1	0.00	22.10	0.00	22.10	22.10	0.00	Std Err of Y Est	5.88	Chamber Area = 1600.40 cm ²
SP08200-B2	48.30	F2	8.00	48.30	8.00	48.30	48.01	1.00	R Squared	0.95	
SP08200-B3	59.80	F3	16.00	59.80	16.00	59.80	59.21	2.00	No. of Observations	6.00	Flux rate = 8288 umol/m ² /day
SP08200-B4	70.50	F4	24.00	70.50	24.00	70.50	69.82	3.00	Degrees of Freedom	4.00	
SP08200-B5	77.50	F5	32.00	77.50	32.00	77.50	76.33	4.00	X Coefficient(s)	1.5233	90% CI (low) = 8251 umol/m ² /day
SP08200-B6	88.80	F6	40.00	88.80	40.00	88.80	87.13	5.00	Std Err of Coef.	0.1898	90% CI (high) = 10321 umol/m ² /day
0.00	0.00	SED		0.00							
1B								yes	Regression Output		
SP08200-T01	29.30	T0		29.30		29.30			Constant	29.23	Chamber Volume = 40.85 liters
SP08200-B1	54.30	F1	0.00	54.30	0.00	54.30	54.30	1.00	Std Err of Y Est	5.05	Chamber Area = 1600.40 cm ²
SP08200-B2	81.10	F2	8.00	81.10	8.00	81.10	81.10	2.00	R Squared	1.00	
SP08200-B3	60.80	F3	16.00	60.80	16.00	60.80	60.80	3.00	No. of Observations	3.00	Flux rate = 16880 umol/m ² /day
SP08200-B4	33.70	F4	24.00	33.70	24.00	33.70	33.70	4.00	Degrees of Freedom	1.00	
SP08200-B5	61.30	F5	32.00	61.30	32.00	61.30	61.30	5.00	X Coefficient(s)	3.2250	90% CI (low) = 18008 umol/m ² /day
0.00	0.00	SED		0.00					Std Err of Coef.	0.0577	90% CI (high) = 20011 umol/m ² /day
2A								yes	Regression Output		
SP08200-T01	23.10	T0		23.10		23.10			Constant	33.82	Chamber Volume = 40.85 liters
SP08200-B1	25.80	F1	0.00	25.80	0.00	25.80	25.80	0.00	Std Err of Y Est	6.82	Chamber Area = 1600.40 cm ²
SP08200-B2	38.10	F2	8.00	38.10	8.00	38.10	35.78	1.00	R Squared	0.97	
SP08200-B3	78.40	F3	16.00	78.40	16.00	78.40	75.77	2.00	No. of Observations	6.00	Flux rate = 12775 umol/m ² /day
SP08200-B4	82.00	F4	24.00	82.00	24.00	82.00	81.08	3.00	Degrees of Freedom	4.00	
SP08200-B5	101.80	F5	32.00	101.80	32.00	101.80	100.25	4.00	X Coefficient(s)	2.0856	90% CI (low) = 11588 umol/m ² /day
SP08200-B6	118.80	F6	40.00	118.80	40.00	118.80	113.34	5.00	Std Err of Coef.	0.1870	90% CI (high) = 13881 umol/m ² /day
0.00	0.00	SED		0.00							
2B								yes	Regression Output		
SP08200-T01	22.00	T0		22.00		22.00			Constant	48.36	Chamber Volume = 40.85 liters
SP08200-B1	31.80	F1	0.00	31.80	0.00	31.80	31.80	0.00	Std Err of Y Est	10.78	Chamber Area = 1600.40 cm ²
SP08200-B2	91.80	F2	8.00	91.80	8.00	91.80	91.80	1.00	R Squared	0.97	
SP08200-B3	118.40	F3	16.00	118.40	16.00	118.40	117.80	2.00	No. of Observations	6.00	Flux rate = 24388 umol/m ² /day
SP08200-B4	144.70	F4	24.00	144.70	24.00	144.70	143.81	3.00	Degrees of Freedom	4.00	
SP08200-B5	172.20	F5	32.00	172.20	32.00	172.20	171.01	4.00	X Coefficient(s)	3.9874	90% CI (low) = 22404 umol/m ² /day
SP08200-B6	204.40	F6	40.00	204.40	40.00	204.40	202.91	5.00	Std Err of Coef.	0.3222	90% CI (high) = 28332 umol/m ² /day
0.00	0.00	SED		0.00							
3A								yes	Regression Output		
SP08200-T01	42.20	T0		42.20		42.20			Constant	20.51	Chamber Volume = 40.85 liters
SP08200-B1	18.30	F1	0.00	18.30	0.00	18.30	18.30	0.00	Std Err of Y Est	7.81	Chamber Area = 1600.40 cm ²
SP08200-B2	46.30	F2	8.00	46.30	8.00	46.30	45.83	1.00	R Squared	0.93	
SP08200-B3	30.80	F3	16.00	30.80	16.00	30.80	49.88	2.00	No. of Observations	4.00	Flux rate = 14088 umol/m ² /day
SP08200-B4	80.80	F4	24.00	80.80	24.00	80.80	78.89	3.00	Degrees of Freedom	2.00	
SP08200-B5	78.30	F5	32.00	78.30	32.00	78.30	77.22	4.00	X Coefficient(s)	2.3111	90% CI (low) = 11428 umol/m ² /day
SP08200-B6	72.30	F6	40.00	72.30	40.00	72.30	69.85	5.00	Std Err of Coef.	0.4383	90% CI (high) = 16746 umol/m ² /day
0.00	0.00	SED		0.00							
3B								yes	Regression Output		
SP08200-T01	41.00	T0		41.00		41.00			Constant	48.36	Chamber Volume = 40.85 liters
SP08200-B1	36.80	F1	0.00	36.80	0.00	36.80	36.80	0.00	Std Err of Y Est	8.81	Chamber Area = 1600.40 cm ²
SP08200-B2	71.40	F2	8.00	71.40	8.00	71.40	70.85	1.00	R Squared	0.91	
SP08200-B3	88.80	F3	16.00	88.80	16.00	88.80	88.80	2.00	No. of Observations	6.00	Flux rate = 11120 umol/m ² /day
SP08200-B4	88.70	F4	24.00	88.70	24.00	88.70	88.04	3.00	Degrees of Freedom	4.00	
SP08200-B5	107.50	F5	32.00	107.50	32.00	107.50	105.28	4.00	X Coefficient(s)	1.8242	90% CI (low) = 9371 umol/m ² /day
SP08200-B6	118.30	F6	40.00	118.30	40.00	118.30	116.53	5.00	Std Err of Coef.	0.2870	90% CI (high) = 12870 umol/m ² /day
0.00	0.00	SED		0.00							
4A								yes	Regression Output		
SP08200-T01	23.20	T0		23.20		23.20			Constant	16.80	Chamber Volume = 40.85 liters
SP08200-B1	18.70	F1	0.00	18.70	0.00	18.70	18.70	0.00	Std Err of Y Est	4.27	Chamber Area = 1600.40 cm ²
SP08200-B2	28.00	F2	8.00	28.00	8.00	28.00	25.89	1.00	R Squared	0.98	
SP08200-B3	48.10	F3	16.00	48.10	16.00	48.10	45.47	2.00	No. of Observations	4.00	Flux rate = 10734 umol/m ² /day
SP08200-B4	61.00	F4	24.00	61.00	24.00	61.00	60.08	3.00	Degrees of Freedom	2.00	
SP08200-B5	35.20	F5	32.00	35.20	32.00	35.20	33.84	4.00	X Coefficient(s)	1.7608	90% CI (low) = 9277 umol/m ² /day
SP08200-B6	63.40	F6	40.00	63.40	40.00	63.40	63.83	5.00	Std Err of Coef.	0.2388	90% CI (high) = 12190 umol/m ² /day
0.00	0.00	SED		0.00							
4B								yes	Regression Output		
SP08200-T01	40.20	T0		40.20		40.20			Constant	54.85	Chamber Volume = 40.85 liters
SP08200-B1	43.80	F1	0.00	43.80	0.00	43.80	43.80	0.00	Std Err of Y Est	8.43	Chamber Area = 1600.40 cm ²
SP08200-B2	88.80	F2	8.00	88.80	8.00	88.80	88.08	1.00	R Squared	0.98	
SP08200-B3	111.70	F3	16.00	111.70	16.00	111.70	110.61	2.00	No. of Observations	6.00	Flux rate = 19438 umol/m ² /day
SP08200-B4	136.80	F4	24.00	136.80	24.00	136.80	135.27	3.00	Degrees of Freedom	4.00	
SP08200-B5	161.30	F5	32.00	161.30	32.00	161.30	159.32	4.00	X Coefficient(s)	3.1888	90% CI (low) = 17903 umol/m ² /day
SP08200-B6	177.40	F6	40.00	177.40	40.00	177.40	174.88	5.00	Std Err of Coef.	0.2320	90% CI (high) = 20075 umol/m ² /day
0.00	0.00	SED		0.00							
5A								yes	Regression Output		
SP08200-T01	16.80	T0		16.80		16.80			Constant	21.49	Chamber Volume = 40.85 liters
SP08200-B1	20.80	F1	0.00	20.80	0.00	20.80	20.80	0.00	Std Err of Y Est	5.41	Chamber Area = 1600.40 cm ²
SP08200-B2	37.00	F2	8.00	37.00	8.00	37.00	36.46	1.00	R Squared	0.98	
SP08200-B3	42.30	F3	16.00	42.30	16.00	42.30	41.41	2.00	No. of Observations	6.00	Flux rate = 8252 umol/m ² /day
SP08200-B4	63.30	F4	24.00	63.30	24.00	63.30	63.67	3.00	Degrees of Freedom	4.00	
SP08200-B5	65.40	F5	32.00	65.40	32.00	65.40	63.22	4.00	X Coefficient(s)	1.3177	90% CI (low) = 6288 umol/m ² /day
SP08200-B6	88.10	F6	40.00	88.10	40.00	88.10	85.38	5.00	Std Err of Coef.	0.1818	90% CI (high) = 10238 umol/m ² /day
0.00	0.00	SED		0.00							
5B								yes	Regression Output		
SP08200-T01	33.10	T0		33.10		33.10			Constant	31.88	Chamber Volume = 40.85 liters
SP08200-B1	31.30	F1	0.00	31.30	0.00	31.30	31.30	0.00	Std Err of Y Est	2.09	Chamber Area = 1600.40 cm ²
SP08200-B2	32.50	F2	8.00	32.50	8.00	32.50	31.86	1.00	R Squared	0.98	
SP08200-B3	67.30	F3	16.00	67.30	16.00	67.30	66.21	2.00	No. of Observations	4.00	Flux rate = 13858 umol/m ² /day
SP08200-B4	89.00	F4	24.00	89.00	24.00	89.00	87.37	3.00	Degrees of Freedom	2.00	
SP08200-B5	78.70	F5	32.00	78.70	32.00	78.70	78.32	4.00	X Coefficient(s)	2.2733	90% CI (low) = 13147 umol/m ² /day
SP08200-B6	65.80	F6	40.00	65.80	40.00	65.80	62.88	5.00	Std Err of Coef.	0.1168	90% CI (high) = 14589 umol/m ² /day
0.00	0.00	SED		0.00							

Appendix 2. Analytical Procedures

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ANALYTICAL METHODS FOR TRACE METALS

SAMPLE STORAGE

Sea Water

Water samples to be analyzed for dissolved metals are initially filtered through a 0.45 um nitrocellulose membrane filter in disposable polystyrene filter units. Before use the filter units are cleaned with 4 N nitric acid followed by copious rinsing with 18 mega-ohm deionized water until the rinses are pH neutral.

The samples are then transferred to precleaned I-Chem polyethylene bottles and acidified with an amount of high purity (Ultrex) nitric acid equivalent to 0.2% of the sample volume. This brings the pH level down to below 2. The filtered and acidified samples are stored in a refrigerator at 4 degrees C until they are removed for analysis.

Sediments

Short term sediment sample storage is in the same precleaned I-Chem polyethylene jars used for field collection. The samples are stored refrigerated at 4 degrees C. For storage beyond 30 days, the samples are frozen.

WATER ANALYSIS

APDC Chelation - MIBK Extraction for Cd, Cu, Cr(VI), Pb, Ni, and Zn

Matrix separation and analyte preconcentration is achieved by chelation with ammonium pyrrolidine dithiocarbamate (APDC) followed by metal chelate extraction with methyl isobutyl ketone (MIBK). The extent of preconcentration is determined by the ratio of sample to MIBK. Any amount of sample not exceeding a ratio of 30:1 may be used.

Generally, 40 ml of sample is pipetted into a stoppered graduated cylinder. To this is added 250 ul of sodium citrate - citric acid buffer along with 1.0 ml of 1% APDC in 18 mega-ohm water. The buffer is added to maintain a pH level between 3 and 4. The sample is then extracted with 2.0 ml of MIBK. All work is performed within a class 100 laminar flow clean hood. The sample extract is analyzed by graphite furnace atomic absorption spectroscopy (GFAA).

A calibration curve is generated by spiking a series of replicates (prior to extraction) from one or more samples per batch with small volumes of successively increasing concentrations of a mixed standard. The response curve to

these standard additions is then used to determine analyte concentrations in other samples within the batch.

Arsenic

Arsenic analysis is performed by direct injection of sea water into the Zeeman corrected GFAA spectrometer. To isolate the atomic absorption signal from light scattering background interferences, five ul of each of the following matrix modifiers are employed: 0.3% Pd(NO₃)₂ in 2% Ultrex nitric acid, 1% Mg(NO₃)₂, and 50% NH₄NO₃.

Mercury

Mercury analysis is by cold-vapor atomic absorption. Sn(II)Cl₂ in 10% HCL is used as the reducing agent. Sample solutions are stabilized by addition of one drop of % KMnO₄. Note that the samples are not digested prior to analysis.

SEDIMENT ANALYSIS

Acid digestion for total metals

Sediment samples are first dried then digested in nitric acid by heating with microwave energy. 0.5 grams of each of the dried samples is weighed into an acid cleaned Teflon lined digestion vessel. To this is added 10.0 ml of 50% Ultrex nitric acid. The vessel is sealed and again weighed. The sample is then subjected to microwave heating sufficient to maintain an internal pressure of 165 psi within the reaction vessel for approximately one hour.

After the digestion process, the sample vessels are again weighed to ensure that no material was lost during heating. The samples are then diluted to a volume of 40 mls and transferred to precleaned polyethylene bottles for refrigerated storage at 4 degrees C.

Digested sediment analysis for As, Cd, Cr, Cu, Ni, Pb, and Zn

The digested sediment samples are analyzed by Zeeman background corrected GFAA. 0.3% Pd(NO₃)₂ and 1% Mg(NO₃)₂ were employed as matrix modifiers. Certified standard solutions are used to create calibration curves.

Digested sample analysis for Hg

Sediment digestates are diluted 50% with ultrapure water then analyzed for mercury by cold-vapor AA. The method is essentially the same as that for water samples.

DETERMINATION OF REACTIVE SILICATE

To determine reactive silicate, refer to the following handbook: "Determination of Reactive Silicate" In: *A Practical Handbook of Seawater Analysis*, Bulletin 167, pp. 65-70. 1968. Fisheries Research Board of Canada, Ottawa.

Acid volatile sulfide determination in sediments using sulfide-specific electrode detection

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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 a 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^{2-} 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

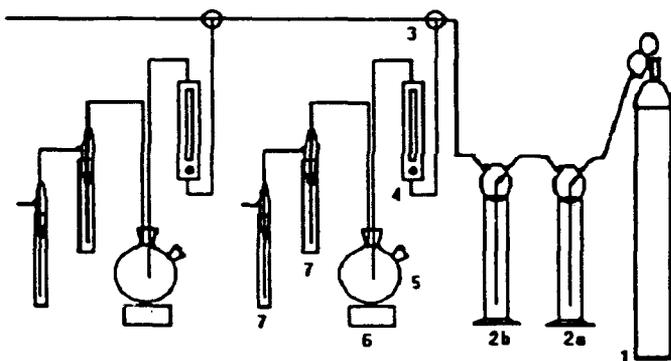


Figure 1. Apparatus for AVS determination: 1. N_2 cylinder; 2. Gas washing bottles: (a) oxygen scrubbing solution, (b) deionized water; 3. Three-way stopcock; 4. Purge flow controller; 5. Reaction flask; 6. Magnetic stirrer; 7. Sulfide traps.

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 Delaware (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 the 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_5^{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:

$$\begin{aligned} \text{AVS}(\mu\text{mol/g dry sediment}) &= \frac{(C_{S^{2-}}) \times V_{\text{vap}}}{\text{g wet sediment} \times R} \\ &= \frac{0.1 \times C_{S^{2-}}}{\text{g wet sediment} \times R} \end{aligned}$$

when $C_{S^{2-}} = \mu\text{mole liter}^{-1}$ (μM) and $V_{\text{vap}} = 100 \text{ ml}$.

D. Calibration of sulfide-specific electrode

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 \uparrow and \downarrow 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 must be 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. $1500 \mu\text{M}$). 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		Calibration Standard	
Volume	Volume	Concentration	
ml	ml	uM	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 (NH₄VO₃) 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 $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ of sufficient concentration may be used as 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 $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ with deionized water and blot dry.
- b. Weigh approximately 12 g of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ 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:

$$\text{Sulfide } (\mu\text{mol/ml}) = \frac{(T_{\text{blank}} - T_{\text{sample}}) \times N_{\text{S}_2\text{O}_3^{2-}}}{V_{\text{sample}}} \times \frac{1 \text{ mole S}^{2-}}{2 \text{ equiv S}^{2-}} \times \frac{1000 \mu\text{moles}}{1 \text{ mmole}}$$

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

N = concentration of $\text{S}_2\text{O}_3^{2-}$ 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 $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ 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:

$$N(\text{S}_2\text{O}_3^{2-}) = \frac{\text{g K}_2\text{CrO}_7}{\text{ml S}_2\text{O}_3^{2-}} \times \frac{1 \text{ mole K}_2\text{CrO}_7}{294.19 \text{ g K}_2\text{CrO}_7} \times \frac{6 \text{ equiv K}_2\text{CrO}_7}{1 \text{ mole K}_2\text{CrO}_7} \times \frac{1000 \text{ ml}}{1 \text{ l}}$$

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) Rabin, 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 3. QA/QC Protocol

**Benthic Flux Sampling Device
Bremerton Survey**

Shipping Custody Sheet

Date Shipped:

Date Recieved:

Released by:

Recieved by:

Sample #	description	date collected

ANALYTICAL QUALITY ASSURANCE

Method Blanks

Throughout the analyses, method blanks are employed as a means of verifying contamination free preparation and reagents. Each batch of extracted and digested samples is accompanied by a blank which is analyzed in parallel with the rest of the samples being carried through the entire preparation and analysis procedure.

Instrument calibration

Instruments are calibrated at the start of each analytical batch. With water samples and extracted water samples, the method of standard additions is used to generate each calibration curve. Successive dilution of a standard is used to generate standard curves for the analysis of the digestates. Initial calibration is verified by subsequent measurement of an independently prepared standard. The calibration is confirmed at regular intervals during an analytical run.

Accuracy

Standard reference sediments are digested and analyzed periodically as a check on general method accuracy. Additionally, spiked replicates of field samples are processed with each analytical batch in order to validate method accuracy within the context of varying matrices.

With water and extracted water samples, which are analyzed by the method of standard additions, spiked samples are not used.

Precision

Analytical precision and method detection limits are determined by replicate storage, preparation, and analysis of standard sea water. Further verification of precision is achieved by splitting one in twenty field samples. The limited volume available from each field sample restricts the number of split duplicates available to analyze.

19 DEC. 91

MEMORANDUM FOR BART
FROM JOHN ANDREWS

SUBJECT: PRECISION OF BREMERTON SEA WATER SAMPLE ANALYSIS

The following precision data is based upon three replicate analyses of a single sample. The sample was split so that each replicate was independently filtered, acidified, stored, extracted, and analyzed. The 90% confidence interval is based upon a two sided T-test with 2 (3-1) degrees of freedom. I feel that these numbers are conservative in that analyzing a larger number replicates would yield a narrower confidence interval.

	<u>Relative</u> <u>Standard Deviation</u>	<u>90% Confidence</u> <u>Interval</u>
Cu	21%	+/- 61%
Cd	10%	+/- 29%
Ni	5.7%	+/- 17%
Pb	3.7%	+/- 11%
Zn	9.4%	+/- 27%

Cr(VI) and Hg precision data not available as sample concentrations were below the method detection limits.

As precision was not tested.

Call me with questions or if you decide that you need to have tighter confidence limits.

Appendix 4. PAH/PCB Report

Appendix 4. PAH and PCB Data for July 1991 Sinclair Inlet Survey

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The PAH and PCB data obtained from the July 1991 survey of Sinclair Inlet are listed in Tables 4-1 through 4-11. Therein follows a summary of associated QA/QC data and related tables and figures.

Table 4-1. Positions (GPS latitude and longitude) of NOSC stations sampled for sediment and/or overlying water in Puget Sound - Sinclair Inlet, July 1991.

<u>NOSC STATION</u>	<u>LATITUDE (N)</u>		<u>LONGITUDE (W)</u>	
	<u>Degrees</u>	<u>Minutes</u>	<u>Degrees</u>	<u>Minutes</u>
1A	47	33.47	122	36.04
1B	47	33.64	122	37.48
2A	47	33.56	122	37.67
2B	47	33.43	122	38.94
3A	47	33.26	122	39.32
3B	47	33.29	122	38.74
4A	47	33.20	122	39.11
4B	47	32.08	122	40.76
5A	47	33.38	122	38.96
5B	47	33.46	122	38.16

Table 4-2. Concentrations¹ of Aroclor 1254², p,p'-DDE³, and PAHs (ug/kg dry wt.) in surficial sediments collected⁴ from Station 3B in Sinclair Inlet of Puget Sound, July 1991. Values for percent water and percent TOC also are listed.

NOSC STA. #	3B-T0	3B-T40	Ave.	S.E.	T0+T40
EPA RIBBS #	013	006			
GC/MS BF #	310	297			
Percent Water	57.9	61.9	59.9	2.0	-
Percent TOC	2.19	2.59	2.39	0.20	-
Aroclor 1254	214	100 ¹	157 ¹	57	2.1
p,p'-DDE	3 ¹	-	3 ¹	-	-
naphthalene	33 ¹	42 ¹	38 ¹	5	0.8
2-methylnaphthalene	29	31	30	1	0.9
1-methylnaphthalene	19	19	19	0	1.0
biphenyl	7	6	6	1	1.2
2,6-dimethylnaphthalene	37	68	52	16	0.5
2,3,5-trimethylnaphthalene	10	14	12	2	0.7
acenaphthylene	62	44	53	9	1.4
acenaphthene	19	11	15	4	1.7
fluorene	34	22	28	6	1.5
phenanthrene	253	123	188	65	2.1
anthracene	125	91	108	17	1.4
1-methylphenanthrene	43	20	32	12	2.2
dimethylphenanthrene	-	-	-	-	-
fluoranthene	858	453	656	203	1.9
pyrene	1160	561	860	300	2.1
benzo[a]anthracene	360	244	302	58	1.5
chrysene	630	416	523	107	1.5
benzo[b]fluoranthene	397	362	380	18	1.1
benzo[k]fluoranthene	596	423	510	87	1.4
benzo[e]pyrene	433	303	368	65	1.4
benzo[a]pyrene	420	300	360	60	1.4
perylene	94	76	85	9	1.2
indeno[1,2,3-cd]pyrene	331	264	298	34	1.3
dibenz[ah]anthracene	50 ¹	59	54 ¹	5	0.8
benzo[ghi]perylene	291	207	249	42	1.4
				AVE:	1.4
				SE:	0.1

¹Footnoted values lack GC/MS second-ion confirmation; all values are "blank-corrected" (no blanks detected).

²Estimated from PCB congener IUPAC number 110.

³No detectable p,p'-DDT or p,p'-DDD.

⁴Separate grab samples collected upon deployment (T0) and retrieval (T40) of the Benthic Flux Sampling Device.

Table 4-3. Concentrations¹ of Aroclor 1254², DDT residues, and PAHs (ug/kg dry wt.) in surficial sediments from Sinclair Inlet of Puget Sound, July 1991.

NOSC STA. #	1A	1B	2A	2B	3A	3B-T0/40 ³	4A	4B	5A	5B
EPA RIBBS #	001	011	002	012	003	013/006	004	014	005	015
GC/MS BF #	266	302	274	305	277	310/297	413	316	286	330
Percent Water	24.5	24.7	39.7	66.3	75.0	59.9	69.7	71.5	55.2	54.7
Percent TOC	0.25	1.34	1.60	3.68	3.04	2.39	4.05	5.46	5.05	2.37
Aroclor 1254	-	-	89	144	211	157 ¹	749	66 ¹	450	965
p,p'-DDE	-	-	-	-	-	3 ¹	-	-	-	3
p,p'-DDD	-	-	7	-	-	-	-	-	16	-
naphthalene	38 ¹	20 ¹	27	149	234	38 ¹	148	38 ¹	73	46
2-methylnaphthalene	32	12	13	111	116	30	123	44	83	35
1-methylnaphthalene	19	8	10	56	65	19	78	25	34	29
biphenyl	2 ¹	4	4	25	20	6	21	6	18	11
2,6-dimethylnaphthalene	6	15	26	107	120	52	85	153	123	117
2,3,5-trimethylnaphthalene	-	11	6	22	34	12	-	8	15	11
acenaphthylene	-	15	28	128	72	53	57	20	135	41
acenaphthene	4	21	10	80	53	15	34	10	33	19
fluorene	3	11	19	97	57	43	43	11	142	28
phenanthrene	8	72	80	757	209	188	346	71	463	183
anthracene	4 ¹	53	71	240	114	108	184	37	511	100
1-methylphenanthrene	-	20	15	62	37	32	73	44	71	34
dimethylphenanthrene	-	-	-	-	-	-	-	-	-	-
fluoranthene	2 ¹	482	160	1570	575	656	1040	242	1340	554
pyrene	26	442	220	1520	750	860	1330	321	1580	760
benzo[a]anthracene	16	175	136	596	413	302	669	86	966	228
chrysene	17	219	280	1120	588	523	1010	120	2620	420
benzo[b]fluoranthene	18	154	195	812	489	380	1010	117	1010	259
benzo[k]fluoranthene	12	185	192	875	572	510	733	162	1110	379
benzo[e]pyrene	14 ¹	115	164	615	483	368	687	113	870	274
benzo[a]pyrene	18	145	179	620	527	360	775	80	960	267
perylene	5 ¹	43	38	157	143	85	239	50	273	113
indeno[1,2,3-cd]pyrene	15 ¹	116	152	518	516	298	617	125	731	225
dibenz[ah]anthracene	-	23 ¹	41	122	131	54 ¹	146	23	194	34
benzo[ghi]perylene	15 ¹	97	123	423	403	249	539	150	509	176

¹Footnoted values lack GC/MS second-ion confirmation; all values are "blank-corrected" (no blanks detected).

²Estimated from PCB congener number 110.

³Average for grab samples collected upon deployment (T0) and retrieval (T40) of the Benthic Flux Sampling Device.

Table 4-4. Values for the concentrations¹ of Aroclor 1254 (ug/kg dry wt.) in Sinclair Inlet surficial sediments (July 1991) obtained from six major specific PCB congener components of the Aroclor 1254 mixture. Values for percent water and percent TOC also are listed.

NOSC STA. #	1A	1B	2A	2B	3A	3B-TO/40	4A	4B	5A	5B
EPA RIBBS #	001	011	002	012	003	013/006	004	014	005	015
GC/MS BF #	266	302	274	305	277	310/297	413	316	286	330
Percent Water	24.5	24.7	39.7	66.3	75.0	59.9	69.7	71.5	55.2	54.7
Percent TOC	0.25	1.34	1.60	3.68	3.04	2.39	4.05	5.46	5.05	2.37
PCB-095	6.02	-	84	166	170	137 ¹	470	45 ¹	422	794
101	7.94	-	103	198	225	156 ¹	854	97 ¹	626	1140
099	3.60	-	124	264	267 ¹	189 ¹	763	-	503	1190
110	5.85	-	89	144	211	157 ¹	749	66 ¹	450	965
118	6.39	-	90	166	182	126 ¹	916	77 ¹	477	1160
105	3.83	-	98 ¹	248	312 ¹	142 ¹	1190	-	555	1260
Median	-	-	94	182	218	149	808	72	490	1150
110/Median	-	-	0.95	0.79	0.97	1.05	0.93	0.92	0.92	0.84

¹Footnoted values lack GC/MS second-ion confirmation.

²From Schulz, D. E., G. Petrick, and J. C. Duinker. 1989. Complete characterization of polychlorinated biphenyl congeners in commercial Aroclor and Clophen mixtures by multidimensional gas chromatography-electron capture detection. *Environ. Sci. Technol.* 23(7): 852-859.

Table 4-5. Concentrations¹ of specific PCB congeners (ug/kg dry wt.) in surficial sediments from Sinclair Inlet of Puget Sound, July 1991. Values were obtained from Aroclor 1254 standardization and percent congener values reported by Schulz et al. (1989).

NOSC STA. #	1A	1B	2A	2B	3A	3B-TO/40	4A	4B	5A	5B
EPA RIBBS #	001	011	002	012	003	013/006	004	014	005	015
GC/MS BF #	266	302	274	305	277	310/297	413	316	286	330
PCB - 018	0.41	-	-	-	-	-	-	-	-	-
028 + 031	0.47	-	-	-	-	-	-	-	-	-
052	5.18	-	-	-	-	4.9 ¹	19.0 ¹	-	10.9	28.0
049	1.64	-	-	-	9.3 ¹	7.4 ¹	20.8 ¹	-	12.2	11.3 ¹
044	2.03	-	-	-	-	2.8 ¹	17.1 ¹	-	5.5	10.9
074	0.78	-	-	1.5 ¹	-	-	11.7 ¹	-	5.0 ¹	6.3 ¹
070 + 076	3.21	-	-	-	-	3.8 ¹	33.9	3.0 ¹	11.8	20.7
066	0.59	-	-	-	-	1.8 ¹	15.7 ¹	2.0 ¹	5.0 ¹	4.3 ¹
095	6.02	-	5.0	10.0 ¹	10.2	8.2 ¹	28.2	2.7 ¹	25.3	47.6
101	7.94	-	8.1	15.6 ¹	17.8	12.4 ¹	67.5	7.7 ¹	49.5	90.1
099	3.60	-	4.5	9.5 ¹	9.6 ¹	6.8 ¹	27.5	-	18.1	42.8
110	5.85	-	5.3	8.5	12.4	9.2 ¹	44.2	3.9 ¹	26.6	57.0
118	6.39	-	5.8	10.6 ¹	11.6	8.0 ¹	58.6	4.9 ¹	30.5	74.2
105	3.83	-	3.7 ¹	9.4 ¹	11.9 ¹	5.4 ¹	45.2	-	21.1	47.9
136	1.12	-	3.1 ¹	4.8 ¹	6.0 ¹	5.8 ¹	14.2	-	15.0	12.5
149	2.21	-	4.0	6.9 ¹	14.2	9.2	29.7	5.4 ¹	37.4	28.8
132 + 153	6.24	3.3 ¹	12.9	25.3	55.6	33.7	110	22.1	154	110
141	1.04	-	2.6 ¹	-	6.6 ¹	3.6 ¹	16.3 ¹	-	14.8	9.5
138	3.20	-	5.9	9.9	18.6	13.2	37.1	7.3	49.9	52.2
176	0.32	-	3.8	7.8	13.5	6.8 ¹	-	-	29.9	10.1
183	0.17	-	-	-	8.0 ¹	4.6	-	-	15.7	4.9
174	0.34	-	-	-	10.2	4.6 ¹	11.9	-	22.6	5.9
180	0.38	-	2.6	4.0	9.8	5.6	14.9	2.5	32.8	9.7
170 + 190	0.39	-	-	-	9.8 ¹	5.0 ¹	-	1.7 ¹	22.9	5.1

¹Footnoted values lack GC/MS second-ion confirmation.

Table 4-6. Concentrations (ng/liter) of Aroclor 1254¹ and PAHs in seawater procedural blank samples from Puget Sound Sinclair Inlet survey, July 1991.

ID # GC/MS BF #	QAB1 227	QAB2 238	Ave. ± S.E.
Aroclor 1254	0.1 ¹	0.5 ¹	0.3 ¹ ± 0.2
naphthalene	2.2	2.3	2.2 ± 0.1
2-methylnaphthalene	1.4	1.7	1.6 ± 0.2
1-methylnaphthalene	0.9	0.9	0.9 ± 0.0
biphenyl	0.4	0.4	0.4 ± 0.0
2,6-dimethylnaphthalene	0.8	0.8	0.8 ± 0.0
2,3,5-trimethylnaphthalene	0.4	0.3	0.4 ± 0.1
acenaphthylene	-	-	-
acenaphthene	0.3 ¹	0.7 ¹	0.5 ¹ ± 0.2
fluorene	0.3	0.2	0.2 ± 0.1
phenanthrene	0.5	0.3	0.4 ± 0.1
anthracene	0.06	0.03 ¹	0.0 ¹
1-methylphenanthrene	-	-	-
dimethylphenanthrene	-	-	-
fluoranthene	0.1	0.07	0.1 ± 0.0
pyrene	0.06 ¹	0.05	0.1 ¹ ± 0.0
benzo[a]anthracene	-	-	-
chrysene	0.05 ¹	-	0.0 ¹
benzo[b]fluoranthene	-	-	-
benzo[k]fluoranthene	-	-	-
benzo[e]pyrene	-	-	-
benzo[a]pyrene	-	-	-
perylene	-	-	-
indeno[1,2,3-cd]pyrene	-	-	-
dibenz[ah]anthracene	-	-	-
benzo[ghi]perylene	-	-	-

¹Estimated from PCB congener number 110.

Table 4-7. Concentrations¹ of Aroclor 1254² and PAHs (ng/liter) in T0 pumped seawater samples from Sinclair Inlet: Puget Sound Naval Shipyard NOSC Station 5B (19 July 1991).

ID #	R1	R2	R3	Median	Ave.	± S.E.
EPA R1BBO #	001	002	003			
GC/MS BF #	209	210	211			
Aroclor 1254	0.0 ¹	0.3 ¹	0.1 ¹	0.1 ¹	0.1 ¹	± 0.1
naphthalene	2.9	3.6	5.8	3.6	4.1	± 0.9
2-methylnaphthalene	1.8	1.9	3.8	1.9	2.5	± 0.7
1-methylnaphthalene	1.4	1.5	2.5	1.5	1.8	± 0.4
biphenyl	0.4	0.3	0.5	0.4	0.4	± 0.1
2,6-dimethylnaphthalene	1.6	1.4	2.5	1.6	1.8	± 0.3
2,3,5-trimethylnaphthalene	0.9	1.3	2.0	1.3	1.4	± 0.3
acenaphthylene	0.3	0.4	0.6	0.4	0.4	± 0.1
acenaphthene	2.5	2.1	3.6	2.5	2.7	± 0.4
fluorene	1.6	1.6	2.5	1.6	1.9	± 0.3
phenanthrene	2.7	1.9	3.5	2.7	2.7	± 0.5
anthracene	0.4	0.4	0.6	0.4	0.5	± 0.1
1-methylphenanthrene	0.6	0.6	0.9	0.6	0.7	± 0.1
dimethylphenanthrene	-	0.3	-	0.3	0.3	
fluoranthene	5.0	4.3	7.2	5.0	5.5	± 0.9
pyrene	2.5	2.2	3.9	2.5	2.9	± 0.5
benzo[a]anthracene	0.4 ¹	0.4	0.6 ¹	0.4 ¹	0.5 ¹	± 0.1
chrysene	0.6	0.6	0.9	0.6	0.7	± 0.1
benzo[b]fluoranthene	0.5	0.6	0.7 ¹	0.6	0.6 ¹	± 0.1
benzo[k]fluoranthene	0.4	0.4 ¹	0.4 ¹	0.4 ¹	0.4 ¹	± 0.0
benzo[e]pyrene	0.4 ¹	0.5	0.6 ¹	0.5 ¹	0.5 ¹	± 0.1
benzo[a]pyrene	0.2 ¹	0.3 ¹	0.3 ¹	0.3 ¹	0.3 ¹	± 0.0
perylene	0.1 ¹	± 0.0				
indeno[1,2,3-cd]pyrene	0.2 ¹	0.3 ¹	0.3 ¹	0.3 ¹	0.3 ¹	± 0.0
dibenz[ah]anthracene	-	-	-	-	-	
benzo[ghi]perylene	0.2	0.3	0.3	0.3	0.3	± 0.0

¹Footnoted values lack GC/MS second-ion confirmation; all values corrected for average blank.

²Estimated from PCB congener number 110.

Table 4-8. Concentrations¹ of TOC (mg/liter), and Aroclor 1254² and PAHs (ng/liter) in T40 pumped seawater samples from Sinclair Inlet: Puget Sound Naval Shipyard NOSC Station 5B (21 July 1991).

ID #	R1	R2	R3	Median	Ave. ± S.E.
EPA R1BBO #	010	011	012		
GC/MS BF #	220	221	242		
TOC	0.98	0.81	0.80	0.81	0.86 ± 0.06
Aroclor 1254	0.3 ¹	0.2 ¹	0.4 ¹	0.3 ¹	0.3 ¹ ± 0.1
naphthalene	5.8	4.7	5.7	5.7	5.4 ± 0.4
2-methylnaphthalene	4.3	5.1	3.9	4.3	4.4 ± 0.4
1-methylnaphthalene	2.8	3.4	2.8	2.8	3.0 ± 0.2
biphenyl	0.9	0.7	0.6	0.7	0.7 ± 0.1
2,6-dimethylnaphthalene	2.7	2.7	2.6	2.7	2.7 ± 0.0
2,3,5-trimethylnaphthalene	1.2	1.1	1.0	1.1	1.1 ± 0.1
acenaphthylene	0.4	0.4	0.3	0.4	0.4 ± 0.0
acenaphthene	3.5	3.2	3.6	3.5	3.4 ± 0.1
fluorene	2.2	2.2	2.2	2.2	2.2 ± 0.0
phenanthrene	3.5	2.8	3.7	3.5	3.3 ± 0.3
anthracene	0.6	0.6	0.7	0.6	0.6 ± 0.0
1-methylphenanthrene	0.8	0.5	0.8	0.8	0.7 ± 0.1
dimethylphenanthrene	0.3	-	0.4 ¹	0.3	0.4 ± 0.0
fluoranthene	6.0	5.8	6.4	6.0	6.1 ± 0.2
pyrene	3.5	3.7	3.8	3.7	3.7 ± 0.1
benzo[a]anthracene	0.6	0.6	0.5	0.6	0.6 ± 0.0
chrysene	0.9	0.9	0.6	0.9	0.8 ± 0.1
benzo[b]fluoranthene	0.6	0.6	0.6	0.6	0.6 ± 0.0
benzo[k]fluoranthene	0.3	0.4 ¹	0.4	0.4	0.4 ± 0.0
benzo[e]pyrene	0.5 ¹	0.5 ¹	0.4 ¹	0.5 ¹	0.5 ¹ ± 0.0
benzo[a]pyrene	0.2 ¹ ± 0.0				
perylene	0.1 ¹	0.2 ¹	0.1 ¹	0.1 ¹	0.1 ¹ ± 0.0
indeno[1,2,3-cd]pyrene	0.2 ¹	0.2 ¹	0.1 ¹	0.2 ¹	0.2 ¹ ± 0.0
dibenz[ah]anthracene	-	-	-	-	-
benzo[ghi]perylene	0.3 ¹	0.2 ¹	0.1 ¹	0.2 ¹	0.2 ¹ ± 0.1

¹Footnoted values lack GC/MS second-ion confirmation; all values corrected for average blank.

²Estimated from PCB congener number 110.

Table 4-9. Concentrations¹ of TOC (mg/liter), and Aroclor 1254² and PAHs (ng/liter) in TO pumped seawater samples from Sinclair Inlet: Puget Sound Naval Shipyard NOSC Station 3B (21 July 1991).

RIBBO #	023
GC/MS #	243
TOC	0.93
Aroclor 1254	0.6 ¹
naphthalene	11.3
2-methylnaphthalene	4.2
1-methylnaphthalene	3.3
biphenyl	1.0
2,6-dimethylnaphthalene	3.4
2,3,5-trimethylnaphthalene	1.5
acenaphthylene	0.5
acenaphthene	8.7
fluorene	4.2
phenanthrene	5.5
anthracene	1.4
1-methylphenanthrene	1.2
dimethylphenanthrene	0.4
fluoranthene	8.3
pyrene	6.3
benzo[a]anthracene	0.7
chrysene	1.0
benzo[b]fluoranthene	1.0
benzo[k]fluoranthene	0.7
benzo[e]pyrene	0.7
benzo[a]pyrene	0.3 ¹
perylene	0.1 ¹
indeno[1,2,3-cd]pyrene	0.2 ¹
dibenz[ah]anthracene	-
benzo[ghi]perylene	0.3 ¹

¹Footnoted values lack GC/MS second-ion confirmation; all values corrected for average blank.

²Estimated from PCB congener number 110.

Table 4-10. Concentrations¹ of TOC (mg/liter), and Aroclor 1254² and PAHs (ng/liter) in Benthic Flux Sampling Device seawater samples from Sinclair Inlet: Puget Sound Naval Shipyard NOSC Station 5B (19-21 July 1991).

ID	#	T0	T8	T16	T24	T32	T40
NOSC	#	B1	B2	B3	B4	B5	B6
EPA R1BBO	#	008	029	028	005	025	027
GC/MS BF	#	217	233	232	214	208	230
TOC		6.0	3.9	7.0	4.4	7.2	8.0
Aroclor 1254		0.2	0.2 ¹	0.1 ¹	0.2 ¹	0.1 ¹	0.4 ¹
naphthalene		2.1	2.1	1.2	1.7	4.4	4.0
2-methylnaphthalene		1.6	1.9	1.5	1.9	4.3	4.2
1-methylnaphthalene		1.2	1.0	1.2	1.5	2.4	2.9
biphenyl		0.2	0.3	0.4	0.7	1.1	0.9
2,6-dimethylnaphthalene		0.9	1.4	1.2	1.4	2.2	1.9
2,3,5-trimethylnaphthalene		0.5	0.7	0.7	0.8	1.1	0.5
acenaphthylene		0.4	0.4	0.4 ¹	0.4	0.4	0.4
acenaphthene		6.2	6.1	6.3	6.5	4.9	4.3
fluorene		3.1	3.6	3.3	3.2	2.7	2.3
phenanthrene		1.3	1.8	2.0	2.5	3.2	2.2
anthracene		0.7	0.6	0.7	0.8	0.8	0.5
1-methylphenanthrene		0.3	0.6	0.6	0.5	0.5	0.3
dimethylphenanthrene		0.3	0.6	0.9	1.3	1.2	0.7
fluoranthene		4.7	5.9	6.3	7.3	6.3	4.0
pyrene		3.2	4.1	4.6	5.5	4.5	2.8
benzo[a]anthracene		0.5	0.5	0.5	0.5	0.5	0.3
chrysene		0.5	0.7	0.7	0.8	0.6	0.4
benzo[b]fluoranthene		0.6	0.5	0.5	0.5	0.4	0.3 ¹
benzo[k]fluoranthene		0.3	0.4 ¹	0.3	0.4	0.3 ¹	0.2 ¹
benzo[e]pyrene		0.3 ¹	0.4 ¹	0.4 ¹	0.4	0.3 ¹	0.2 ¹
benzo[a]pyrene		0.2 ¹	0.1 ¹				
perylene		0.1 ¹	0.2 ¹	0.2 ¹	0.2 ¹	0.1 ¹	0.1 ¹
indeno[1,2,3-cd]pyrene		0.1	0.1 ¹	0.1 ¹	0.1 ¹	0.1 ¹	0.0 ¹
dibenz[ah]anthracene		-	-	-	-	-	-
benzo[ghi]perylene		0.1 ¹	0.2	0.2	0.1 ¹	0.1	0.1 ¹

¹Footnoted values lack GC/MS second-ion confirmation; all values corrected for average blank.

²Estimated from PCB congener number 110.

Table 4-11. Concentrations¹ of TOC (mg/liter), and Aroclor 1254² and PAHs (ng/liter) in Benthic Flux Sampling Device seawater samples from Sinclair Inlet: Puget Sound Naval Shipyard NOSC Station 3B (21-23 July 1991).

ID #	T0	T8	T16	T24	T32	T40
NOSC #	B1	B2	B3	B4	B5	B6
EPA R1BBO #	024	007	009	004	026	006
GC/MS BF #	244	216	218	207	229	215
TOC	7.3	8.0	7.4	10.4	8.0	10.9
Aroclor 1254	0.6 ¹	0.6 ¹	1.2 ¹	1.0 ¹	0.6 ¹	0.9 ¹
naphthalene	1.9	15.0	21.0	23.0	25.0	37.0
2-methylnaphthalene	1.4	14.0	21.0	22.0	24.0	35.0
1-methylnaphthalene	1.3	8.1	12.0	12.0	13.0	20.0
biphenyl	0.3	2.5	3.7	3.9	3.6	6.0
2,6-dimethylnaphthalene	1.1	5.0	6.7	7.4	6.5	11.2
2,3,5-trimethylnaphthalene	0.6	2.2	2.9	3.0	2.8	4.3
acenaphthylene	0.4	0.6	0.7	0.6	0.5	0.8 ¹
acenaphthene	5.8	11.1	15.0	18.0	21.0	26.0
fluorene	3.3	7.9	11.4	13.0	12.0	21.0
phenanthrene	4.2	9.4	13.0	16.0	14.0	16.0
anthracene	1.1	0.9	1.2	1.1	1.1	1.1
1-methylphenanthrene	0.9	1.6	1.4	1.2	1.1	1.3
dimethylphenanthrene	0.9	1.1	1.6	1.8	1.7	2.0
fluoranthene	11.5	8.1	11.0	12.0	10.0	12.0
pyrene	10.0	6.8	8.8	9.1	7.5	8.8
benzo[a]anthracene	1.3	0.9	1.4	1.4	1.2	1.9
chrysene	1.7	1.5	2.4	2.1	1.5	2.8
benzo[b]fluoranthene	1.8	1.3	2.7	2.4	1.4	3.4
benzo[k]fluoranthene	1.5 ¹	0.9	1.6	1.6	1.2	2.2
benzo[e]pyrene	1.6	1.1	2.3	2.1	1.4	2.7
benzo[a]pyrene	0.6 ¹	0.4 ¹	0.9 ¹	0.8	0.4 ¹	1.0 ¹
perylene	0.2 ¹	0.2 ¹	0.4 ¹	0.2	0.3	0.7 ¹
indeno[1,2,3-cd]pyrene	0.5	0.3 ¹	0.6 ¹	0.5	0.3 ¹	0.7 ¹
dibenz[ah]anthracene	0.2	0.1 ¹	-	0.3 ¹	0.2 ¹	0.4 ¹
benzo[ghi]perylene	0.7	0.3 ¹	0.6 ¹	0.5	0.3 ¹	0.7 ¹

¹Footnoted values lack GC/MS second-ion confirmation; all values corrected for average blank.

²Estimated from PCB congener number 110.

QUALITY ASSURANCE - QUALITY CONTROL

INTRODUCTION. Here we present information related to the reliability of the chemistry data listed above. Some of this information is in graphical form. In order to include as many of the target compounds as possible in the graphs, brief codes arbitrarily have been selected to represent these analytes (Table 4-12). An outline of the procedures used to identify and quantify the analytes in overlying water is presented in Table 4-13.

SAMPLING OF OVERLYING WATER. In this survey of Puget Sound's Sinclair Inlet, estuarine water overlying the bottom sediment outside the Benthic Flux Sampling Device (BFSD) was collected via a Teflon tubing - submerged pump Seawater Pumping System (SPS) developed by the Naval Ocean Systems Center (NOSC). The SPS was cleaned between stations by cycling detergent-containing water through the tube-pump system overnight, and flushed by pumping ambient water for a minimum of 5 minutes before sampling. As part of the development of this system, tests had been conducted in San Diego Harbor during the summer of 1990. Triplicate samples of subsurface water were collected from mid-Bay stations both by the SPS, and by divers who opened pre-cleaned sampling bottles at depth to collect the water and then tightly sealed them before surfacing. Mean and standard error (SE) values for blank-corrected water concentrations of a spectrum of the target PAH compounds are compared in Figure 4-1 (PCB concentrations were too low to provide a reliable assessment). This comparison indicates that the use of the SPS to collect subsurface water samples from active harbor areas does not significantly bias the resultant PAH concentrations.

SENSITIVITY OF GC/MS ANALYSIS OF OVERLYING WATER. The analytical capability of the Selected Ion Monitoring Gas Chromatography - Mass Spectrometry procedure developed by ERL-N/PEB for identifying and quantifying trace organic compounds in small-volume (0.5 liter) water samples is extremely sensitive. Figures 4-2 and 4-3 illustrate the strong signals obtained in overlying water from Benthic Flux Station 5B for 1-methylnaphthalene at about 2 parts-per-trillion (ng/L) in both the first or "quantification" ion, and the second or "confirmation" ion. Further, the ratios of these two signals agree with that obtained from corresponding standards within 4 percent, well within the +/- 20 percent agreement criterion established for second ion confirmation at this GC/MS laboratory. In contrast, Figure 4-4 illustrates the apparent signature of PCB congener number 110 at an equivalent Aroclor 1254 concentration of 0.7 ng/L in overlying water from Station 3B. Clearly, no second-ion confirmation was obtained (Figure 4-5). However, since PCB - 110 constitutes only about 6 percent of the Aroclor 1254 mixture, the peak illustrated in Figure 4-4 corresponds to a specific congener concentration of 0.04 ng/L. As no second-ion confirmation was obtained, this observation is accepted only as an upper limit value. Nevertheless, upper limit values for pollutants do constitute valuable information, especially when such values are below guidelines (here, EPA's Water Quality Criterion of 1 ng/L for PCB). If enough such results are

obtained for a given water body, concern over damage to that ecosystem component by the pollutant lessens. Thus, the analytical sensitivity demonstrated here is significant from the environmental management perspective. In addition, the ability to detect a possible concentration of an individual compound (congener no. 110) at 0.04 parts-per-trillion in a half-liter water sample provides for this laboratory an entree to a new arena of environmental research opportunities.

ACCURACY OF WATER PAH CONCENTRATIONS: A routine component of the laboratory's QA/QC program for water samples is the spiking of a relatively clean representative matrix (addition of standards at levels far above ambient concentrations). In this study, estuarine water pumped from Yaquina Bay, Oregon, into the flowing seawater system of the Hatfield Marine Science Center was selected, because previous studies had shown that the PAH levels were similar to the low (sub-part-per-trillion) procedural blank values typically obtained. Thus, uncertainties in the contribution of ambient PAH concentrations to those measured in the spiked water samples is negligible. Figure 4-6 illustrates the comparison of measured and spiked values for the spectrum of target PAH compounds. The median recovery efficiency is about 90 percent. It should be noted that the use of internal standards as part of the laboratory's GC/MS procedures automatically corrects for recovery efficiency, to the first order. The fact that recoveries are high indicates that uncertainties in this recovery correction step are relatively small.

ACCURACY OF SEDIMENT PCB AND PAH CONCENTRATIONS: Reference sediment (SRM 1941) containing known PCB and PAH concentrations (the latter class certified) was obtained from the National Institute for Science and Technology (NIST). Replicate analyses provided the comparison between values measured by this EPA laboratory and those reported by NIST, illustrated in Figure 4-7. In general, very good agreement was obtained, typically within about 15 percent.

ACCURACY AND PRECISION OF SEDIMENT TOC CONCENTRATIONS: The sediment Total Organic Carbon (TOC) values listed in this appendix have been corrected for a very small procedural blank value (n=2), which averaged 0.015 ± 0.001 (SE) percent (g TOC per 100 g sediment on a dry weight basis). In general this constituted a correction of less than one percent of a TOC gross value. Two TOC reference sediments also were analyzed. The mean (± 1 standard deviation) obtained for the first (Code BCSS-1) was 2.20 ± 0.09 percent vs. the reference value of 2.19 ± 0.09 percent. Corresponding values for the second reference sediment (Code PACS-1) were 3.61 ± 0.04 vs. 3.69 ± 0.11 percent.

PRECISION OF GC/MS INJECTION STEP: One area of uncertainty in GC/MS analysis is the precision of the sample solvent injection and compound measurement step. Therefore, periodically during a run, a sample is programmed to be injected three times to determine the relative standard deviation (%RSD) values for its target compounds.

The results obtained from this survey's sediment and overlying water samples are illustrated in Figures 4-8a and 4-8b. The median %RSD values is about 15 percent for each of these matrices.

PRECISION OF SEDIMENT PCB AND PAH ANALYSES: Replicate aliquots were taken from within one jar of surficial sediment collected from Site 1A; the resultant GC/MS analyses were used to calculate "Within Sample" %RSD values for Aroclor 1254 and the target PAH compounds. In addition, surficial sediment samples were collected at Benthic Flux Station 3B upon the deployment of the BFS, and again at its retrieval two days later. Thus, this sample set includes field variability between the slightly different locations (uncertainty in meters) of the vessel and sediment grab sampler for the two grab samples. Analyses of these two samples yielded "Between Grabs" %RSD values. Both types of %RSD values are illustrated in Figures 4-9a and 4-9b. These results show that, in this case, much higher variability was obtained within a single sediment sample jar than between separate jars of sediment collected two days apart. Median %RSD values for the two cases are approximately 80 and 25 percent, respectively. We speculate that this was caused by heterogeneity of the Within Sample sediment, possible owing to soot particles that were sampled disproportionately. However, the fact that the Within Sample aliquots were selected for the sediment sample from Site 1A, the site of lowest contamination, may have contributed to the relatively high variance observed for the sediment PAH concentrations there.

PRECISION OF OVERLYING WATER PCB AND PAH CONCENTRATIONS AND PROCEDURAL BLANKS: Triplicate samples of overlying water were collected at Benthic Flux Station 5B upon deployment of the BFS. Duplicate procedural blanks also were analyzed. Mean and one standard error (SE) values obtained for the target compounds from these analyses are summarized in Table 4-14. These results illustrate the high precision obtained even at these very low (generally sub-part-per-trillion) concentrations. The median SE value for the water samples is 0.1 ng/L; the corresponding value for the procedural blanks also is 0.1 ng/L.

PRECISION OF MEAN BENTHIC FLUX VALUES FOR PAH COMPOUNDS: The mean flux values obtained by Bart Chadwick of NOSC, from the Benthic Flux Station 3B BFS water concentrations measured by this laboratory, are illustrated in Figure 4-10. These results were obtained from linear regression of the time-series water concentrations, corrected for the secondary effect of dilution by outside water upon withdrawal of the 0.5 liter sample (using either Outside or T0 sample values). Corresponding "r-square" values, which represent the proportion of variance explained by the linear regression, also are shown. For the first eight PAH compounds (naphthalene through phenanthrene), measurable flux rates (i.e., greater than zero at the 80 percent confidence level) were obtained; corresponding r-squared values ranged from 0.77 to 0.99, with a median value of 0.84. This indicates that, for these lower molecular weight PAH compounds, a measurable flux from the

contaminated surficial sediments to the overlying water was observed, and that the linear regression model explains a relatively high proportion of the variance obtained in the time-series sample set.

PRECISION OF BFSB TIME-SERIES SAMPLE CONCENTRATIONS OF PCB:
Although the PCB values in the overlying water (Outside and BFSB) samples generally were too low to obtain second-ion confirmation, the set of blank-corrected concentrations (Table 4-15) does suggest that the level of Aroclor 1254 in the overlying water at Benthic Flux Stations 3B and 5B generally did not exceed 1 ng/L at the time of sampling during our Sinclair Inlet survey. This illustrates the utility of reporting near-detection-limit GC/MS values that lack second-ion confirmation (thus considered here to be upper limit concentrations). The standard error of the six time series values for each station is a few tenths of a ng/L, and the SE values for the triplicate set of Outside water samples collected upon deployment (T0) and retrieval (T40) of the BFSB at station 5B each is 0.1 ng/L.

Table 4-12. Codes used to represent target PCB mixture or PAH compounds in figures of Appendix 4.

<u>CODE</u>	<u>COMPOUND</u>
1254	Aroclor 1254
NA	naphthalene
C1NA	1-methylnaphthalene
BIPH	biphenyl
C2NA	2,6-dimethylnaphthalene
C3NA	2,3,5-trimethylnaphthalene
ACEY	acenaphthylene
ACE	acenaphthene
FLEN	fluorene
PHE	phenanthrene
ANT	anthracene
C1PH	1-methylphenanthrene
FLAN	fluoranthene
PYR	pyrene
BaA	benzo[a]anthracene
CRY	chrysene
BbF	benzo[b]fluoranthene
BkF	benzo[k]fluoranthene
BeP	benzo[e]pyrene
BaP	benzo[a]pyrene
PER	perylene
IND	indeno[1,2,3-cd]pyrene
B2aA	dibenz[ah]anthracene
BgP	benzo[ghi]perylene

Table 4-13.

**LIQUID/LIQUID EXTRACTION
OF TOTAL ORGANICS (HYDROPHOBIC)
FROM SEAWATER SAMPLES**

Method Summary

1. Collect ~ 500 mL of sample, determine the exact volume.
2. Add 25 μ L per 500 mL sample of internal standards in methanol. Concentrations in samples are 50 pptr of deuterated PAH's and 5 pptr of PCB congeners. Equilibrate for four hours.
3. Add 12 mL per 500 mL of sample of 10% Isooctane in Hexane. Extract on shaker table for 12 to 18 hours.
4. Remove and discard the water layer.
5. Concentrate the sample to 50 μ L using high purity N_2 .
6. Recovery standard added equivalent to 50 pptr d^{10} phenanthrene and 5 pptr of PCB congener 79.
7. Transfer to GC vial with micro insert.
8. GC/MS Analysis:

GC: HP 5890 Series II.

Column: J&W 30 meter * 0.25 mm ID
* 0.25 μ M DB-5 coating.

Detector: HP 5970B Mass Selective Detector
Selective Ion Monitoring.

Table 4-14.

SINCLAIR INLET FLUX STA. 5B: T-0	WATER		BLANK	
	Ave	± SE	Ave	± SE
ALOCOR 1254	0.1*	± 0.1	0.3*	± 0.2
NAPHTHALENE	4.1	± 0.9	2.2	± 0.1
2-CH3-NAPHTHALENE	2.5	± 0.7	1.6	± 0.2
1-CH3-NAPHTHALENE	1.8	± 0.4	0.9	± 0.0
BIPHENYL	1.4	± 0.1	0.4	± 0.0
2,6-DI-CH3-NAPHTHALENE	1.8	± 0.3	0.8	± 0.1
2,3,5-TRI-CH3-NAPHTHALENE	1.4	± 0.3	0.4	± 0.1
ACENAPHTHYLENE	0.4	± 0.1	-	
ACENAPHTHENE	2.7	± 0.4	0.5*	± 0.2
FLUORENE	1.9	± 0.3	0.2	± 0.1
PHENATHRENE	2.9	± 0.5	0.4	± 0.1
ANTHRACENE	0.5	± 0.1	0.0*	
1-CH3-PHENATHRENE	0.7	± 0.1	-	
FLUORANTHENE	5.5	± 0.9	0.1*	± 0.0
PYRENE	2.9	± 0.5	0.1	± 0.0
BENZO[a]ANTHRACENE	0.5*	± 0.1	-	
CHRYSENE	0.7	± 0.1	0.0*	
BENZO[b]FLUORANTHENE	0.6	± 0.1	-	
BENZO[k]FLUORANTHENE	0.4*	± 0.0	-	
BENZO[e]PYRENE	0.5*	± 0.1	-	
BENZO[a]PYRENE	0.3*	± 0.0	-	
PERYLENE	0.1*	± 0.0	-	
INDENO[123cd]PYRENE	0.3*	± 0.0	-	
BENZO[ghi]PERYLENE	0.3	± 0.0	-	

* Lacks 2nd ion confirmation

Table 4-15.

AROCLOR 1254 IN WATER (ng/L)

<u>Time (hr)</u>	<u>3B</u>	<u>5B</u>
Ambient (0)	0.6 *	0.1 *±0.1
BFSO 0	0.6 *	0.2
BFSO 8	0.6 *	0.2 *
BFSO 16	1.2 *	0.2 *
BFSO 24	1.0 *	0.2 *
BFSO 32	0.6 *	0.1 *
BFSO 40	0.9 *	0.4 *
Ambient (40)	-	0.3 *±0.1
Sediment (ug/kg)	160	960

* Upper limit (no 2nd ion confirmation)

Figure 4-1.

SAN DIEGO HARBOR PAH (ng/L)

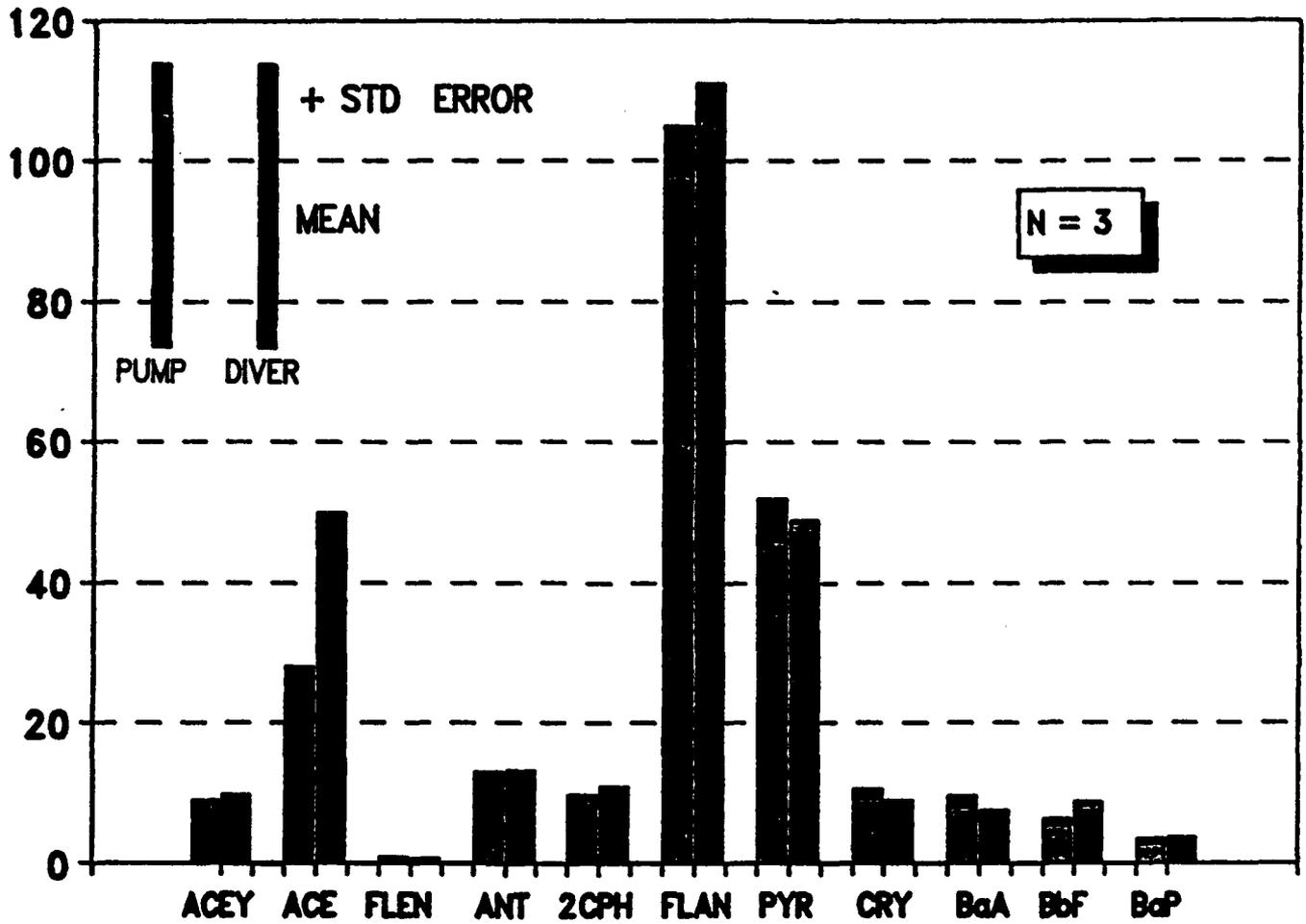
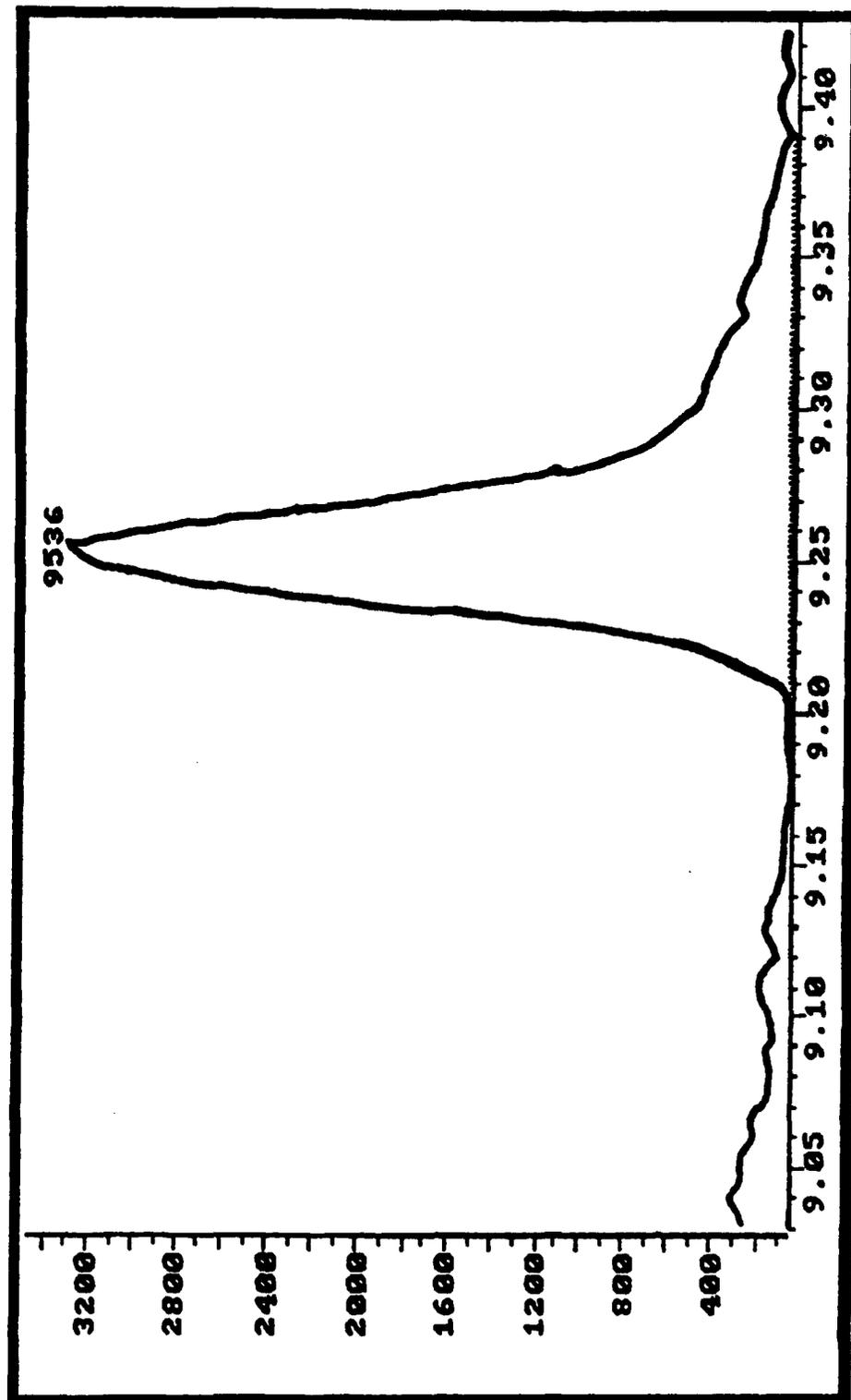


Figure 4-2.

QUANT ION : 142 AMU

1-CH₃-NAPHTHALENE : 2.3 ng/L

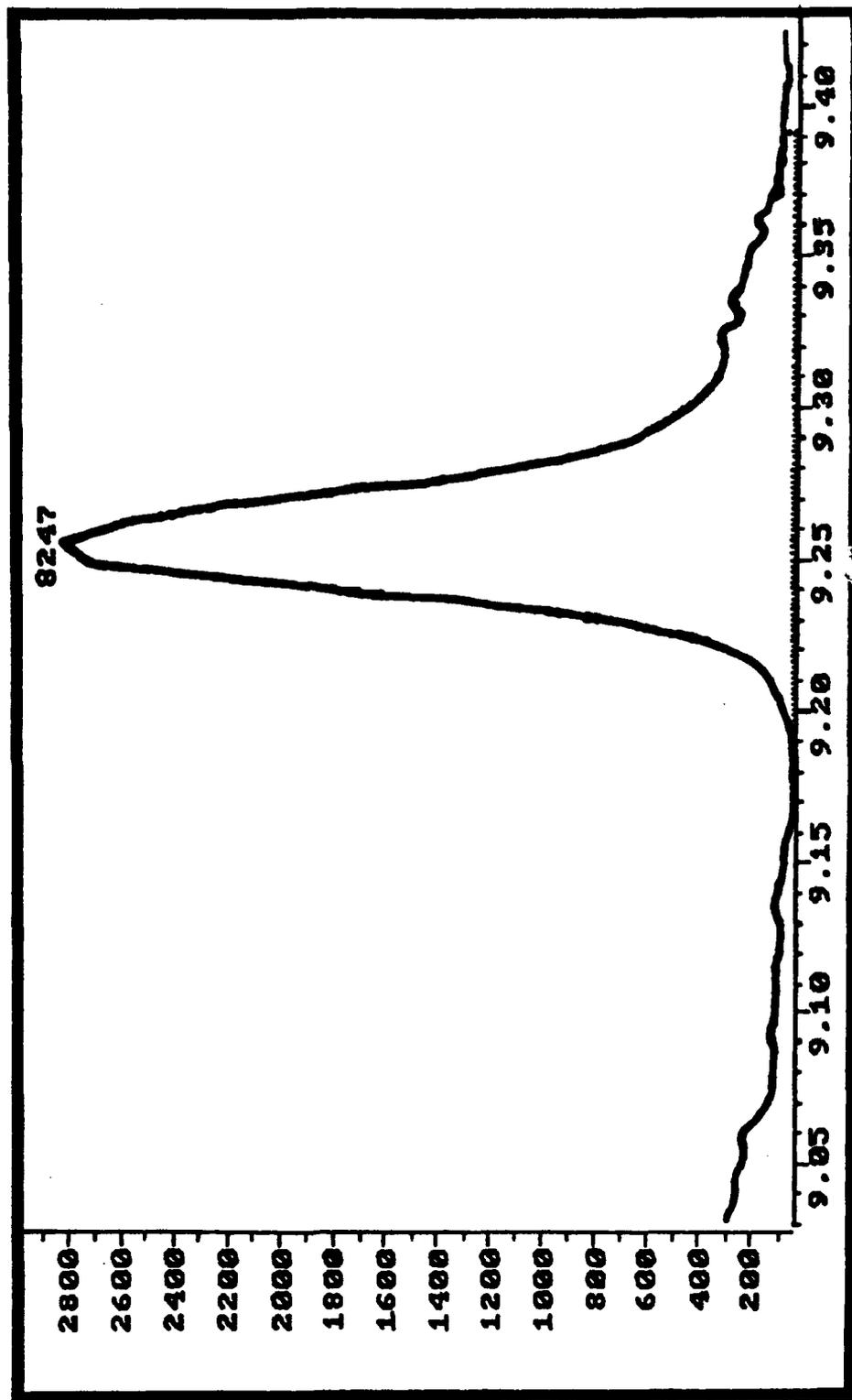


PSNS WATER : 5B

Figure 4-3.

CONFIRM ION : 141 AMU

1-CH₃-NAPHTHALENE : EXPECT/OBSERVE = 0.96

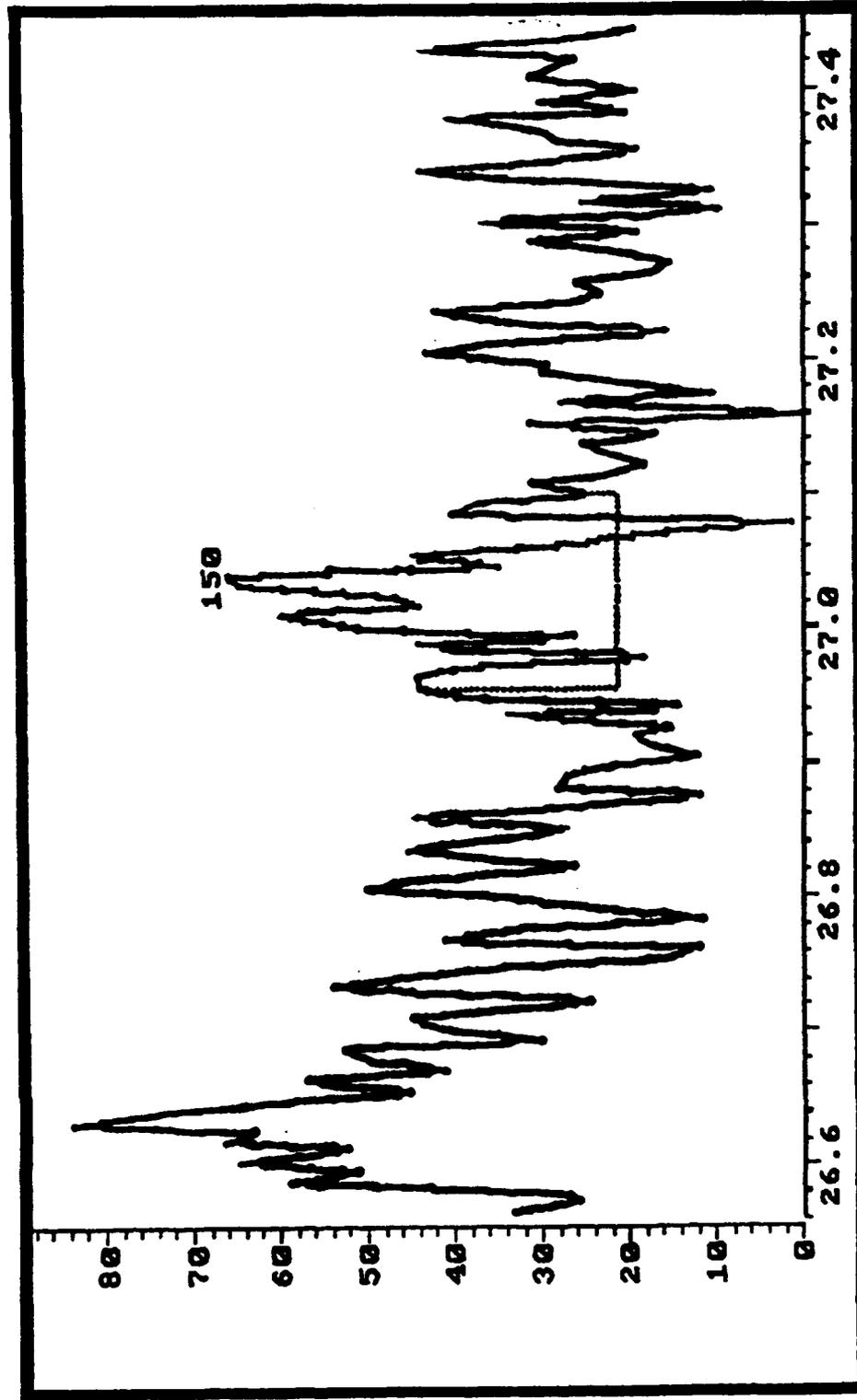


PSNS WATER : 5B

Figure 4-4.

QUANT ION : 326 AMU

AROCLOR 1254 : 0.7 ng/L PCB - 110 : 0.04 ng/L

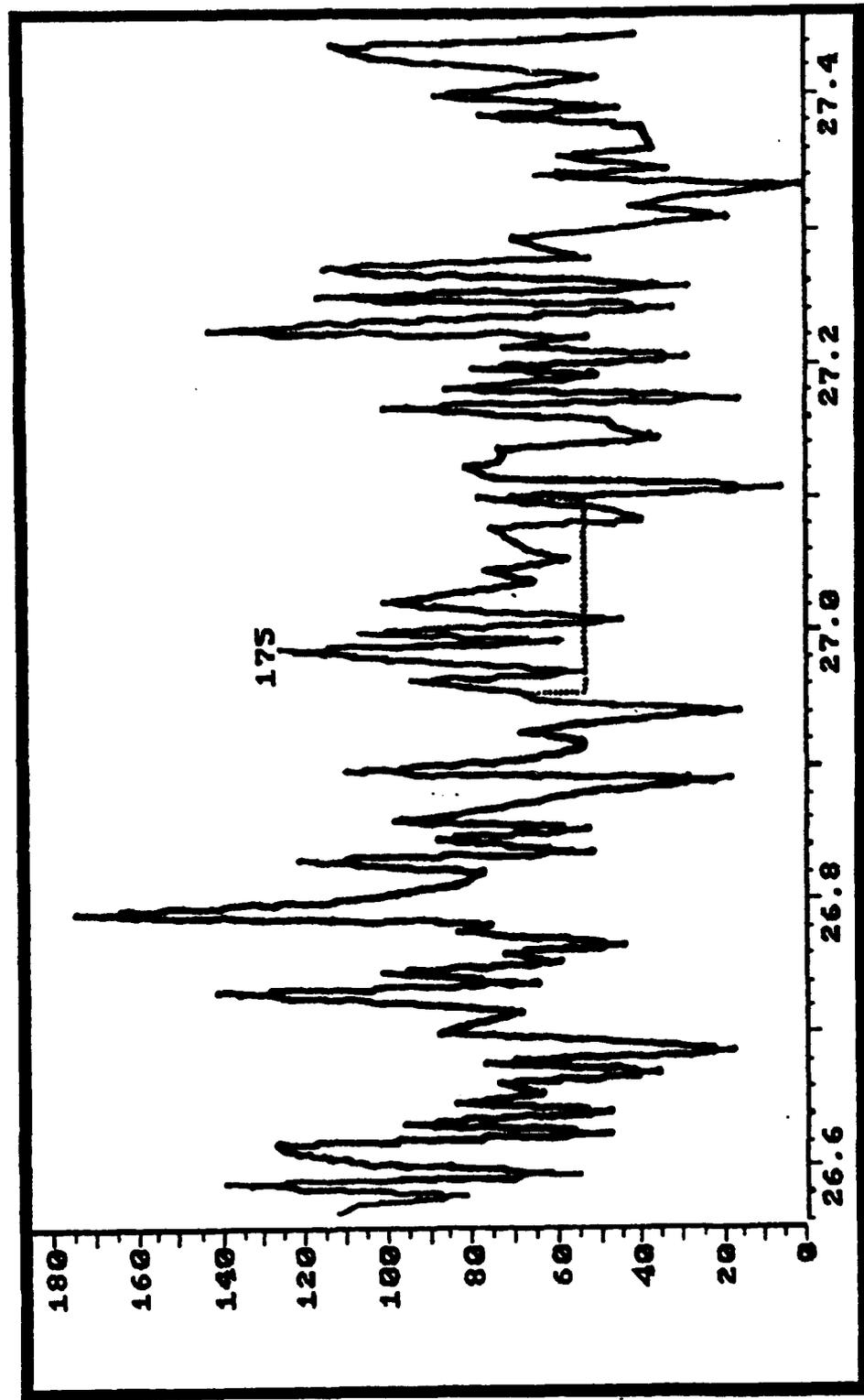


PSNS WATER : 3B

Figure 4-5.

CONFIRM ION : 256 AMU

PCB - 110 : NO SECOND ION



PSNS WATER : 3B

Figure 4-6.

Accuracy of Water PAH (ng/L)

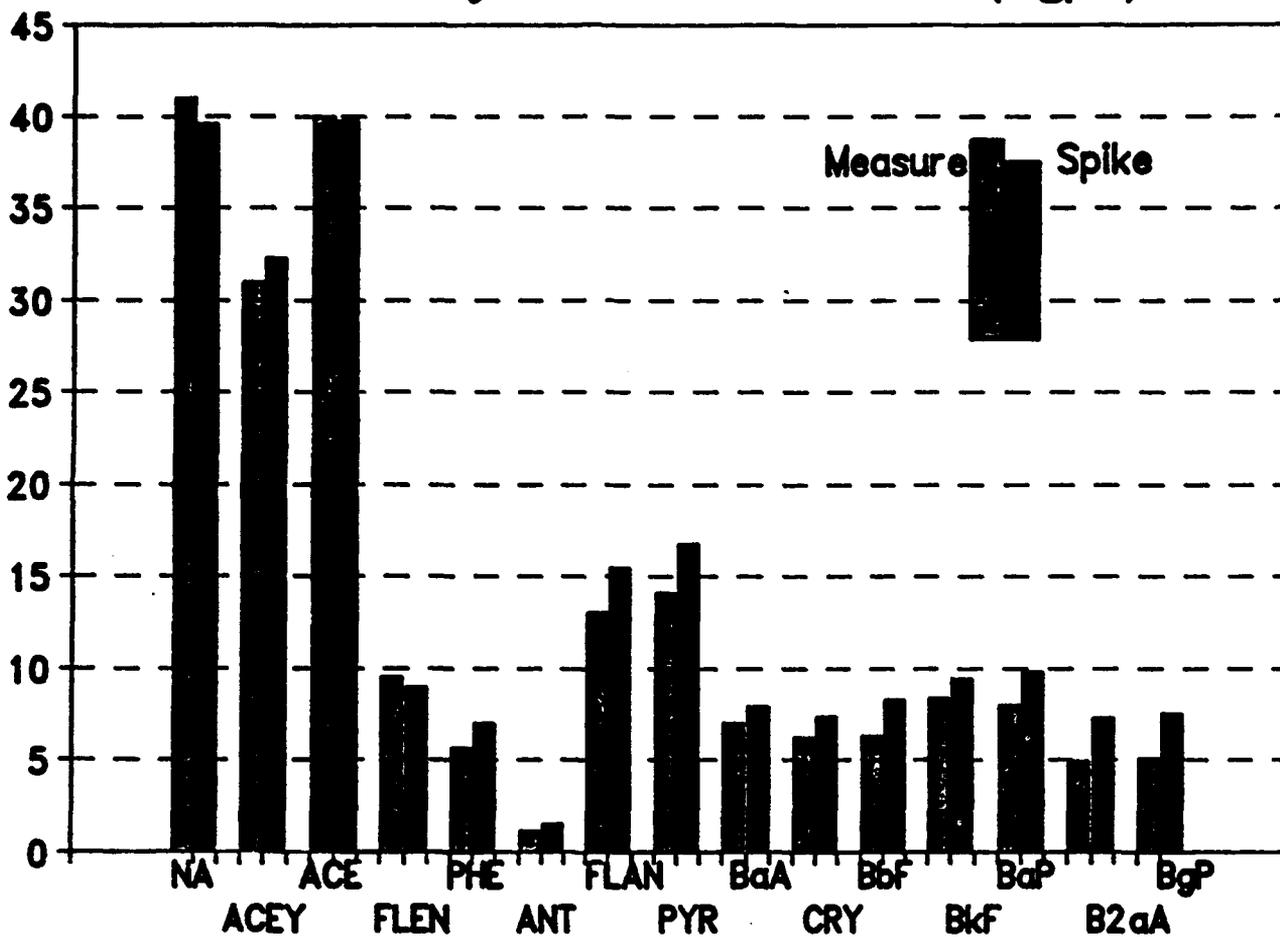


Figure 4-7.

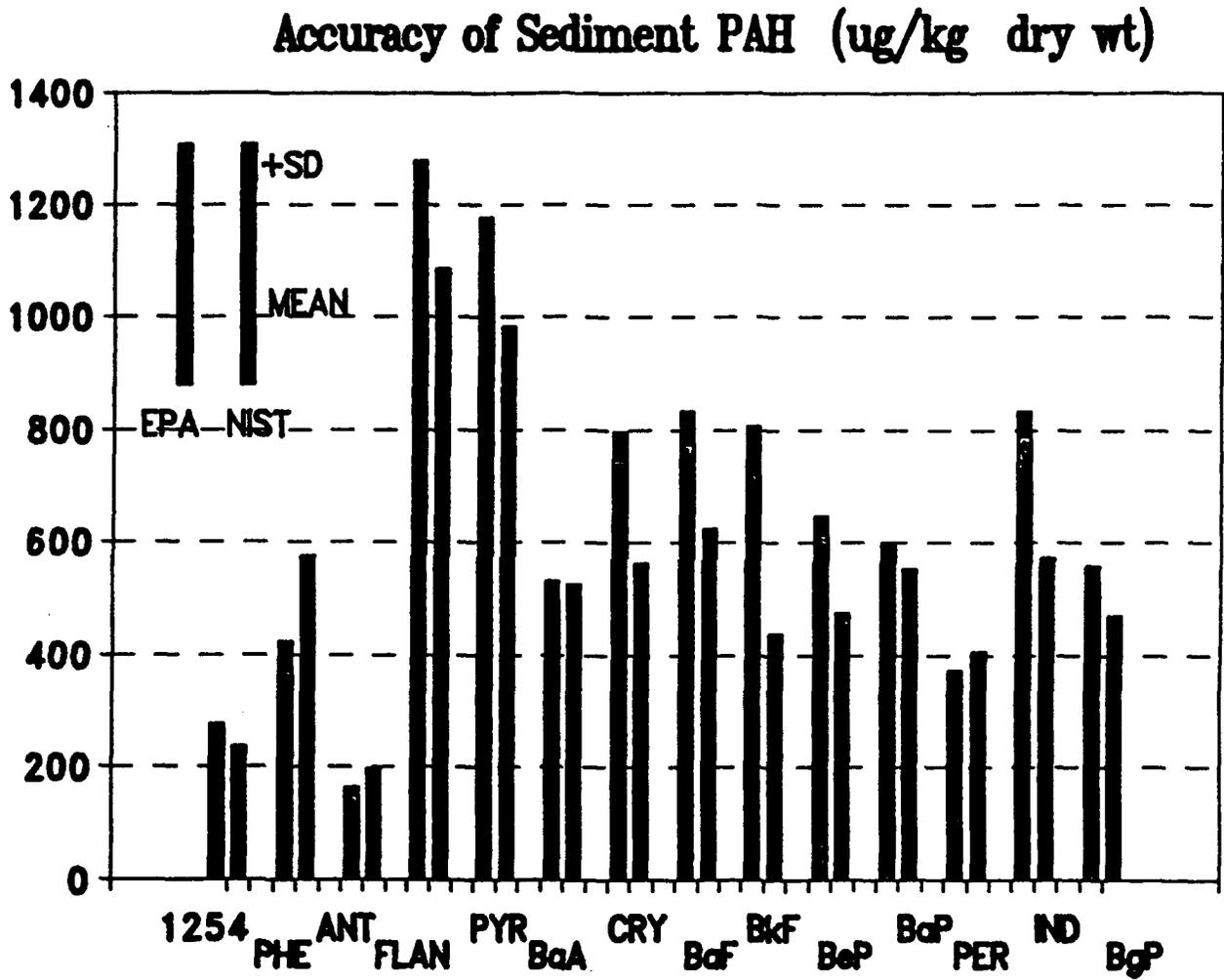


Figure 4-8a.

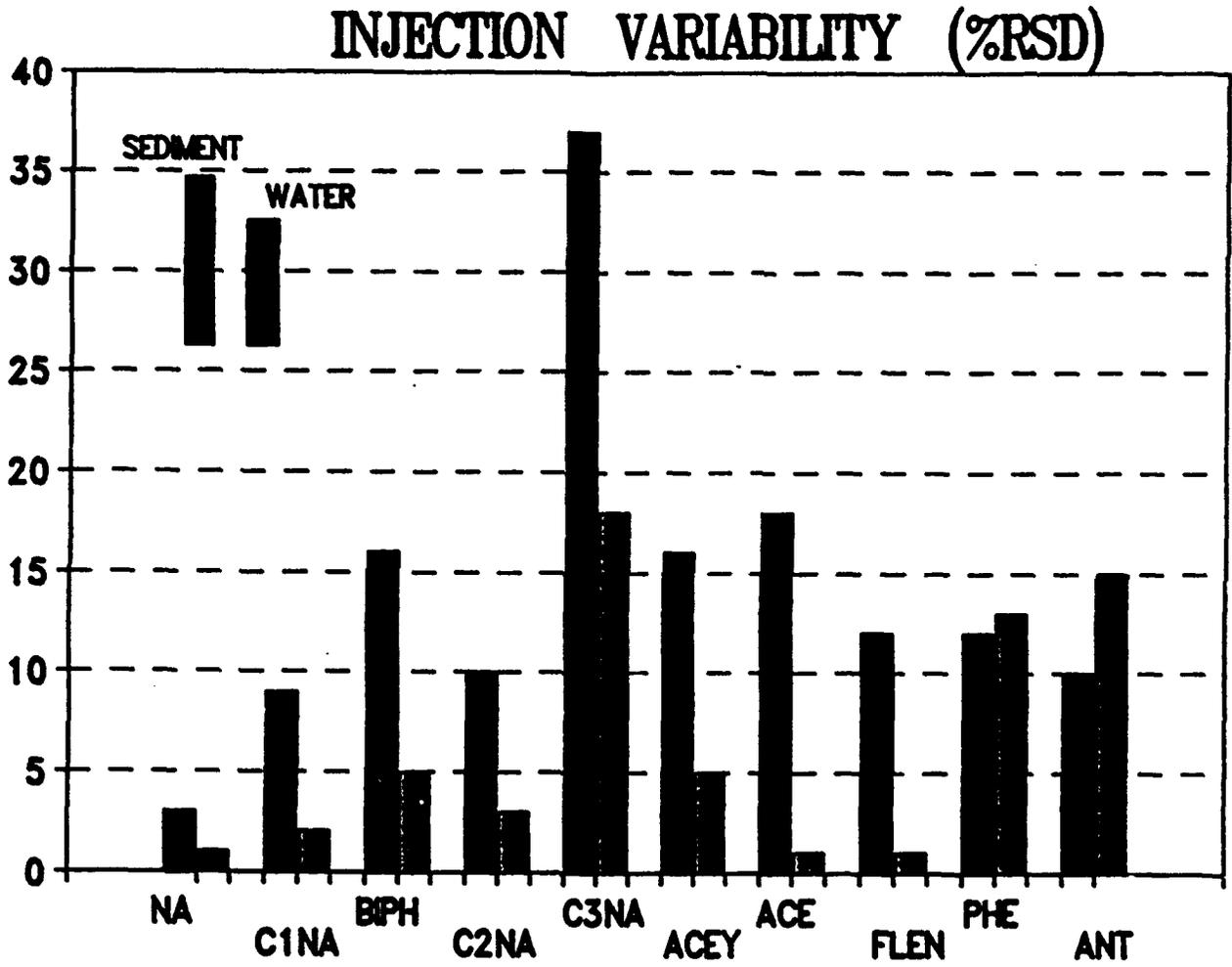


Figure 4-8b.

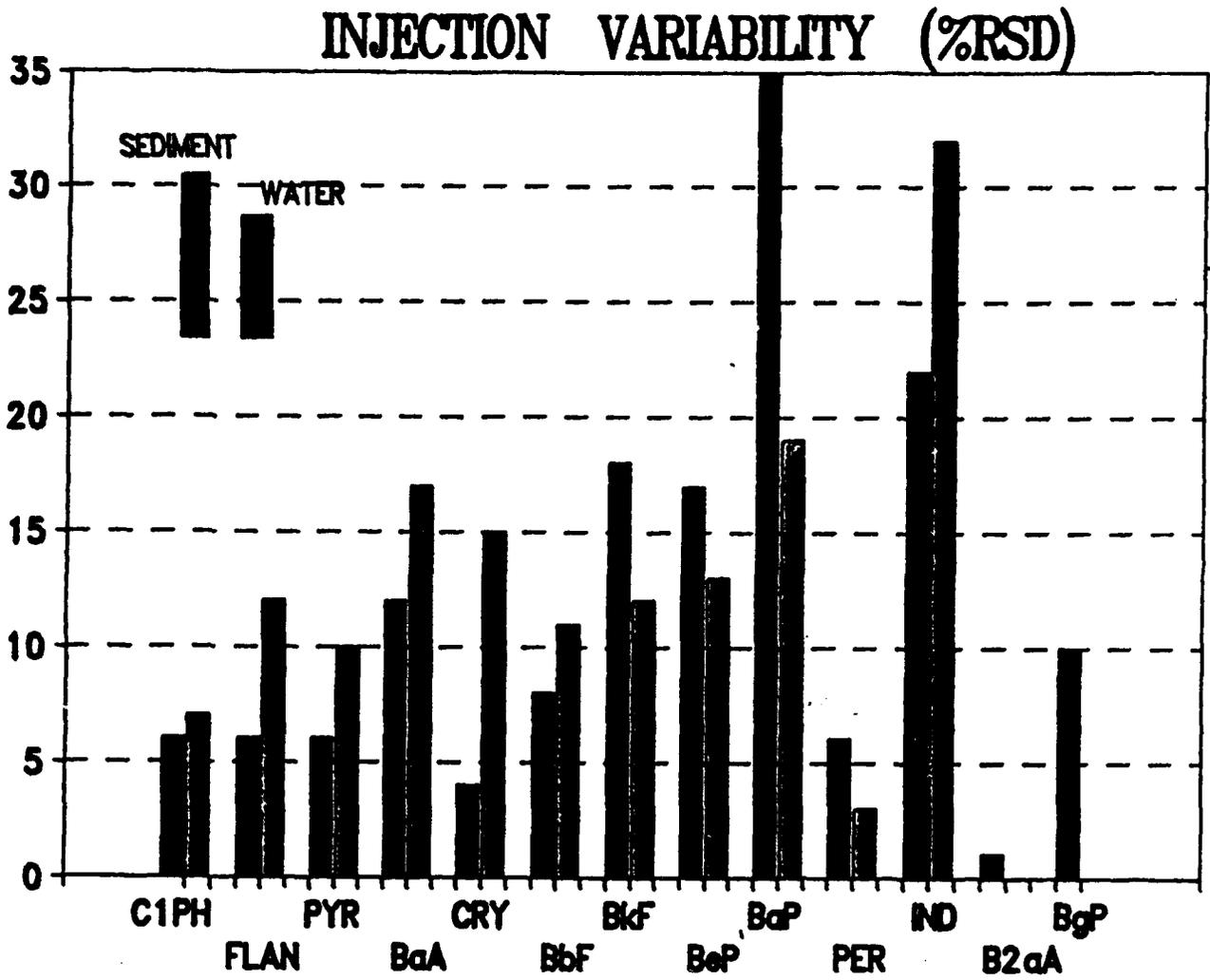


Figure 4-9a.

SEDIMENT PAH VARIABILITY (%RSD)

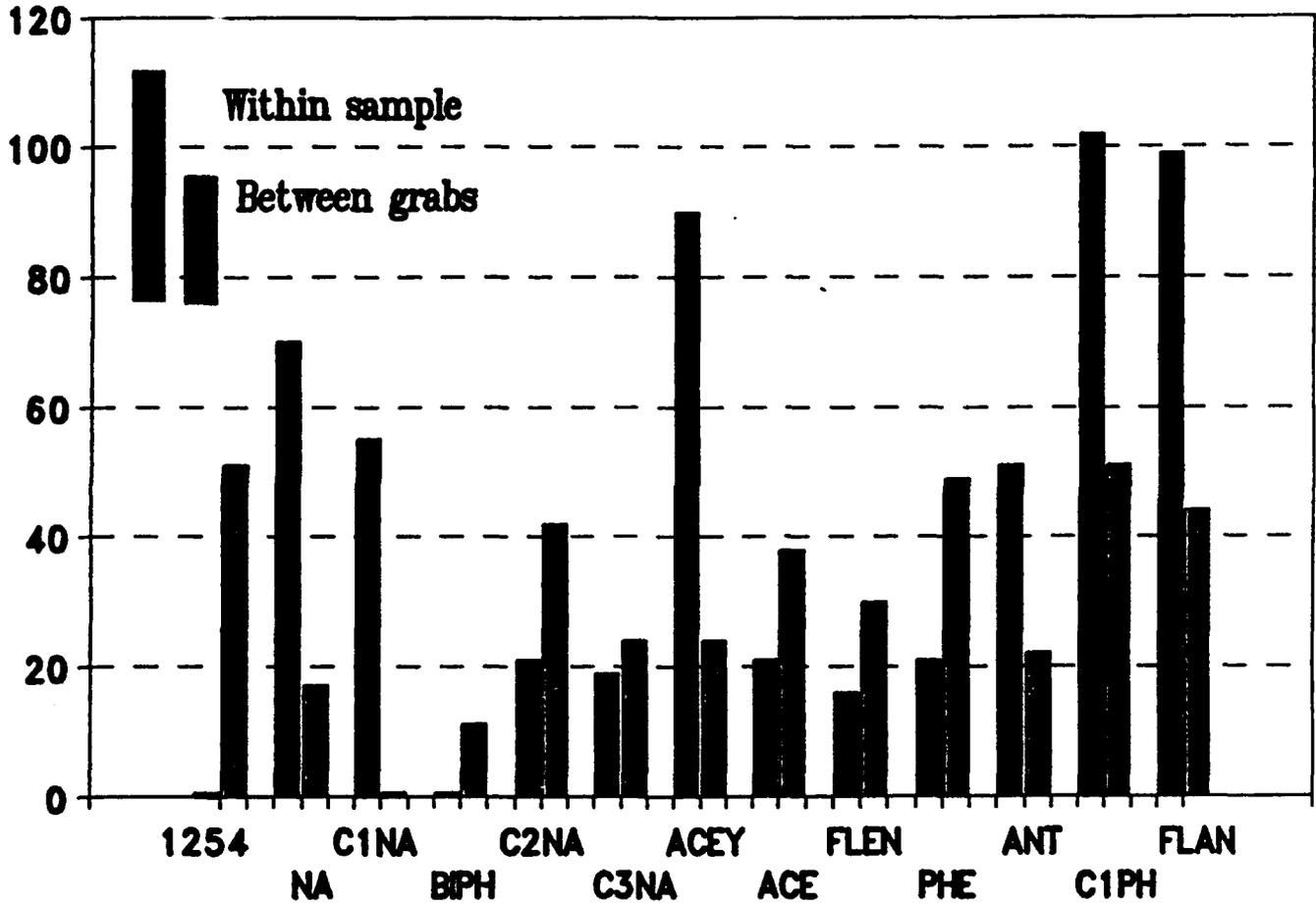


Figure 4-9b.

SEDIMENT PAH VARIABILITY (%RSD)

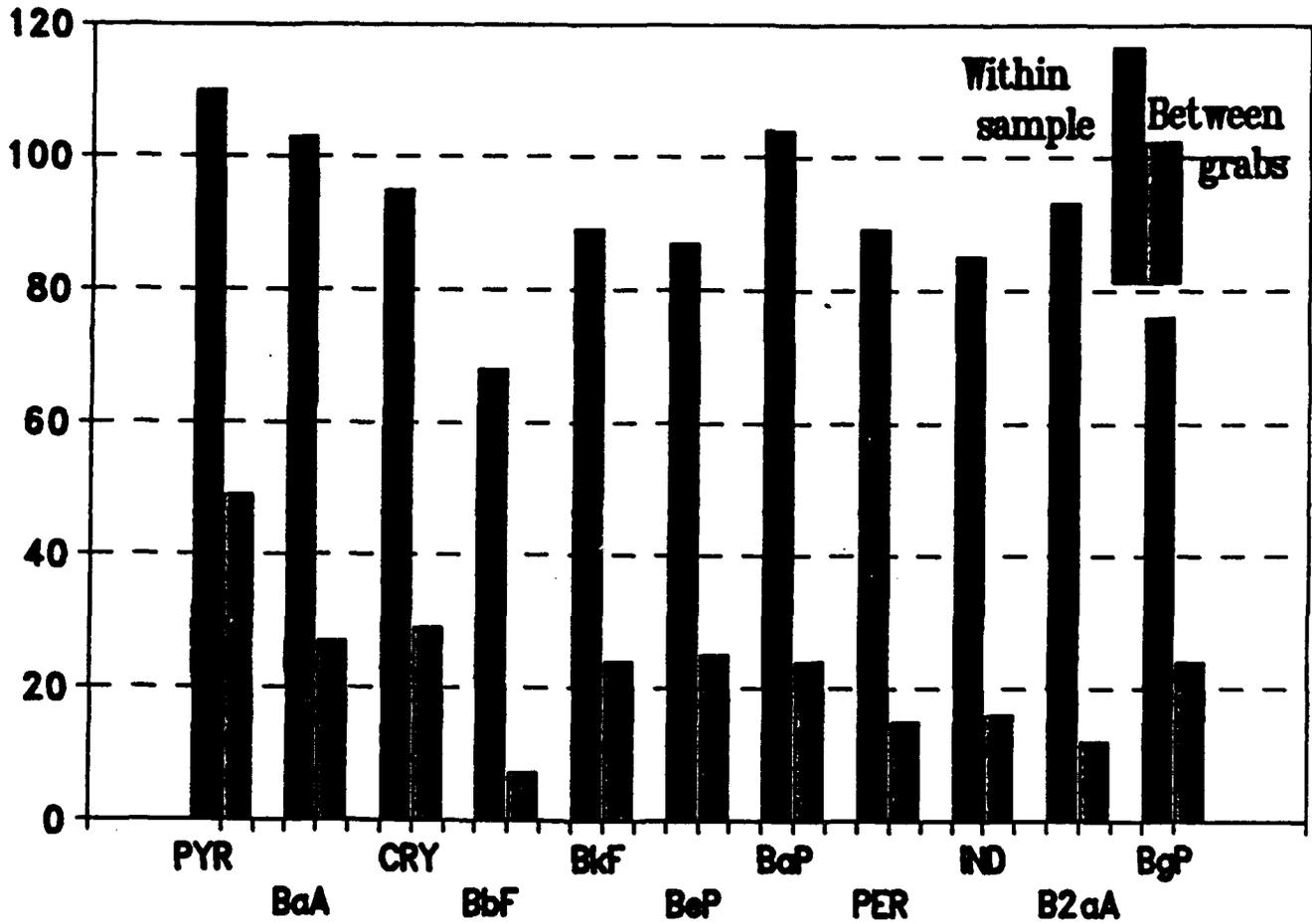
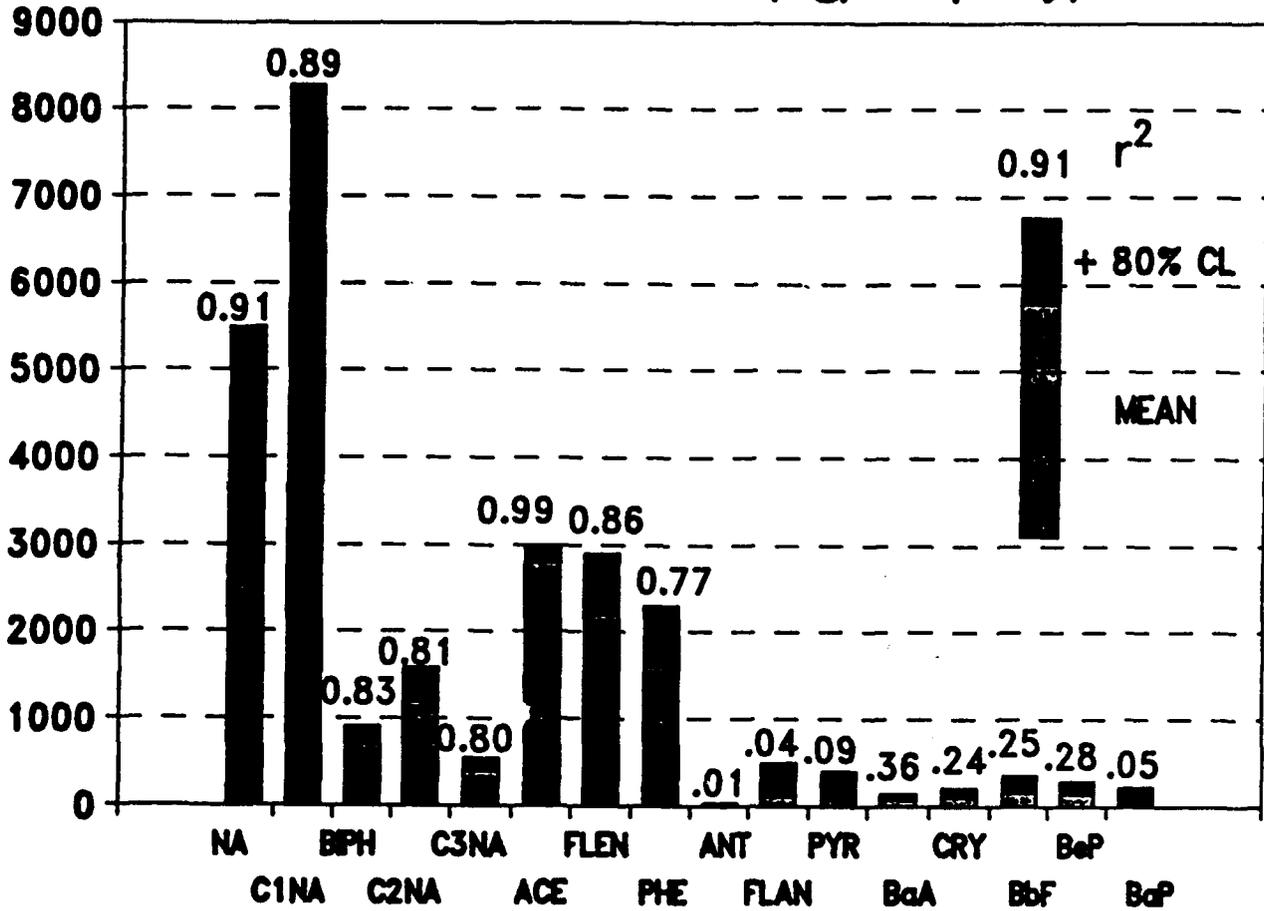


Figure 4-10.

3B PAH FLUX (ng/m²/day)



Appendix 5. Pore-Water Chemistry Report

FINAL REPORT Award N66001-91-M-L256

TITLE: Pore-Water Chemistry in Sinclair Inlet

PRINCIPAL INVESTIGATOR: Clare E. Reimers

DATE: December 2, 1991

1. SUMMARY OF EFFORT

During July 1991 the Marine Environment Branch at NOSC (Code 522) conducted a study of the flux rates of contaminants from sediments in Sinclair Inlet, the location of the Puget Sound Naval Shipyard, using an *in situ* benthic chamber instrument. Recognizing that the mobility of contaminant metals and organic compounds may depend in large part on the redox chemistry and pH of the sediments, this investigator deployed an instrument to measure with microelectrodes *in situ* high resolution, pore-water profiles of dissolved O₂, pH, electrical resistivity, and at some sites also hydrogen sulfide and pCO₂ (the partial pressure of carbon dioxide). The instrument's design is described in Reimers (1987). Seven deployments were completed, although only five resulted in usable data (Table 1). The major causes of lost data were: 1) sensor breakage (apparently by benthic megafauna), and 2) sensor malfunction.

Benthic chamber time-series samples were analyzed for dissolved silica and in some cases total alkalinity. The intent of this effort was to provide additional measures which could be used to assess the benthic chamber's performance.

2. RESULTS

2a. *Microprofiler results*

In situ microprofiles of O₂, pH and resistivity were measured successfully at four sites, 2B (two deployments), 3B, 4A and 5B (Figures 1-3). Sulfide and pCO₂ were successfully measured only at station 2B (Figure 4).

Resistivity- Measurements of the electrical resistivity of sediments are widely used to estimate sediment porosity and diffusion coefficients. For a wide range of sediments, a simple relation has been found between the ratio of the resistivity in the sediment and the resistivity of the water (R_s/R_w; a term called the formation factor, F) and porosity. This relation is:

$$F = \phi^{-n}$$

where ϕ is the porosity (cm³_{water}/cm³_{bulk}), and n is typically ≈ 2.5 to 3 for high porosity muds, whereas n ≈ 2 for unlithified sands (Ullman and Aller, 1982).

The bulk sediment diffusion coefficient for dissolved species in the pore waters may be approximated as:

$$D_s = \frac{D_o}{\phi F}$$

where D_o is the free solution diffusion coefficient of the solute (Ullman and Aller, 1982). Values of D_s are needed to estimate benthic fluxes from pore water gradients and Fick's law of diffusion.

The sediments in Sinclair Inlet were observed to be primarily muddy sands, although some sites were littered with shell or shipyard debris (e.g. cables). Bioturbation appeared restricted largely to the uppermost ~ 1 cm. Our resistivity measurements yielded formation factor profiles that tended to increase to F values of 2 to 2.5 in the first 6 cm, suggesting porosities decreased to approximately 0.7 by 6 cm depth. At site 4A, a high resistivity layer was encountered between 2 and 3 cm depth. Since both the resistivity and pH electrodes penetrated this layer, it probably consisted of densely-packed sand (a storm deposit?). Layering was also suggested by the formation factor profile at site 2B.

Oxygen- Oxygen microprofiles are shown in Figure 2. In the plots representing stations 3B and 4A, some data points from above the sediment-water interface have been omitted because the records were unusually noisy (due to an unknown source of signal interference). The oxygen profiles illustrate that in Sinclair Inlet the sediments are a sink for dissolved oxygen. Oxygen was generally observed to be completely consumed in the first 0.5 cm of the sediment column. Of the four sites profiled, site 5B had the steepest O₂ gradient.

pH- There were some problems with the pH measurements. At station 2B there were a number of noise spikes that occurred at the same time in both profiles. These data points were omitted before constructing the profiles in Figure 3. At stations 3B and 5B the pH microelectrodes performed well, but readings right at the sediment-water interface were not recorded because the pH microelectrodes crossed the interface a few millimeters before the resistivity probe located the interface. (The microprofiler has a search program based on the resistivity output. In this program mode, pH and all the other sensors except resistivity are read only every 10 mm until the interface is detected, see Figure 1). However, the pH profile at station 4A is the one which is the most questionable. The electrode potential recorded was shifted roughly 200 mV above its normal value (at pH 8). We have observed this problem before and believe it is caused by a stray low resistance path that develops across the penetrator that passes the signal through the microprofiler pressure housing. When this potential shift occurs, the electrode may not exhibit a full response.

In spite of the above qualifications, the pH profiles in Figure 3 illustrate that pore water pH decreases abruptly in the first 0.5 cm of sediment in Sinclair Inlet. The pH decrease is greatest at site 5B, and the level value reached at 5B of ~6.2 is unusually low for marine systems.

Sulfide- A silver-silver sulfide microelectrode was successfully deployed at site 2B. The potential of the microelectrode versus depth in the sediment is illustrated in Figure 4. This potential is ideally a direct function of the logarithm of the activity of the sulfide ion, $a_{S^{2-}}$ (Berner, 1963). A lowering of the sulfide electrode's EMF corresponds to an increase in the activity of sulfide ion. At sediment depths greater than 39 mm at site 2B the potential of the sulfide electrode was more negative than -503 mV which was the limit of our instrument's input range (Figure 4).

Berner (1963) determined the calibration curve for the silver-silver sulfide electrode versus a calomel electrode at 25°C to be:

$$E_{S^{2-}} = -.890 + 0.0295pS^{2-}$$

where $pS^{2-} = -\log a_{S^{2-}}$.

If this calibration holds for our microelectrodes (laboratory tests still need to be run), we can convert our measured potentials to values of pS^{2-} after correcting the equation above for the potential

difference between a Ag/AgCl and a calomel reference electrode, since we used the Ag/AgCl reference. This changes the constant in the above equation from $-.890V$ to $-.935V$. Thus, we estimate that the pS^{2-} of the bottom water at site 2B ≈ 29 , whereas at a depth of 39 mm in the sediment it ≈ 14.6 .

Since the principal sulfide species at the pH of these sediments (7.5-8.0; Figure 3) is HS^- not S^{2-} , the concentration of total sulfide species (ΣH_2S) may be estimated from the equilibrium relationships between H_2S , HS^- , and H^+ , and HS^- , S^{2-} and H^+ . The equilibrium constants for these relationships are $K_1 = 10^{-13.9}$ and $K_2 = 10^{-7.02}$ at $25^\circ C$. Thus, we calculate the pore water hydrogen sulfide concentration at site 2B increases from zero at the sediment water interface to a concentration which is only $\sim 0.01 \mu M$ below 4 cm depth. This latter value seems unrealistically low. Once our sulfide microelectrodes have been properly calibrated, these calculations will need to be redone.

pCO_2 - This investigator has been developing pCO_2 microelectrodes for pore water studies. The reason for this work is that with this parameter and pH one can calculate the concentrations of all the inorganic carbon species, i.e. $CO_{2(aq)}$, CO_3^{2-} , and HCO_3^- in pore waters. Two pCO_2 profiles were measured during separate deployments at site 2B (Figure 4). Both profiles indicate an increase in pCO_2 , but a greater increase was determined at the first 2B deployment site.

The calibration of the pCO_2 measurements requires an estimation of the pCO_2 of the bottom water above the sediment. At site 2B, bottom water alkalinity was measured as $2153.6 \mu mol kg^{-1}$; pH as 8.058 (NBS), and ΣCO_2 as $1920 \mu mol kg^{-1}$ (measured by CO_2 coulometer). If we use alkalinity and ΣCO_2 to calculate pCO_2 , the estimate is $283 \mu atm$; if we use pH and alkalinity, it is $561 \mu atm$; whereas if we use pH and ΣCO_2 , it is $530 \mu atm$. These estimates should be consistent. They may differ because 1) one of the measurements is in error (e.g. how good is the pH calibration of the benthic flux chamber electrode?); or 2) each parameter was measured in a different water parcel, collected at different times from above the site. In Figure 4, we have used the intermediate value ($530 \mu atm$) as the estimate of the pCO_2 of the bottom water. This was concluded because we suspect the bottom water pCO_2 to be $\geq 355 \mu atm$, the approximate value of water in equilibrium with the atmosphere.

2b. Benthic Flux Chamber Analyses

The results of our analyses of the benthic chamber time-series samples are given in Table 2. If we assume that a steady increase in dissolved silica over the time course of a deployment is a good indicator of a problem-free chamber deployment, sites 1A, 2A, 2B, 3B, 4A, 4B and 5A appear "problem-free". The chamber results from sites 1B, 3A and 5B are unusual. Alkalinity determinations at site 3A were also highly variable suggesting a sampling problem (Table 2). For sites 2B and 3B, ΣCO_2 concentrations were estimated from alkalinity measurements and the pH records of the chamber's pH electrode. These yield flux rates of 10.7 and $8.75 \mu mol cm^{-2} day^{-1}$. These fluxes are about equal to the highest rates of organic carbon oxidation ($8.2-9.4 \mu mol cm^{-2} day^{-1}$) given for shallow marine sediments in a review article by Henrichs and Reeburgh (1987).

3. FURTHER INTERPRETATIONS

The sediments in Sinclair Inlet are highly anoxic and their black color indicates iron sulfide precipitation. The consistently low pore water pH values, the smell of sulfide given off by the muds, and the sulfide electrode profile at station 2B, suggest that excess sulfide is present in solution. Thus, based on solubility considerations, we would predict that the concentrations of trace metals as

free ions in these pore solutions are extremely low.

There are inconsistencies between the chamber ΣCO_2 flux estimates and estimates that may be derived from the pore water profiles that call for follow-up work. At station 2B, the oxygen gradient at the sediment-water interface suggests a diffusive oxygen flux into the sediment of $\sim 1.0 \mu\text{mol cm}^{-2}\text{day}^{-1}$. If all of the oxygen consumption was due to aerobic respiration (when it is likely that much of the oxygen flux is driven by the oxidation of sulfides), this could produce a ΣCO_2 flux of at most $0.8 \mu\text{mol cm}^{-2}\text{day}^{-1}$ (assuming "Redfield" stoichiometry). If we accept the chamber-derived ΣCO_2 flux of $10.6 \mu\text{mol cm}^{-2}\text{day}^{-1}$ as real, we must conclude that there is a high rate of ΣCO_2 production in association with one or more other process(es) such as anaerobic sulfate reduction and methanogenesis. This seems plausible based on the high concentrations of acid-volatile sulfur in the solids and the smell of sulfide given off by the muds.

The problem is that the pH and pCO_2 pore water profiles from station 2B do not indicate such a high ΣCO_2 flux if we assume the flux is driven primarily by molecular diffusion and not advective exchange (e.g. via bioturbation or bubble ebullition). Assuming the pore water pH and pCO_2 at 1 cm depth in the sediments at station 2B were ~ 7.56 and $2000 \mu\text{atm}$ (Figures 3 and 4), respectively, the pore water ΣCO_2 at this horizon is calculated to equal approximately $2320 \mu\text{mol kg}^{-1}$. The measured bottom water ΣCO_2 was $1920 \mu\text{mol kg}^{-1}$. Thus, a gradient of $\sim 400 \mu\text{mol kg}^{-1}\text{cm}^{-1}$ suggests a diffusive flux of ΣCO_2 out of the sediment of only roughly $0.3 \mu\text{mol cm}^{-2}\text{day}^{-1}$. This is considerably smaller than the chamber estimate, but suspicious because it is less than the oxygen flux alone. In the future, we need to perfect our methods for calibrating our pCO_2 and sulfide microelectrodes to improve the usefulness of these measurements for resolving such discrepancies. We should also measure the pH of the chamber samples immediately after collection and compare these to the *in situ* time-course records. If the chamber pH electrode is not functioning properly, the ΣCO_2 fluxes derived from pH and alkalinity will be in error.

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Table 1. in situ Microprofiler Results Summary. The microprofiler has 8 available sensor channels: 1 that may be used for resistivity, 3 for oxygen, 2 for pH or sulfide, and 2 for pCO₂.

Deployment	Date	Site	Sensor Performance				
			Resistivity	Oxygen	pH	pCO ₂	Sulfide
1	7-20-91	4A	E	VG; P; P	G; P	NU; NU	NU
2	7-21-91	5B	E	VG; B; B	VG; G	NU; NU	NU
3	7-22-91	3B	F	B; B; B	B	NU; NU	B
4	7-23-91	3B	E	G; G; P	VG; VG	P; NU	NU
5	7-24-91	2B	E	G; P; B	G; G	E; NU	NU
6	7-25-91	1B	F	F; F; F	F; F	F; F	NU
7	7-26-91	2B	F	VG; P; B	P	E; NU	E

KEY- NU indicates not utilized; B= electrode broken in situ before profiling; F= failed; E= excellent results; VG=very good results; G= good results (i.e. interpretable, but affected by noise of drift); P=poor results (unacceptable noise, interference or drift levels).

Table 2. Flux chamber Time-Course Sample Analyses

SAMPLE	SILICA $\mu\text{mol kg}^{-1}$	Total Alkalinity $\mu\text{mol kg}^{-1}$	pH (NBS) in situ	ΣCO_2 $\mu\text{mol kg}^{-1}$ (calculated)
2B T01	22.0	2153.6	8.058	2027
2B 1	31.9	2260.2	8.059	2129
2B 2	91.9	2402.5	7.942	2307
2B 3	118.4	2581.7	7.736	2553
2B 4	144.7	2672.1	7.555	2706
2B 5	172.2	2766.1	7.447	2845
2B 6	204.4	2822.5	7.369	2937
3B T01	41.0	2127.7	8.009	2020
3B 1	36.9	2125.3	7.962	2033
3B 2	71.4	2185.5	7.571	2207
3B 3	89.8	2235.1	7.291	2357
3B 4	99.7	2228.3	7.143	2421
3B 5	107.5	2318.9	6.994	2620
3B 6	119.3	2388.6	6.914	2769
3A T0	42.2	2143.6		
3A 1	18.5	1597.5		
3A 2	46.5	2070.3		
3A 3	50.8	1814.4		
3A 4	80.6	2087.5		
3A 5	79.5	2053.7		
3A 6	72.5	2110.3		
1A T0	21.7			
1A 1	22.1			
1A 2	46.3			
1A 3	59.8			
1A 4	70.5			
1A 5	77.5			
1A 6	88.6			
1B 1	29.5			
1B 2	54.5			

Table 2. (Contd).

1B 3	81.1
1B 4	60.9
1B 5	53.7
1B 6	61.3
2A T0	23.1
2A 1	25.9
2A 2	56.1
2A 3	76.4
2A 4	82.0
2A 5	101.8
2A 6	116.9
4A T0	23.2
4A 1	19.7
4A 2	26.0
4A 3	46.1
4A 4	61.0
4A 5	55.2
4A 6	65.4
4B T0	40.2
4B 1	43.8
4B 2	88.6
4B 3	111.7
4B 4	136.9
4B 5	161.5
4B 6	177.4
5A T0	16.6
5A 1	20.9
5A 2	37.0
5A 3	42.5
5A 4	65.3
5A 5	65.4
5A 6	88.1

Table 2. (Contd).

5B T0	29.0
5B T01	33.1
5B 1	31.5
5B 2	52.5
5B 3	67.3
5B 4	89.0
5B 5	78.7
5B 6	65.6

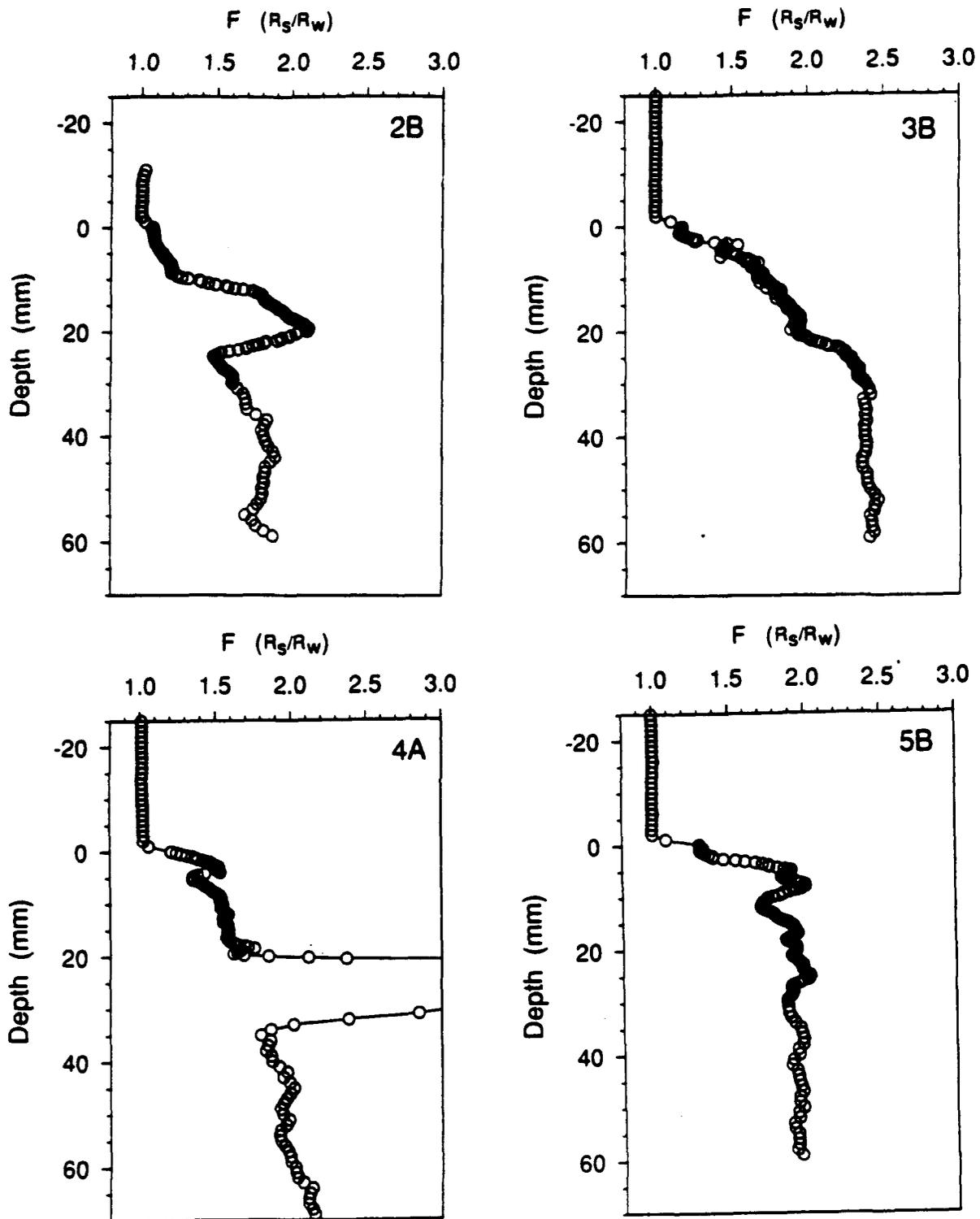


Fig. 1. Formation factor profiles measured in situ in Sinclair Inlet sediments. Resistivity readings were made every 1 mm until the sediment-water interface was detected. Below the interface, readings were taken every 0.25 mm to 30 mm and then every 1 mm to 60 or 70 mm.

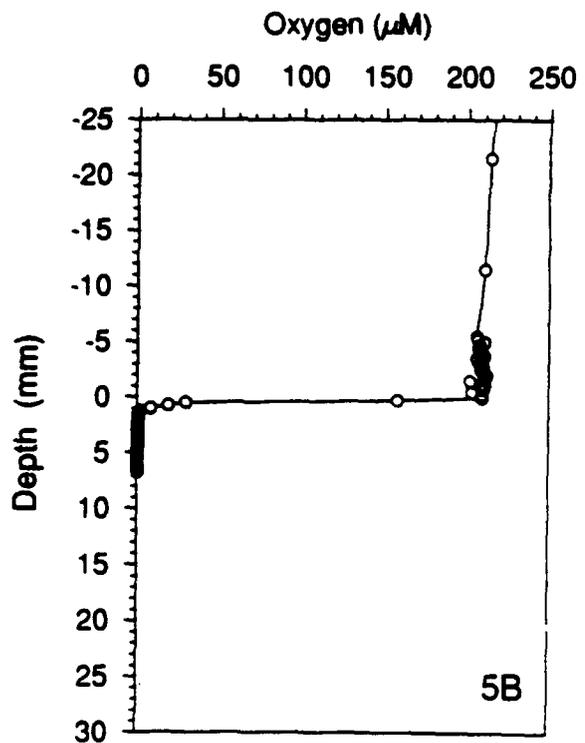
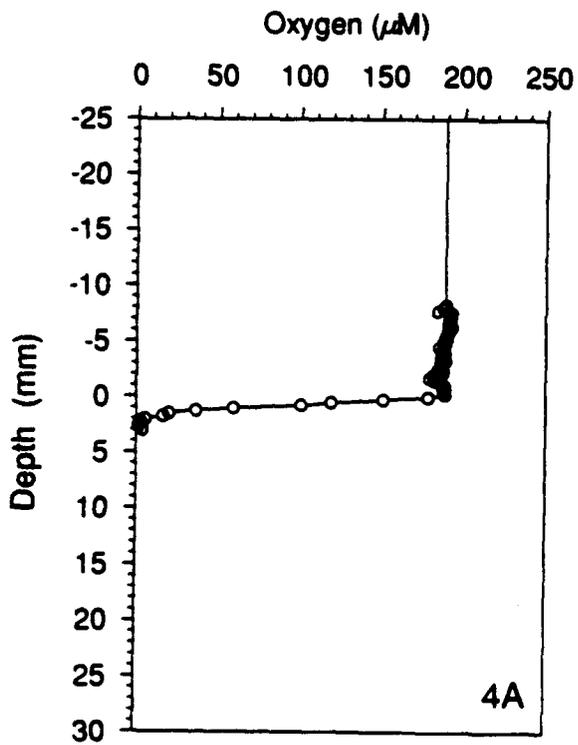
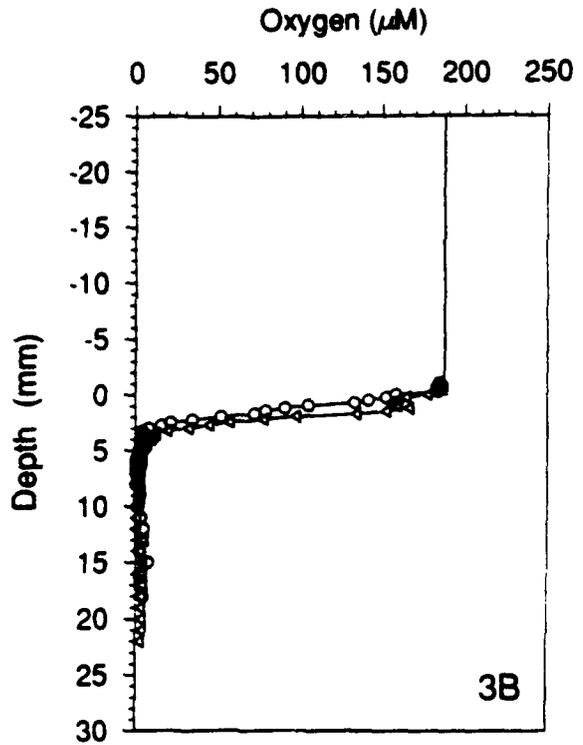
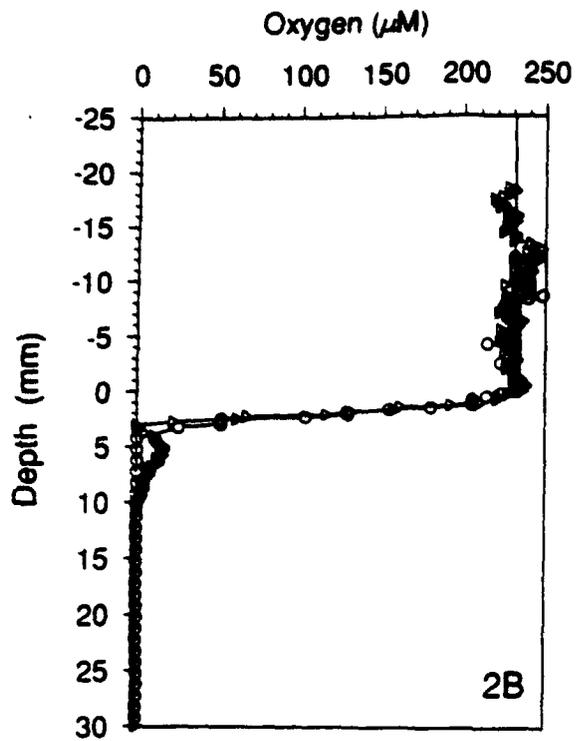


Fig. 2. Oxygen microprofiles from Sinclair Inlet. Many profiles do not extend very far into the sediment because the microelectrodes were broken by the coarse sand or debris.

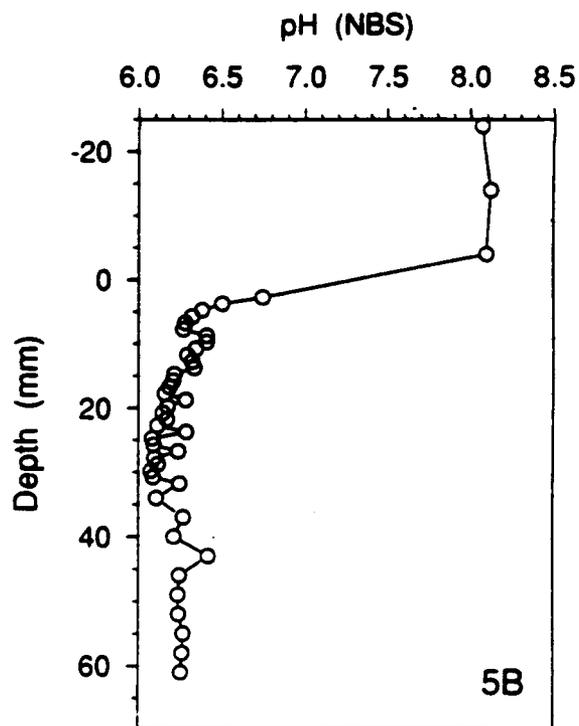
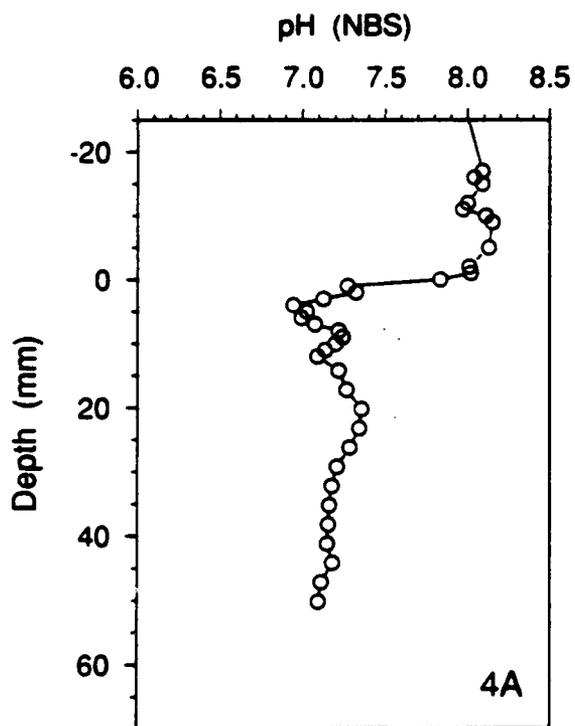
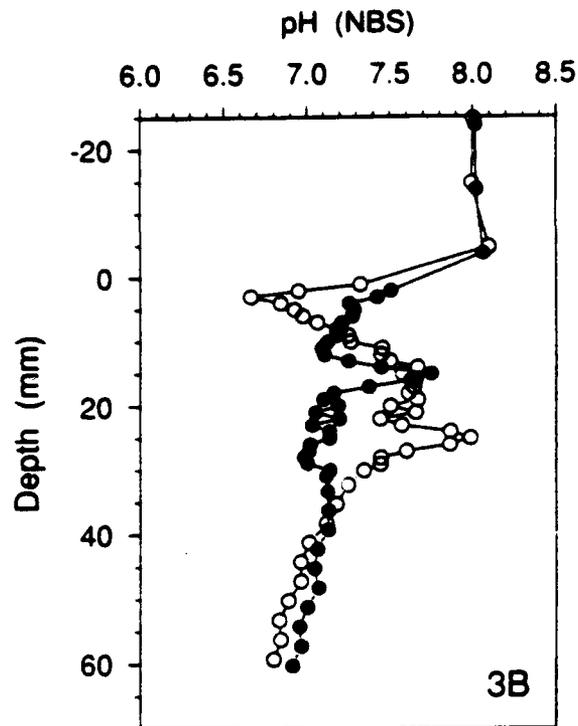
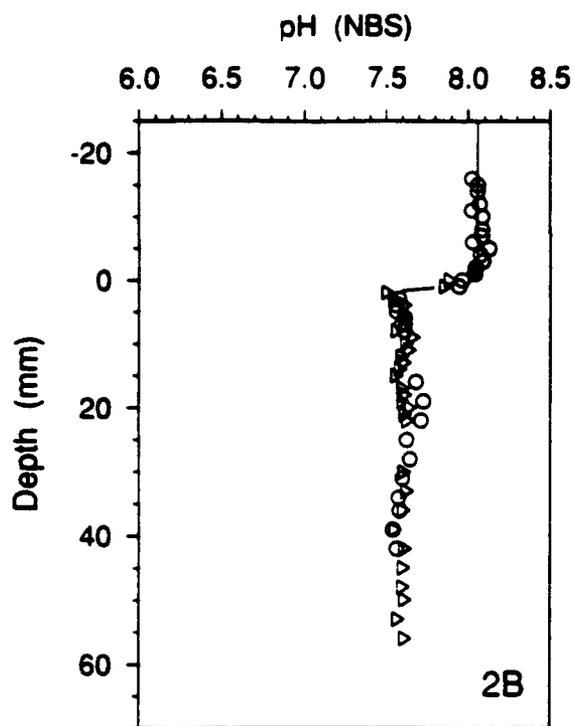


Fig. 3. Profiles of pore water pH measured in Sinclair Inlet in July 1991.

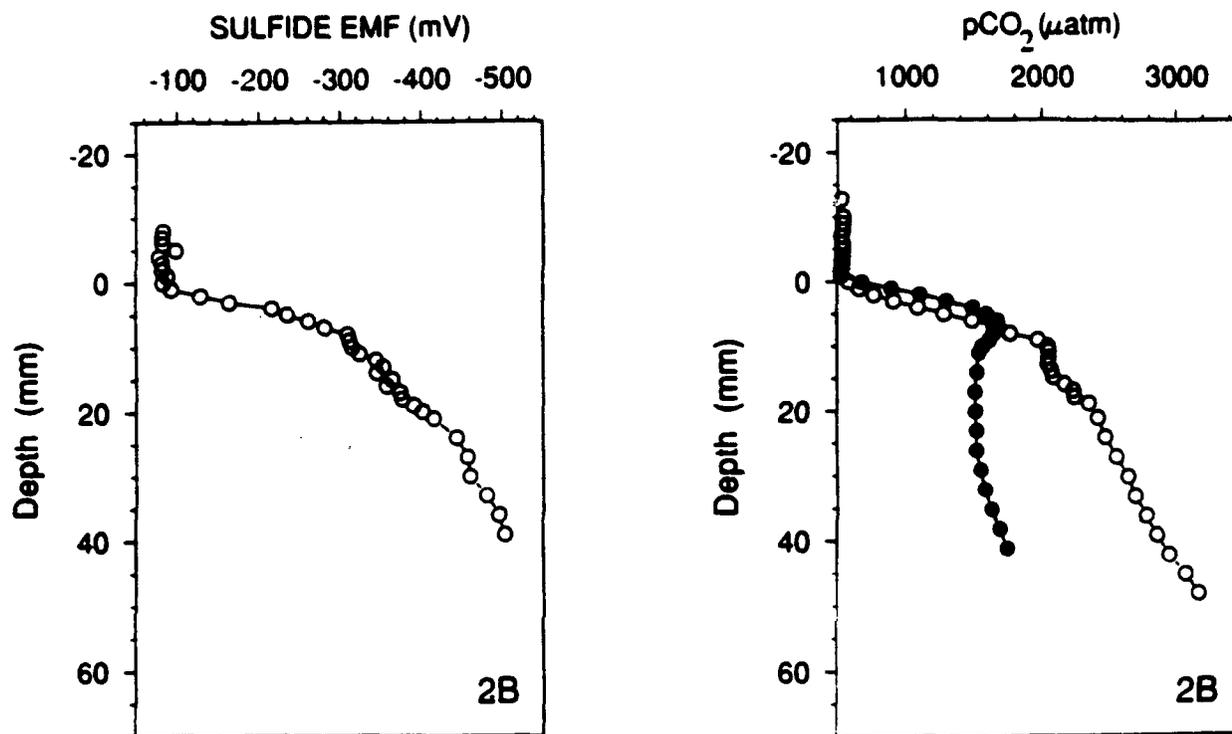


FIGURE 4. Microelectrode profiles of sulfide (EMF) and pCO₂ at station 2B. The calibration of these sensors is uncertain and needs verification.

Appendix 6. Source Budget Calculations

PUGET SOUND NAVAL SHIPYARD SEDIMENT FLUX

The Puget Sound Naval Shipyard occupies approximately 1.1 by 10⁶ m². The following flux values result from averaging contaminant flux rates from the current study for regressions with r² values greater than 0.5 (from sites 1B, 2A, 2B, 3A, 3B, 4A, 5A, and 5B):

Element	Average Sediment Flux Rate from Current Study (µg/m ² /day)	Sediment Flux (dissolved) (kg/day)
As	256 ± 143	0.28 ± 0.16
Cd	9 ± 8	0.01 ± 0.01
Cu	21 ± 90	0.02 ± 0.09
Ni	341 ± 92	0.41 ± 0.09
Pb	-20 ± 8	*
Zn	655 ± 384	0.72 ± 0.42

* Flux rate < 0.

SINCLAIR INLET SEDIMENT FLUX

The inlet is approximately 4 nautical square miles from the west end to the east edge of the Puget Sound Naval Shipyard (PSNS). Subtracting out the area of PSNS leaves an area of 1.261 by 10⁷ m². The flux rate calculated from site 4B is then applied over this area to obtain the approximate total sediment discharge of Sinclair Inlet:

Element	Average Sediment Flux Rate from Site 4B of Current Study (µg/m ² /day)	Sediment Flux (dissolved) (kg/day)
As	152 ± 82	1.9 ± 1.0
Cd	*	
Cu	*	
Ni	308 ± 241	3.9 ± 3.0
Pb	*	
Zn	*	

* No quantifiable flux.

Site 4B (at the west end of Sinclair Inlet) of the current study agrees with sites 3, 4, and 5 (from the west end of Sinclair Inlet to the east edge of the Puget Sound Naval Shipyard) in Weston, 1990.

NAVY VESSELS

Zinc

Historically, Navy vessels used zinc anodes for cathodic protection at a rate of approximately one 23-lb anode per 100 ft² of vessel. These anodes are 95 percent Zn by weight and when they are replaced (generally every 3 years) they are anywhere from 50–75 percent spent.¹

While conducting this study, the following vessels were at PSNS:

Hull Number	Wetted-Surface Area (ft ²)
647	27,000
601, 588, 585, 591, 593	24,378 × 5
623, 616	43,650 × 2
609	42,000
Total	278,190

At the rates mentioned above, these vessels collectively contribute 12.7 kg Zn/day (total).

Copper

The budget for copper includes the vessels mentioned in the above zinc analysis in addition to the following ships:

Hull Number	Wetted-Surface Area (ft ²)
Total from above	278,190
CGN 35	40,260
CGN 36	37,755
CVN 70	159,500
AS 12	22,000
AOE 1, 2	103,520 × 2
Total	744,745

A value of 50,000 µg Cu/m²day was yielded by copper leach-rate tests carried out for many years here at NCCOSC, NRaD, on panels coated with F121 paint (a common antifouling paint historically used by the Navy). Currently, less toxic antifouling methods are being employed; however, the vessels listed above were more than likely painted with F121 paint. Using this information, the Navy vessels collectively discharge approximately 3.5 kg Cu/day (dissolved).

1. Personal communication, Gordon Smith, DTRC.

NON-NAVY VESSELS

Zinc

Approximately 900 non-Navy vessels are estimated to be moored in the Sinclair Inlet.² The average vessel uses approximately 100 lbs of zinc anode protection (shaft zincs and plate zincs) per year. (Anodes totaling 10 lbs are replaced every 6 months and are about 50 percent spent.³ The total discharge from non-Navy vessels is thus **11.3 kg Zn/day** (total).

Copper

If the average submerged surface area is 35 by 10 feet, and antifouling paint leaches copper at a rate of 50,000 $\mu\text{g Cu/m}^2\text{day}$, non-Navy vessels discharge approximately **2.1 kg Cu/day** (dissolved).

CITY OF BREMERTON EFFLUENT DISCHARGE

According to the 11 August 1993 NPDES permit for the City of Bremerton (permit number WA-002928-9),⁴ the 1992 yearly average flow of the Bremerton outfall was 6.0 mgd. The 1990 yearly average effluent concentrations of copper and zinc were 39.8 and 102 $\mu\text{g/l}$, respectively, for a final discharge of:

Element	Effluent Discharge (total) (kg/day)
Cu	0.90
Zn	2.3

PUGET SOUND NAVAL SHIPYARD OUTFALL DISCHARGE

Outfalls 18 and 19 of the PSNS were monitored in December 1992 for copper, lead, and zinc (Technical Information Fact Sheet in association with NPDES permit WA-000206-2).⁵ The average discharge rates for these two outfalls are 2.8 and 5.24 mgd, respectively. Results are given as total/dissolved.

Element	Outfall 18 ($\mu\text{g/l}$)	Outfall 19 ($\mu\text{g/l}$)	Outfall 18 Discharge (kg/day)	Outfall 19 Discharge (kg/day)	Combined Discharge (total/dissolved) (kg/day)
Cu	35/16	19/7	0.37/0.17	0.38/0.14	0.75/0.31
Pb	28/1	5/1	0.28/0.01	0.10/0.02	0.38/0.03
Zn	1176/32	708/10	12.1/0.33	14.2/0.20	26.3/0.53

2. Personal communication, Harbor Master.

3. Personal communication, Dave Bear, Bear Underwater Services, San Diego, CA.

4. Washington State Department of Ecology, 1993. National pollutant discharge elimination system waste discharge permit #WA-002928-9 for the City of Bremerton, WA, issued 11 August 1993.

5. Washington State Department of Ecology, 1993. National pollutant discharge elimination system waste discharge permit #WA-000206-2 for the Department of Defense, Department of the Navy, Puget Sound Naval Shipyard, Bremerton, WA, Technical Information Fact Sheet Public Notice, dated 23 July 1993.

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