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Quantifying *In Situ* Metal Contaminant Mobility in Marine Sediments

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EXECUTIVE SUMMARY

This report summarizes the work conducted to demonstrate and validate the use of the Benthic Flux Sampling Device (BFSD) for quantifying *in situ* metal contaminant mobility in marine sediments. A complete description of the equipment, processes, and methods is given. Test and demonstration results along with analysis and interpretation are included in the report. Performance and cost analysis is also included. The specific objectives of the project were as follows:

1. Evaluate the quality of water samples collected using the BFSD, specifically for use in determining if a statistically significant flux was occurring at the test locations in comparison to the blank flux results for the BFSD.
2. Evaluate the BFSD for repeatability.
3. Evaluate the logistical and economic resources necessary to operate the BFSD.
4. Evaluate the range of conditions in which the BFSD can be operated.

The California Environmental Protection Agency’s Technology Certification Program was selected for independent evaluation of the performance objectives. A set of detailed performance claims that embodied the above project objectives were established. A replicate series of three full system blank equipment tests were conducted to statistically establish system baseline performance. Two formal demonstrations were then conducted with evaluator oversight. The demonstrations used contaminated sites in San Diego Bay, CA, and in Pearl Harbor, HI, where fundamental differences allowed the evaluators a broad set of results to compare with claimed performance. Standardized processes and methods were followed. Pre- and post-deployment preparations, logistics, material, and labor costs were also evaluated.

The project met its objectives. The two demonstrations were successful and provided evaluators adequate results for comparison with claimed performance. The Benthic Flux Sampling Device has been certified by the California EPA. Sponsorship for this 3-year project was provided by the Environmental Security Technology Certification Program under the Office of the Deputy Undersecretary of Defense (Environmental Security).

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1. INTRODUCTION

1.1 BACKGROUND

Contaminants enter shallow coastal waters from many sources, including ships, shoreside facilities, municipal outfalls, spills, and non-point-source runoff. Sediments are typically considered a primary sink for these contaminants. Sediments in many bays, harbors, and coastal waters used by the Department of Defense (DoD) are contaminated with potentially harmful metal and organic compounds. DoD is required by the Comprehensive Environmental Resource Conservation and Liability Act, as amended by the Superfund Amendment and Reauthorization Act of 1986 (CERCLA/SARA), to assess and, if necessary, remove and remediate these sites and discharges to protect the public health or welfare of the environment.

To determine whether contaminants are moving into, out of, or remaining immobilized within the sediments, contaminant flux must determined. Variations in sediment chemical and physical properties make it impossible to rely on bulk sediment contaminant concentrations alone to predict contaminant flux, bioavailability and, therefore, toxicity. Diagenetic reactions in surface sediments control contaminant pore water gradients, and the direction and magnitude of these gradients control the diffusive flux across the sediment–water interface. These fluxes can be calculated from measurements of contaminant pore water gradients and sediment physical properties. However, in some coastal areas pore water gradients are very steep and, therefore, difficult to measure. Flux calculations based on pore water gradients also only provide the diffusive component of a contaminant flux. An additional concern in coastal areas is that biological irrigation by infauna and wave- or current-induced flushing may provide a larger flux component through advection of water through the sediments. To avoid these problems, a direct measurement of contaminant flux in coastal areas is often the best method to assess contaminant mobility across the sediment–water interface. This direct measurement can be made with a flux chamber that isolates a volume of seawater over the sediments to quantify contaminant flux across the sediment–water interface.

The Benthic Flux Sampling Device 2 (BFSD2) is an instrument for measuring contaminant fluxes from marine sediments. The instrument is a commercialized version of the original prototype BFSD used during development and is adapted from benthic flux chamber technology developed in oceanography for studying the cycles of major elements and nutrients on the seafloor. The BFSD2 is an autonomous instrument for *in-situ* measurement of toxicant flux rates from sediments. The BFSD2 measures a flux out of or into the sediment 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.

Figure 1 shows the BFSD2, including its pyramid-shaped tubular frame, open-bottomed chamber, and associated sampling and control equipment. At the top of the frame is an acoustically released buoy for BFSD2 recovery. At the bottom of the frame is an open-bottomed chamber and associated sampling gear, flow-through sensors, a data acquisition and control unit, a video camera system, a power supply, and an oxygen supply system.

Figure 1. Benthic Flux Sampling Device 2.

The BFSD2 provides a unique way to evaluate the significance of in-place sediment contamination. Knowledge of the degree to which contaminants remobilize is essential in defining the most cost-effective remedial action at impacted sites. No other viable method exists for direct quantification of sediments as sources. At sites where it can be demonstrated that remobilization of contaminants is limited, significant cost savings might be achieved through reduction of cleanup costs. This limitation may often be the case because many contaminants are strongly sequestered within the sediment and not likely to leach out. Estimated disposal costs for contaminated sediments range from $100 to $1000/cubic yard. A recent survey of Navy shoreside facilities indicated that of the 31 facilities that responded, 29 reported contaminated sediment sites. The actual volume of contaminated sediment at these sites is not well-documented; however, even conservative estimates suggest that millions of cubic yards of material may exceed typical sediment quality guidelines.

1.2 OFFICIAL DoD REQUIREMENT

This project addresses the DoD/Navy requirement for compliance, cleanup assessment, and remediation decisions using innovative technology to directly quantify the mobility and bioavailability of contaminants in marine sediments. Marine sediments are a repository for contamination from various sources. The degree to which these contaminants remobilize into the environment largely determines the environmental risks.

1.2.1 Addressing Requirements

The technology demonstrated in this project provides a way to quantify risks and supports the overall goal of cost-effective, risk-based environmental cleanup. This technology provides a basis for risk-based decision-making and potential cost savings by

1. Improving methods for measuring bioavailability for contaminated sediment.
2. Minimizing cleanup requirements at sites where contaminants are not remobilizing.
3. Evaluating the integrity of natural and remedial sediment caps.
4. Providing a direct measure of the time scale of natural attenuation.
5. Documenting the actual contaminant contribution of sediments relative to other sources.

1.3 DEMONSTRATION OBJECTIVES

The primary objective of the BFSD2 demonstration was to perform deployments at contaminated sites in San Diego Bay, California, and Pearl Harbor, Hawaii, under the observation of California Environmental Protection Agency (EPA) certification evaluators. Other observers, including local, state, and federal regulators, Remediation Program Managers, academic, industry, and other DoD agencies also attended. Each site offered different validation opportunities. San Diego Bay showed instrument repeatability and compared historical trends, and Pearl Harbor showed site differences and geochemical trend analysis. The specific planned objectives of the demonstrations were as follows:

1. Evaluate the quality of water samples collected using the BFSD2; specifically for use in determining if a statistically significant flux was occurring at the test locations in comparison to the blank flux results for the BFSD2.
2. Evaluate the BFSD2 for repeatability.
3. Evaluate the logistical and economic resources necessary to operate the BFSD2.
4. Evaluate the range of conditions in which the BFSD2 can be operated.

Other objectives included exposure of various user communities to the technology to encourage continued interest and applications.

1.4 REGULATORY ISSUES

There were no regulatory permitting issues associated with BFSD2 deployment. Collecting sediment samples in a marine environment is considered a nonhazardous activity (although personnel handling samples must follow all safety precautions and limit their exposure to potentially hazardous samples). No hazardous waste was generated during the demonstrations.

BFSD2 is a sample collection instrument and its prototype was the first of its kind to collect sediment–water interface samples for contaminant flux analysis. Because this technology has no equivalent, BFSD2 is evaluated on the internal quality assurance/quality control (QA/QC) for the laboratory analysis and data analysis and interpretation. Although some clean water standards have been set for seawater, only guidelines exist for sediments. Whereas sample handling, preserving, analyzing, and reporting is covered by many established methods and regulations, the primary regulatory issue for BFSD2 involves the integrity of the collected samples to represent ambient conditions. Furthermore, the heterogeneous nature of sediments combined with the complex chemistry of marine aquatic environments requires thoughtful evaluation of all data before making conclusions. The BFSD2 system can routinely produce accurate, precise, and repeatable results; however, the application of these results to site-specific conditions does not lend itself readily to standardized processes. In many cases, BFSD2 results may be used as an additional factor in a "weight-of-evidence" approach for risk-based decisions involving regulator concurrence.

1.5 PREVIOUS TESTING OF THE TECHNOLOGY

Initial development program tests included *ex situ* (laboratory) and *in situ* (field) trials of critical components, subsystems, and systems. Many system development tests were conducted at various locations within San Diego Bay during 1989 through 1991.

Full-scale system trials of the prototype BFSD were conducted in Sinclair Inlet, offshore from Puget Sound Naval Shipyard, Bremerton, Washington, during June 1991 to support an ongoing assessment. Ten deployments of the prototype BFSD were conducted to characterize flux rates of contaminants from seven shipyard sites and three reference sites (no blank test was conducted). Collected samples were analyzed for the trace metals arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn). The tests were successful and results generally showed low release rates (or fluxes) compared to other contaminant sources. Following data review, an active oxygen control subsystem with sensor feedback was developed and implemented along with several other changes to improve operation reliability.

During 1993, four systems tests of the upgraded prototype BFSD were conducted at sites within San Diego Bay: one at Paleta Creek (at its entrance to the bay within Naval Station San Diego), two at a commercial yacht harbor (Shelter Island), and one at a industrial shipping terminal (PACO Industries). The deployments were preceded by a system blank test to determine the lower limits of flux that could be resolved with the prototype BFSD. Several experimental subsystems, including a sensor for laser-induced fluorescence (LIF) investigation of polycyclic aromatic hydrocarbon (PAH) contaminants and an electrode for potentiometric stripping analysis (PSA) of trace metal (Cu and Zn) contaminants were also tested. Results from these deployments showed significant flux rates when compared to blank test results and clear differences between the sites as related to potential trace metal sources. Paleta Creek results showed the highest flux levels for Cd, Cu, Ni, and Zn. See Leather, Chadwick, and Koon (1995).

Seven more prototype BFSD deployments in San Diego Bay supported a sediment quality assessment at Naval Station San Diego during 1995. Paleta Creek was again included along with five other sites near piers and quay walls, and one site outside the study was used as a reference. The work, preceded by a blank test, yielded results that were consistent with the previous study and showed Cd, Ni, Zn, and Mn all to have positive fluxes. Paleta Creek again showed the highest trace metal fluxes, with levels that were generally consistent with those measured 2 years before. Correlations between measured trace metal flux levels and complex marine chemistry processes were studied and informative trends were identified. For example, in the complex oxidation-reduction (redox) marine environment, trace metal fluxes were consistent with oxidation of solid metal sulfides as a sediment source. See Leather, Chadwick, and Koon (1995) for the complete report; an extract is included in quotes below to illustrate an initial interpretation of the Naval Station San Diego results:

"Some of these trace metal flux relationships may be better illustrated with bar charts showing the trends along a series of transects across the study area. Figures 2 and 3 show the trace metal fluxes for the 1995 deployments along with data from the earlier 1993 deployments. The Zn fluxes in figure 2 are so large that the other trace metal fluxes are barely visible, so the other metal fluxes are replotted in figure 3 without Zn. This demonstrates that Zn is, by far, the trace metal with the largest flux out of the sediments. The first site displayed in both figures is the blank run, followed by the east-west transects near Pier 4 (Sites 3, 3r, 1r, and 2) and Paleta Creek (Sites 5, 4, and 6), and finally the 1993 data. Zn, Ni, and Cd fluxes in the 1995 data are high in the east (Sites 3 and 5) and decrease toward the west, and in the 1993 data higher in the central bay sites compared to north bay sites. The trends for Cu and Pb fluxes are less clear, with some sites showing fluxes into the sediments. Cu does, however, show the highest fluxes out of the sediments at Sites 3 and 5 where the sediment concentrations of most metals are high.

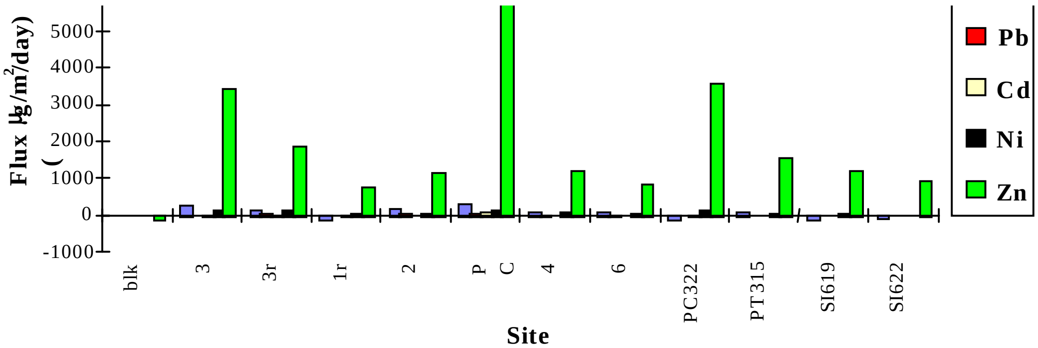


Figure 2. Plot of metal fluxes along east–west transects.

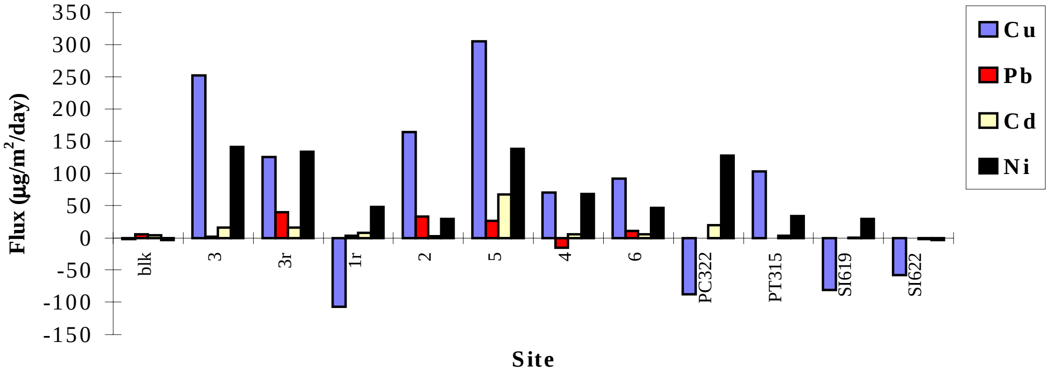


Figure 3. Plot of metal fluxes along east–west transects, excluding Zn.

As the metal showing the consistently highest fluxes from the sediment, Zn serves as the best example to demonstrate the relative remobilization of metals from the sediment back into the water column. To make these estimates of sediment flux from the NAVSTA area, several assumptions must be made. First, the Zn flux will be assumed to be related to the bulk Zn levels in the sediment. This assumption ignores the role played by AVS [acid volatile sulfides] binding or other factors controlling metal fluxes from the sediment. For Zn this may not be a major concern since it is the most soluble metal sulfide and Zn fluxes show the best correlation of any of the metals to bulk metal levels in the sediments. The second assumption is that the six sites where fluxes were measured represent the overall range of fluxes in the NAVSTA area, and bulk metal levels at these sites can be used to extrapolate the fluxes throughout the area depending on bulk metal levels.

Looking at the NAVSTA area sediments out to the west side of the navigation channel, a surface area of approximately 3 million square meters (m^2) is present. From the contour map of Zn concentrations in the sediment chemistry chapter, only approximately 500,000 m^2 are above the ERM value of 410 ppm. The four Zn flux measurements from sediments with these high Zn levels (Sites 1R, 3, 3R, and 5) average 3100 ± 2500 μg/m^2/day. Sediments in the NAVSTA area with Zn levels below ERM values cover approximately 2.5 million m^2 and three flux measurements from sediments with lower Zn levels average 1100 ± 200 μg/ m^2 / day. The overall flux of zinc directly from the sediments in the NAVSTA area is therefore 1500 ±600 kg Zn/ yr."

Finally, as mentioned above, blank tests of the prototype BFSD were conducted to determine the lowest levels of contaminants that could be resolved with the system.

With the prototype BFSD prepared as it would be for a normal deployment, the test was conducted in seawater with the chamber sealed. A time-sequence for sample collection comparable to the planned deployments was used, and the samples were analyzed identical to later site-collected samples. Table 1 lists results for the San Diego Bay tests discussed in this section.

Table 1. San Diego Bay test results.

Compound	Flux ± S. E.	(µg/m^2/day)
	1993	1995
Cadmium	6 ±7	5 ±3
Copper	-71 ±62	-2 ±47
Iron	--	160 ±235
Lead	- 4 ±8	7 ±67
Manganese	--	-52 ±26
Nickel	65 ±69	-4 ±27
Zinc	-227 ±65	-149 ±26

Whereas the prototype BFSD performed successfully and was considered mature enough to begin technology transfer, the process of data analysis and interpretation revealed complexities requiring careful consideration before reaching conclusions. Technology transfer, which is discussed in section 8, began with a competitively awarded firm-fixed-priced contract for BFSD2, which incorporated many changes from the prototype BFSD. A series of *ex situ* and *in situ* tests and checkouts ensured that the instrument retained critical prototype BFSD performance attributes and established functionality of the changed features. A complete series of laboratory (e*x situ*) tests and checkouts were conducted. *Ex situ* tests included the new rotary valve sampling system to ensure reliable performance, the pump and diffuser system with dye-dispersion to ensure adequate mixing, the flow-through sensor system to assure responsive and accurate readings, the vacuum-filled, *in situ*-filtered sample bottles to ensure clog-free operation and adequate fill volume, and the data acquisition and control system to ensure required performance.

2. TECHNOLOGY DESCRIPTION

2.1 DESCRIPTION

Contaminants enter shallow coastal waters from many sources, including ships, shoreside facilities, municipal outfalls, spills, and non-point-source runoff. Sediments are typically considered a primary sink for these contaminants. Where previous shoreside practices have resulted in high concentrations of contaminants in the sediments, contaminants may flux out of the sediments. In areas where pollution prevention and remediation practices have removed other contaminant sources, remaining contaminated sediments may also serve as a primary contaminant source to the water column.

To determine whether contaminants are moving into, out of, or remaining immobilized within the sediments, contaminant flux must be determined. Diagenetic reactions in surface sediments control contaminant pore water gradients, and the direction and magnitude of these gradients control the diffusive flux across the sediment–water interface. These fluxes can be calculated from measurements of contaminant pore water gradients and sediment physical properties. However, in some coastal areas, pore water gradients are very steep and, therefore, difficult to measure. Flux calculations based on pore water gradients also provide only the diffusive component of a contaminant flux. An additional concern in coastal areas is that biological irrigation by infauna and wave- or current-induced flushing might provide a larger component of flux through advection of water through the sediments. To avoid these problems, a direct measurement of contaminant flux in coastal areas is required to assess contaminant mobility across the sediment–water interface. This direct measurement can be made with a flux chamber that isolates a volume of seawater over the sediments to quantify contaminant flux across the sediment–water interface.

The Navy-designed and developed, contractor-fabricated BFSD2 is a flux chamber designed specifically for *in situ* measurement of contaminant fluxes in coastal areas. A chamber of known volume encloses a known surface area of sediment. Seawater samples are collected periodically at timed intervals. After a laboratory has analyzed the samples, and with knowledge of the time intervals between samples, a flux rate between the sediment and water in mass per surface area per unit time (micrograms per square meter per day [$\mu g/m^2/day$]) can be calculated.

The BFSD2 with important components labeled (figure 4) consists of an open-bottomed chamber mounted in a modified pyramid-shaped tubular framework with associated sampling gear, sensors, control system, power supply, and deployment and retrieval equipment. The entire device is approximately 1.2 by 1.2 meters from leg to leg and weighs approximately 175 pounds. The lower part of the framework contains the chamber, sampling valves, sampling bottles, and batteries. The upper frame includes a release that is acoustically burn-wire triggered. The BFSD2 is designed for use in coastal and inland waters to a maximum depth of 50 meters. Maximum deployment time is approximately 4 days based on available battery capacity. Figures 5 and 6 show the two basic configurations for landing and sampling events, respectively.

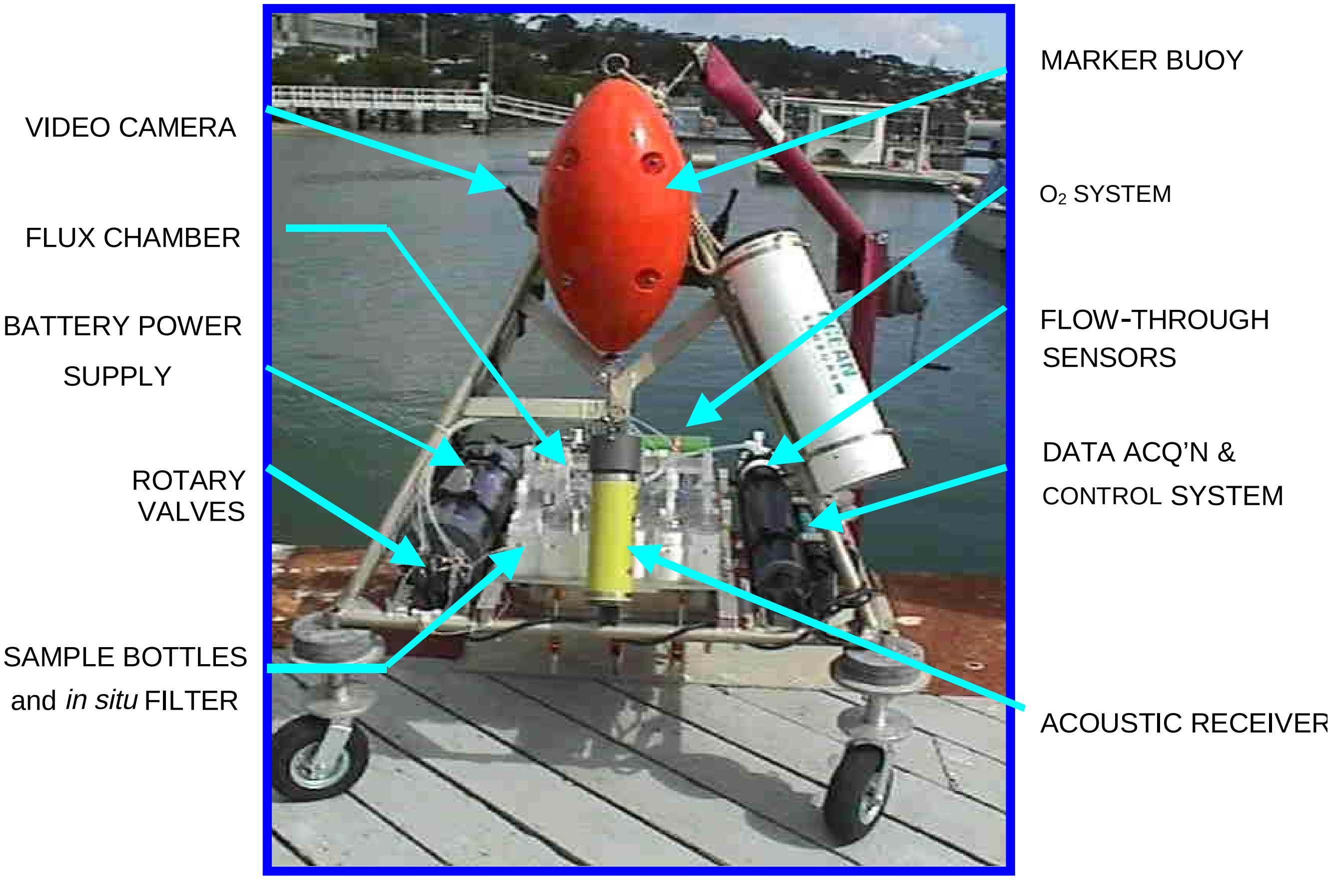
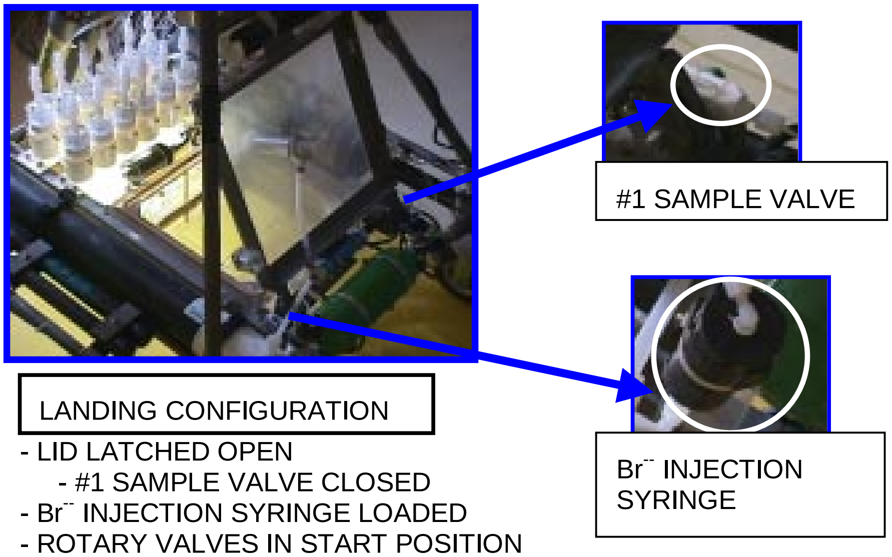


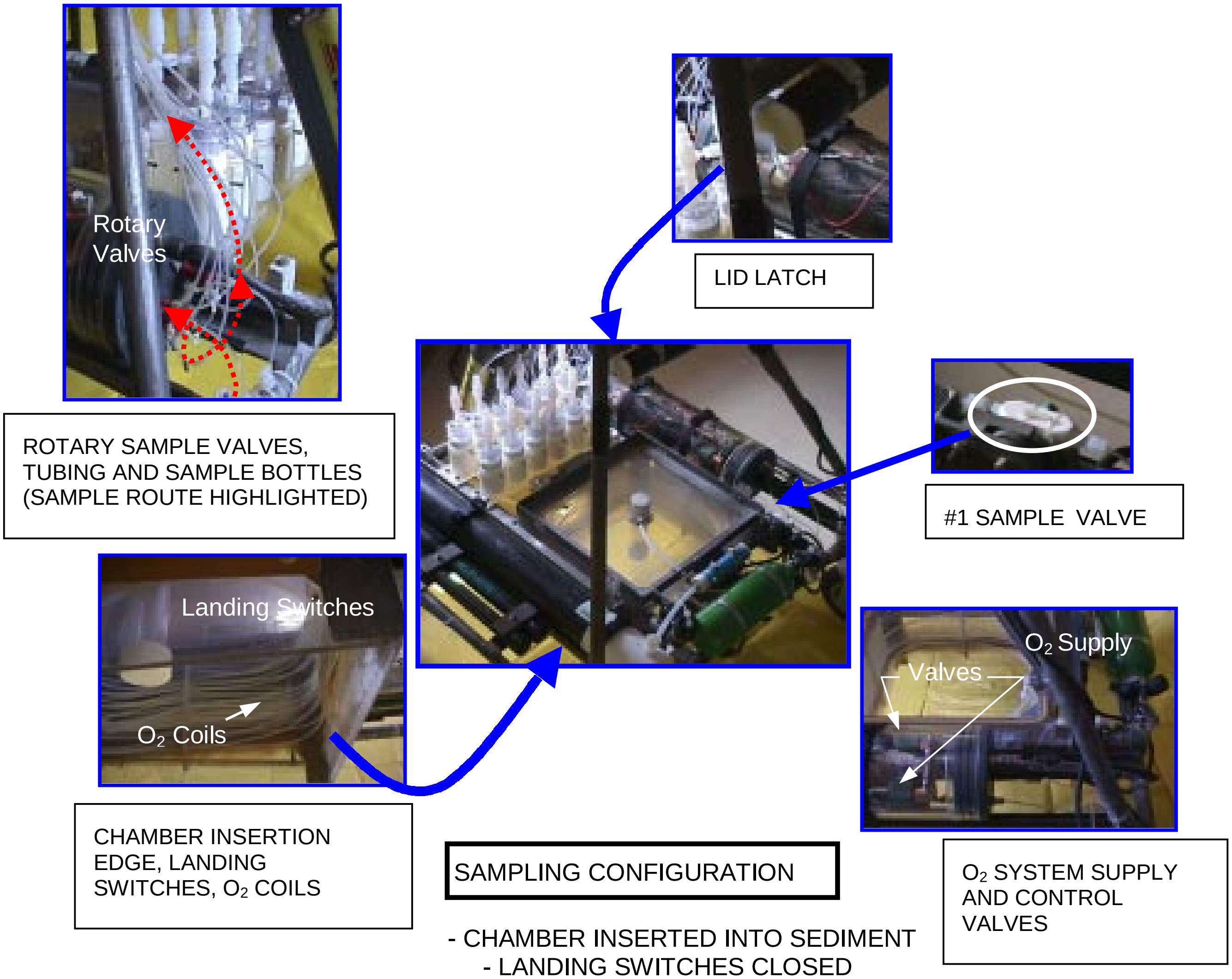
Figure 4. Component breakdown of BFSD2.



LANDING CONFIGURATION

- LID LATCHED OPEN
  - #1 SAMPLE VALVE CLOSED
- Br^{-} INJECTION SYRINGE LOADED
- ROTARY VALVES IN START POSITION
- O_2 SYSTEM LOADED
- SAMPLE BOTTLES >25 in-Hg

Figure 5. BFSD2 landing events.



LID LATCH

#1 SAMPLE VALVE

ROTARY SAMPLE VALVES, TUBING AND SAMPLE BOTTLES (SAMPLE ROUTE HIGHLIGHTED)

CHAMBER INSERTION EDGE, LANDING SWITCHES, O_2 COILS

O_2 SYSTEM SUPPLY AND CONTROL VALVES

SAMPLING CONFIGURATION

- CHAMBER INSERTED INTO SEDIMENT
  - LANDING SWITCHES CLOSED
- LID LATCH ACTIVATED
  - LID CLOSED
- #1 SAMPLE VALVE OPEN
  - SAMPLE BOTTLE #1 FILLED
- Br^{-} INJECTED
- O_2 SYSTEM ACTIVE
  - SUPPLY, VALVES, COILS ENABLED
  - O_2 CONTROL LIMITS SET
- ROTARY SAMPLE VALVES ENABLED
  - SAMPLING PERIOD STARTED

Figure 6. BFSD2 sampling events.

2.1.1 Sampling Chamber

The chamber is a bottomless box, approximately 40 cm square by 18 cm tall, with a volume of approximately 30.0 liters (figure 7). The volume was chosen to allow for a maximum overall dilution of less than 10 percent because of sampling withdrawal into 11 samples of 250 ml each. The chamber is constructed of clear polycarbonate to avoid disrupting any exchanges that may be biologically driven and, thus, light-sensitive. To prevent stagnation in the corners of the chamber, triangular blocks of polycarbonate occupy the 90-degree angles. The top of the chamber is hinged at one edge so that it may be left open during deployment to minimize sediment disturbance. Once the chamber is in place, the computer control system closes the lid. A gasket around the perimeter of the chamber ensures a positive seal between the chamber and the lid. Exact alignment is not required because the lid is slightly larger than the sealing perimeter of the gasket and pivots on two sets of hinges. The lid is held closed by four permanent magnets situated along the chamber perimeter. The bottom of the chamber forms a knife-edge. Pressure-compensated switches mounted on the bottom surface of three sides of a flange circling the chamber at 7.6 cm above the base activate a series of three lights visible with a video camera mounted on the upper frame. Illumination of the lights indicates a uniform minimum sediment penetration depth has been achieved and a that there is good probability that a positive seal between the chamber and the sediment has been achieved.

Figure 7. Chamber enclosure.

Samples are drawn off through a 4-mm Teflon® tube through synchronized parallel rotary valves and into evacuated 250-ml Teflon sampling bottles (figure 8).

Figure 8. Sample bottle assembly.

The first sample is drawn through a 0.45-micron filter into the sample bottle upon closure of the lid at the start of the autonomous operation of the BFSD2; the remaining 11 samples are similarly collected as the synchronized parallel rotary valves are activated at preprogrammed intervals throughout the deployment. The bottles are evacuated to a minimum of 25 inches of mercury before deployment.

2.1.2 Acquisition and Control Subsystem

The acquisition and control unit is an Ocean Sensors Model OS200 conductivity temperature depth (CTD) instrument, modified to allow control of the BFSD2. It consists of a data logger that acquires and stores data from sensors and a control unit that regulates sampling and other functions of the BFSD2. The data logger collects data from a suite of sensors housed in the CTD and connected to the chamber through a flow-through loop. A small constant-volume pump maintains circulation in the flow-through system to the sensors and is also used to maintain homogeneity of the contents of the chamber using a helical diffuser mounted vertically on the central axis of the box. The control unit closes the lid, activates the flow-through/mixing pump, activates dissolved oxygen control valves, and controls activation of the synchronized parallel rotary sampling valves.

Commercial sensors, installed by Ocean Sensors, Inc., are mounted in the CTD instrument housing and are connected to the chamber by a flow-through pump and circulation plumbing. Sensors monitor conditions within the chamber, including conductivity, temperature, pressure, salinity, pH, and dissolved oxygen (figure 9). Circulation in the flow-through sensor system is maintained using a constant flow rate pump adjusted to approximately 15 milliliters per second (ml/sec).

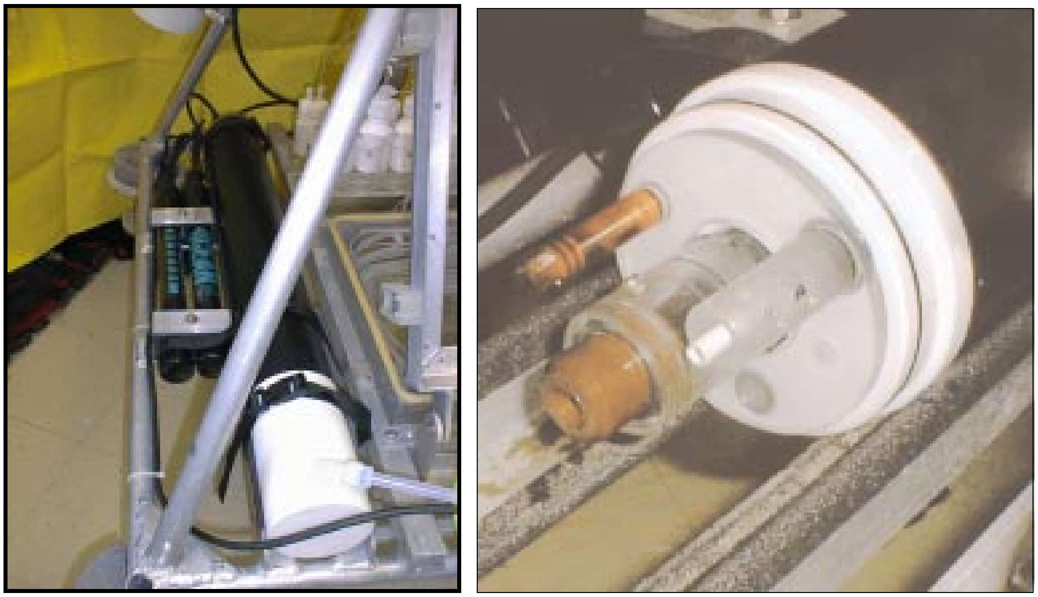


Figure 9. Flow-Through sensor system.

2.1.3 Sampling Subsystem

Discrete samples are obtained using a vacuum collection approach consisting of sample containers, fill lines, in-line filters (with 0.45-micron membrane filters), check valves, and synchronized parallel rotary valves connected to the chamber fill line. Off-the-shelf 250-ml Teflon® collection bottles are modified to allow filling through the cap. Sampling containers of any volume, material, or shape may be used, provided the cap can be modified to accept the fill line connection, the bottle walls are strong enough to withstand the pressure at the sampling depth, and the cap seal is airtight and watertight at the sampling depth pressure. Glass, Teflon®, and polycarbonate bottles have been tested and used successfully with the prototype BFSD. All valves, fittings, and tubes are made of Teflon® or other nonmetallic materials to minimize potential metal contamination of samples and to facilitate cleaning. Samples are drawn from the chamber through a 4-mm Teflon® tube connected to the rotary valves and into the sampling bottles. Sampling is initiated by the control system when it activates the valves at preprogrammed intervals. Seawater samples are drawn through the sampling system by a vacuum of 25 inches of mercury (minimum) that is applied to all sample bottles through check valves mounted in the bottle lids. The check valves are then sealed, and water enters each sample bottle when the rotary valves are activated (number 2 through 12) or when the lid closes and opens a valve attached to its hinge (number 1). Filtered seawater flows into each bottle until pressure is equalized, normally yielding at least 240 ml.

2.1.4 Circulation Subsystem

The BFSD2 has a mixing area called the collection chamber and the process of interest is the exchange of chemical contaminants at the sediment–water interface sequestered within the chamber. The hydrodynamics inside the chamber must adequately simulate movement of water from near-bottom currents outside the chamber. A helical diffuser mounted vertically on the central axis of the chamber mixes the enclosed volume. Tests recorded on video verified that the helical diffuser provided a uniform, gentle mixing action that effectively dispersed dye injected into the chamber without disturbing the sediment layer on the chamber bottom.

The diffuser system includes a standard constant-volume submersible pump. The pump circulates water from an outlet in the chamber wall into the sensor chamber and over the flow-through sensors and back into the chamber through a rigid polycarbonate tube. The vertically mounted tube is capped at the discharge end and has 5-mm holes drilled in a helix pattern along its length. The tests verified that this method visually dispersed a dye injection of Rhodamine in less than 120 seconds.

The acquisition and control unit, the oxygen supply bottle, a video camera and lighting system, circulation pumps, and the retrieval line canister are mounted on the frame members. The oxygen system maintains aerobic conditions within the chamber by diffusing oxygen at a rate sufficient to maintain the initial dissolved oxygen levels through a coil of thin-walled, oxygen-permeable Teflon® tubing.

2.1.5 Oxygen Control Subsystem

During an experiment, conditions in the isolated volume of seawater within the flux chamber begin to change from the initial conditions observed in the bottom water. Oxygen content is one factor that changes rapidly because isolated volumes of seawater in contact with the sediment surface will become anoxic without any resupply of oxygen. Since the fluxes of many contaminants, especially metals, are sensitive to redox conditions, the oxygen content is one of the most important factors that must be monitored and regulated within the flux chamber. Most contaminant fluxes are not large enough to be measured in chambers without oxygen regulation because the isolated volume of seawater will become anoxic before significant contaminant fluxes have occurred. Because of this, an oxygen control system has been built into the BFSD2. This system maintains the oxygen levels in the chamber within a user-selected window about the measured bottom water oxygen level.

The oxygen-regulating system consists of a supply tank, pressure regulator, control valves, diffusion coil, oxygen sensor, and control hardware and software. The supply tank is a 13-cubic-foot aluminum diving tank equipped with a first-stage regulator that allows adjustment of output pressure to the system. The control valves are housed within a watertight pressure case with connections through bulkhead fittings on the end cap. The diffusion coil is thin-walled, 4-mm, oxygen-permeable, Teflon® tubing approximately 15 meters long. Oxygen is monitored using the oxygen sensor in the flow-through system described previously. The oxygen control valves (pressurize or vent) activation is incorporated into the BFSD2 control system.

During a typical deployment, when the flux chamber is initially submerged, the ambient oxygen level in the water is measured with a control program that activates the circulation subsystem and sensors until a stable value of ambient oxygen concentration is obtained. This mesurement is performed with the BFSD2 either on the bottom or suspended less than 1 meter above the sediment (with the lid open). When oxygen stability is obtained, the user then establishes a maximum and a minimum oxygen control level, based on a user-specified range around the stable ambient level. Figure 10 shows a typical set of data obtained from 15 minutes of operation. The control limits are entered into the operational control program and downloaded to the BFSD2 acquisition and control subsystem. When autonomous operations are started and the chamber is closed and sealed, the oxygen level inside the chamber is monitored by the control program. If the level drops below the allowable minimum, a control valve is momentarily opened, the diffusion coil is pressurized, and the oxygen level in the chamber begins to increase. When the oxygen level reaches the maximum allowable level, another control valve is activated and the pressurized tubing is vented. This sequence is repeated continuously during deployment, maintaining the oxygen level in the chamber near the ambient level. Figure 11 is a typical set of data obtained from a 72-hour deployment.

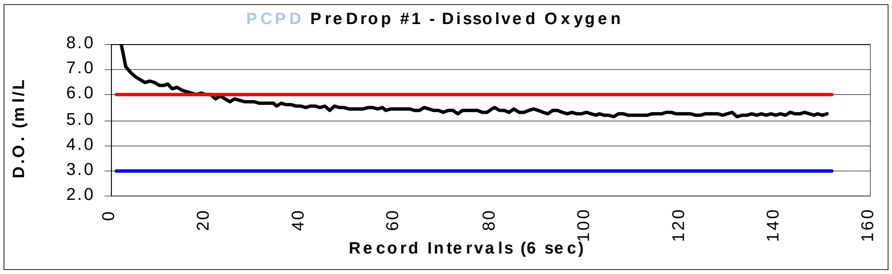


Figure 10. Ambient oxygen data.

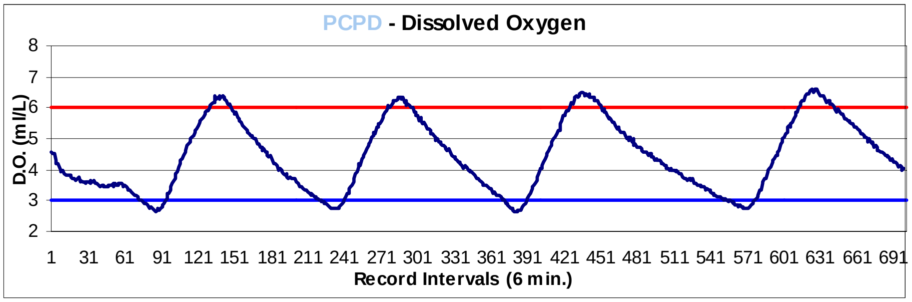


Figure 11. Operational oxygen control data.

2.1.6 DEPLOYMENT AND RETRIEVAL SUBSYSTEMS

During deployment, the test site is surveyed for obstacles with a light-aided video camera mounted on the upper frame of the BFSD2 using an on-deck television monitor. As figure 12 shows, a deployment cable and release line lower the BFSD to its intended depth for the video inspection. Following either rapid or slow descent to the bottom, the minimum depth of collection chamber insertion is sensed by pressure-compensated switches, which activate lights mounted on the chamber frame. These lights are TV-monitored on deck.

Recovery is accomplished by transmitting a coded acoustic signal to the frame-mounted receiver, which, in turn, releases the marker buoy (figure 13). As figure 14 shows, the line attached to the buoy lifts the BFSD2 aboard the vessel. Stored sensor data are uploaded before detaching the cables.

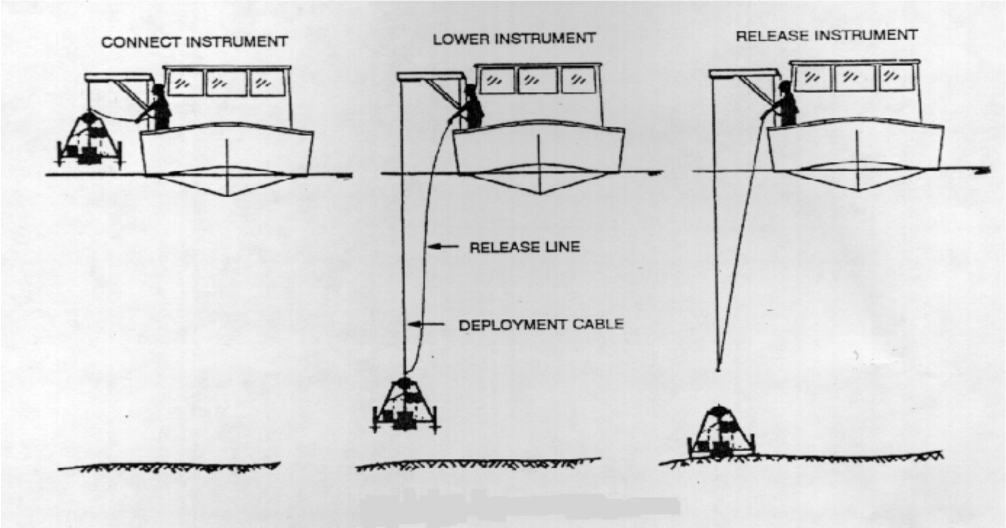


Figure 12. BFSD deployment.

Figure 13. Acoustic release and retrieval buoy.

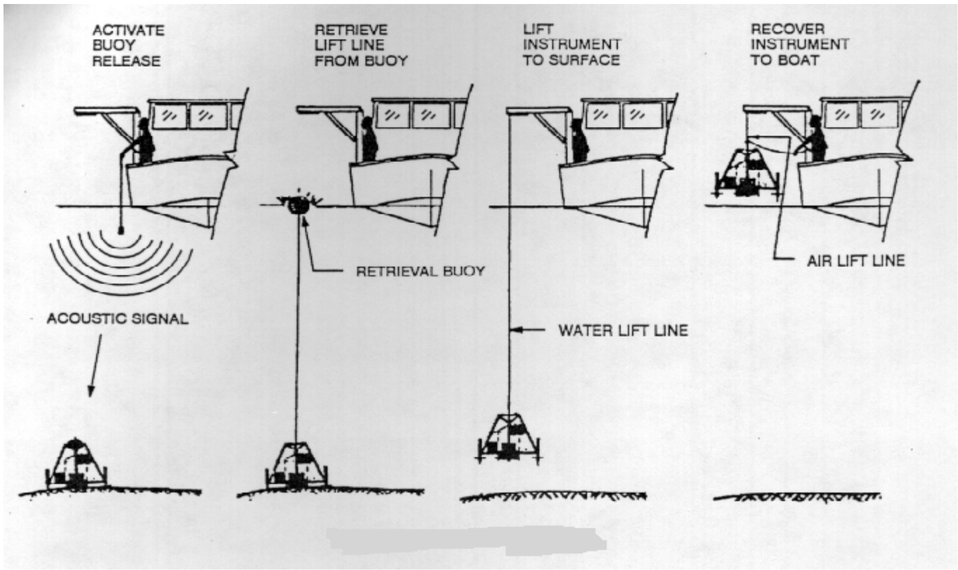


Figure 14. BFSD retrieval.

2.1.7 Analytical Methods

2.1.7.1 Cleaning. Before each deployment, the BFSD2 sample collection system is cleaned and decontaminated. A sequential process of flowing cleaning fluids through the sampling subsystem using a vacuum, soaking disassembled parts (collection bottles and other parts) in prepared solutions, physically brushing and rinsing the collection and sensor chambers and the circulation subsystem with prepared solutions is followed. A nitric acid soak/rinse is used before a final rinse with 18 meg-ohm de-ionized water and sealing/closing off all paths of contamination until deployment.

2.1.7.2 Performance Indicators. A series of performance indicators are used to evaluate the data obtained during operational deployments. One performance indicator is the chemistry time-series data for silica. Silica, a common nutrient used in constructing the hard parts of some planktonic organisms, typically shows a continuous flux out of the sediments because of degradation processes. The linear increase in silica concentration with time in the collected sample bottles is therefore used as an internal check for problems such as a poor chamber seal at the lid or sediment surface. A field analytical test set (Hach Model DR2010) is used to assess the silica concentrations immediately following retrieval and before sending collected samples to the analytical laboratory. Figure 15 is an example of silica flux, indicating an adequate chamber seal with the sediment. Also, with a good chamber seal, the ongoing bacterial degradation of organic material in the sediment consumes oxygen (which must be regulated by the BFSD2) and also generates carbon dioxide. This gradually lowers the chamber pH. Figure 16 is an example of these data for a good chamber seal with the sediment.

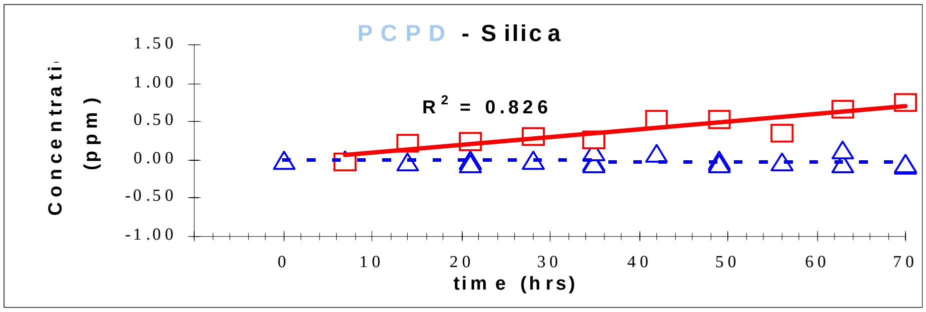


Figure 15. Silica flux for good chamber seal.

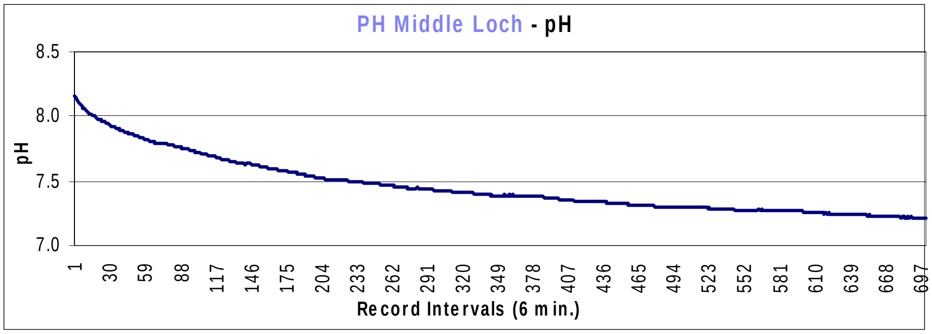


Figure 16. pH data for good chamber seal.

Although the expected relationships of these performance indictors aid in determining normal or successful deployments, natural variability is always present to cloud these relationships. Variations in the pore water reactions at the various sites lead to differences in the observed fluxes of oxygen, silica, and the other contaminants. One major factor contributing to the large variations in fluxes might be burrowing activity. Enhanced biological irrigation (pumping of the overlying seawater through sediment burrows by infaunal organisms) increases the surface area of the sediment–water interface and flow rates across the interface, and might also increase the observed fluxes. The organisms responsible for this biological pumping will also affect oxygen uptake rates and may add to the complex interpretation of the analytical results.

2.1.7.3 Blank Tests. Before the BFSD2 demonstrations, a triplicate blank test was performed to determine the lower limit of resolution for flux determinations of various metals. A polycarbonate panel was sealed across the bottom of the chamber, and the BFSD2 was lowered to within several meters of the sediment surface. A standard operational program identical to the demonstration deployments was run for 70 hours. The results are presented later in this report.

2.1.7.4 Computations. Fluxes are computed from the trace metal concentrations in each sample bottle using a linear regression of concentration versus time after the concentrations are corrected for dilution effects. These dilution effects result from intake of bottom water from outside the chamber to replace the water removed for each collected sample. The corrected concentrations are obtained from the following equation:

$$[C_n] = [s_n] + \frac{v}{V}\left(\left(\sum_{i=1}^{n-1}[s_i]\right) - (n-1)[s_0]\right),$$

where **[*C*]** is the corrected concentration, **[*s*]** is the measured sample concentration, ***n*** is the sample number (1 through 6), ***v*** is the sample volume, and ***V*** is the chamber volume. Fluxes are then calculated as follows:

$$Flux = \frac{mV}{A},$$

where ***m*** is the slope of the regression of concentration versus time, ***V*** is the chamber volume, and ***A*** is the chamber area.

An interactive computational spreadsheet processes most of the data. Analytical laboratory results, sensor and other measured data, performance indicator results, and blank test results are entered into the spreadsheet template and processed. A series of tables, charts, and graphs are computed and displayed, including statistical confidence and other figures of merit. Appendix C provides a set of spreadsheet products for each demonstration.

2.2 STRENGTHS, ADVANTAGES, AND WEAKNESSES

2.2.1 Strengths

The BFSD2 is an *in situ* technology. Benthic contaminant fluxes can provide a unique *in situ* measure of contaminated sediments as well as an indication of bioavailability. Many of the disadvantages cited for various approaches toward assessing sediment contamination relate to removal of the contaminated material to the laboratory for chemical and biological assays. In concert with traditional monitoring and assessment techniques, these flux measurements can lead to a better understanding of marine sediment contamination and transport mechanisms.

2.2.2 Advantages

The BFSD2 is an easily implemented technology, as it is readily deployed from a small boat, and all sampling, data logging, and control functions are performed automatically based on preprogrammed parameters. The BFSD2 can collect samples without diver assistance to minimize costs, sampling time, and safety issues associated with sampling activities. Furthermore, the system collects a wide range of contaminants, nutrients, and dissolved gases and is operational under a various environmental conditions. All materials used in the system are suitable for use and prolonged exposure in the marine environment.

Results obtained using the BFSD2 can be used for the following purposes:

- Source quantification for comparison to other sources and input to models
- Indication of bioavailability because many studies indicate that resolubilized contaminants are more readily available for uptake

- Determination of the cleansing rate of a contaminated sediment site because of natural biogeochemical cycling of in-place contaminants
- Provision of a nonintrusive monitoring tool for sites that have been capped or sealed to minimize biological exposure
- Testing and validation of hypotheses and models for predicting the response of marine sediments to various contaminants

2.2.3 Weaknesses

The BFSD2 is currently validated and certified for metals-contaminated sediments only. It is configured with unique attributes specifically applicable to collection of samples for trace metal analyses. Although the prototype BFSD established the applicability of the technology to organic sediment contaminants, rigorous engineering and validation studies have not been completed.

Another limitation is a lower limit on the flux rates that can be calculated from data collected using the BFSD2 system. Also, the BFSD2 may be deployed to a maximum depth of 50 meters, and the maximum deployment is approximately 4 days, based on available battery capacity. The BFSD2 is stable in bottom currents up to 3 knots.

2.3 FACTORS INFLUENCING COST AND PERFORMANCE

2.3.1 Cost influences

The factors influencing cost include, in order:

1. **Analytical Laboratory Costs.** Laboratory analysis of samples by highly specialized analytical laboratories accounts for approximately 50% of total BFSD2 project costs.
2. **Blank Tests.** The larger the number of sites within a common bay, harbor, or other defined location, the smaller the proportional cost per site for blank tests. It may be possible to eliminate blank testing in some cases, but a cost approaching 50% could occur for only one deployment.
3. **Remote Location.** Acquisition of local resources such as a surface vessel configured with a davit or A-frame and equipment shipping costs influence total project costs the most. Transportation, per diem, materials, and supplies are equivalent for all sites other than local ones. Labor costs are the same.
4. **Work Schedule.** Limited site access or availability can influence cost. Without such restraints, a work schedule taking advantage of *in situ* BFSD2 deployment periods over weekends and/or to accomplish cleaning, sample handling, and other turnaround preparations can be instituted. Extended work hours can be compensated with offsetting periods of inactivity.

2.3.2 Performance Influences

The factors influencing performance include:

1. **Sediment Physical Conditions.** The BFSD2 requires a collection chamber seal with the sediment to function properly. The primary cause for lack, or loss of seal, is porosity of the sediment because of large grain size and distribution. An entire deployment can be lost under

extreme conditions; however, performance indicators can avoid analytical laboratory costs by identifying such cases immediately after retrieval.

2. **Sediment Contamination Levels.** The lower limit for resolving significant flux levels is based on blank test results. Sites having contaminated sediment levels lower than blank test results cannot be resolved with a high degree of confidence. Such results are reported as statistical probabilities with confidence limits and are typically well below water quality limits and do not lead to cleanup issues.

3. **Site Marine Conditions.** As with number 1 above (sediment-chamber seal), the BFSD2 must also maintain a good chamber-lid seal. Surface vessel turbulence and/or prop wash, tidal and/or local currents, or even large fish disturbances can jar the magnetically held lid. A momentary loss of the lid seal can allow ambient seawater to enter the chamber and refresh sequestered sample water. Although such an event will be detected by the previously discussed performance indicators, some or all of the deployment can be negated by loss of lid seal.

4. **Target Analytes.** The BFSD2 is configured for collection of water samples for trace metals analyses. Materials in contact with sample water, minimum sample volume and collection chamber dilution, filtering, hold time, sample preservation and handling, cleaning and decontamination, and numerous other facets of the BFSD2 have been designed specifically for trace metal applications. Use of BFSD2 for collection of water samples for organic contamination analysis would be influenced, as a minimum, by small sample size and *in situ* filtering. Laboratory detection limits for extraction-type analyses would likely be too high for practicable use.

3. SITE/FACILITY DESCRIPTION

3.1 BACKGROUND

Two locations were selected for BFSD2 demonstrations. The first was San Diego Bay, California (Paleta Creek area), and the second was Pearl Harbor, Hawaii (Middle Loch and Bishop Point). The locations/sites were selected based on the following criteria:

1. The sites were known to have metal-contaminated marine sediments and had been at least partially characterized. The sediment contaminant levels were anticipated as high enough to demonstrate statistically significant fluxes at the sediment–water interface.
2. Two deployments at the same San Diego Bay, Paleta Creek site would demonstrate repeatability; two deployments at geographically different Pearl Harbor sites would demonstrate characteristically different data and showcase analysis/interpretation results.
3. The contaminated sediments were located in shallow areas (less than 50 meters deep) and readily accessible.
4. Logistical support requirements would be demonstrated by deployments in Pearl Harbor.
5. Data from prototype BFSD deployments conducted at the Paleta Creek site were available for use as reference data and for comparison with demonstration results (see section 1.5).

3.2 SITE/FACILITY CHARACTERISTICS

3.2.1 San Diego Bay, California

With no major inputs of fresh water, the currents and residence time of water in San Diego Bay are tidally driven. The average depth of the bay is about 5 meters. The tidal range from mean lower low water to mean higher high water is about 1.7 meters. The maximum tidal velocity is about 0.05 to 0.1 meters per second. Sediment pore waters in San Diego Bay typically become anoxic several millimeters below the sediment surface. Dissolved oxygen concentrations range from 4 to 8 milliliters per liter, seawater pH varies from 7.9 to 8.1, and temperatures range from 14 to 25°C.

The sediments of San Diego Bay consist primarily of gray, brown, or black mud, silt, gravel, and sand. The sources of contamination in San Diego Bay have varied over time and include sewage, industrial wastes (commercial and military), ship discharges, urban runoff, and accidental spills. Current sources of pollution to San Diego Bay include underground dewatering, industries in the bay area, marinas, and anchorages; Navy installations; underwater hull cleaning and vessel antifouling paints; and urban runoff. Known contaminants in the bay include arsenic, copper, chromium, lead, cadmium, selenium, mercury, tin, manganese, silver, zinc, tributyltin, polynuclear aromatic hydrocarbons (PAH), petroleum hydrocarbons, polychlorinated biphenyls (PCB), chlordane, dieldrin, and DDT.

The Paleta Creek site (figure 17) is located in San Diego Bay in San Diego County, California, adjacent to Naval Station San Diego. The Paleta Creek site is located on the western shore near Naval Station San Diego where Paleta Creek empties into the bay, slightly inland from the Navy Pier 8 and Mole Pier, and north of Seventh Street. Naval Station San Diego began operations in 1919 as a docking/fleet repair base for the U.S. Shipping Board. In 1921, the Navy acquired the land for use as the San Diego Repair Base. From 1921 to the early 1940s, the station expanded as a result of land acquisitions and facilities development programs.

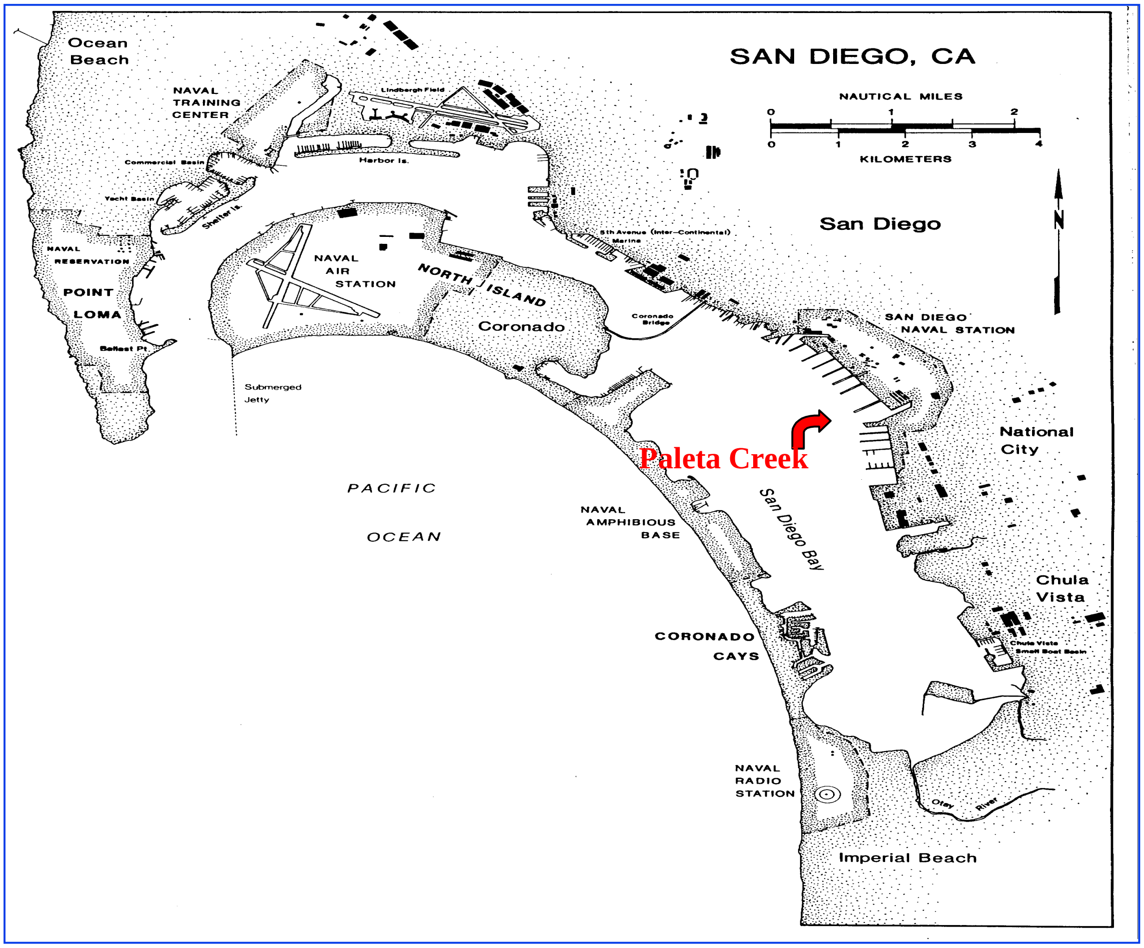


Figure 17. San Diego Bay, Paleta Creek site.

3.2.2 Pearl Harbor, Hawaii

Pearl Harbor contains 21 square kilometers of surface water area; the mean depth is 9.1 meters. Tidal flow and circulation are weak and variable, with a mean tidal current velocity of 0.15 meter per second and a maximum ebb flow of 0.3 meter per second in the entrance channel. Salinity in Pearl Harbor ranges from 10 to 37.5 parts per thousand, with a yearly average of 32.8 parts per thousand. Harbor water temperatures annually range from 22.9 to 29.4°C, and dissolved oxygen values range from 2.8 to 11.0 milligrams per liter. Pearl Harbor is most appropriately described as a high-nutrient estuary.

Middle Loch is located in the northwestern end of Pearl Harbor, north and west of Ford Island, within the Pearl Harbor Naval Base (figure 18).

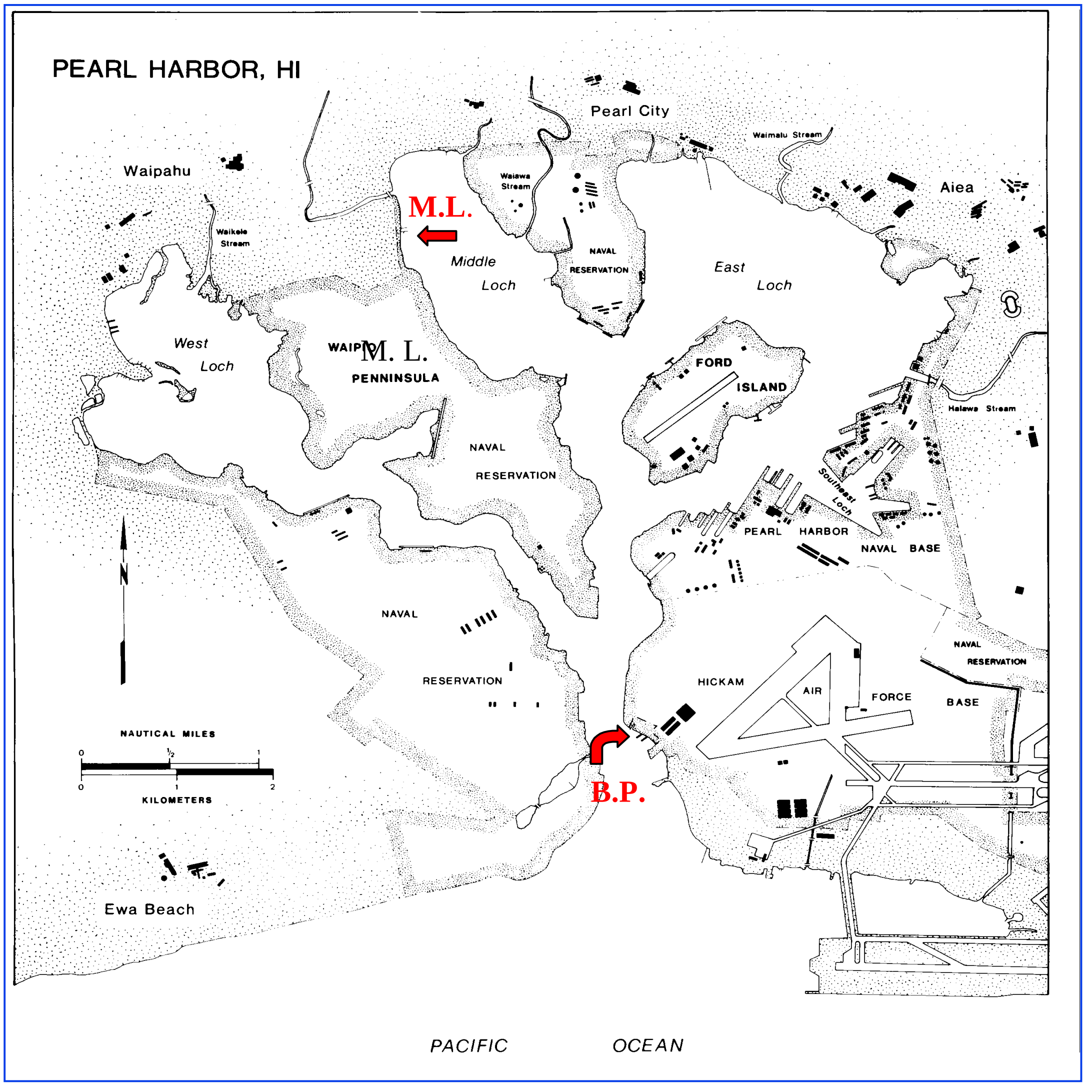


Figure 18. Pearl Harbor, Hawaii (Middle Loch and Bishop Point sites).

In 1901, the U.S. Navy acquired 800 acres of land to establish a naval station at Pearl Harbor. The Pearl Harbor Naval Base has existed since 1919. During World War I, about 12 warships were repaired and overhauled at the Navy Yard. In 1917, a temporary submarine base was relocated to the eastern shoreline of Southeast Loch. Industrial development in the vicinity of Pearl Harbor was greatly accelerated during the late 1930s and early 1940s. During the 1941 Japanese attack on Pearl Harbor during World War II, 21 of the U.S. ships in Pearl Harbor were sunk or severely damaged, and debris resulting from this attack remains buried in harbor sediments (despite initial cleanup efforts). Currently, Pearl Harbor is a major fleet homeport for nearly 40 warships, service-force vessels, submarines, and their associated support, training, and repair facilities.

Middle Loch is moderately contaminated with heavy metals and toxic organic compounds and hydrocarbons. Sediments contain various concentrations of metals such as silver, arsenic, cadmium, chromium, copper, iron, mercury, manganese, nickel, lead, and zinc. Toxic organic compounds include pollutants such as solvents, paints, pesticides, and PCBs. Hydrocarbon contaminants include all petroleum-based fuel products such as diesel, JP-5, JP-4, bunker fuel, gasoline, oils, sludges, and lubricants.

Bishop Point is an active industrial area with ongoing salvage operations and related ship movements. Sediments contain similar contaminants as mentioned above but at higher levels.

4. DEMONSTRATION APPROACH

4.1 PERFORMANCE OBJECTIVES

The demonstrations were intended to verify the performance of the BFSD2 by assessing whether chemicals are adsorbing to or desorbing from sediments at the sediment–water interface. Specifically, the objectives of the BFSD2 technology demonstrations were to:

1. Evaluate the data quality of the water samples collected for use in determining if a statistically significant flux was occurring at the test locations.
2. Evaluate the BFSD2 for repeatability.
3. Evaluate the logistical and economic resources necessary to operate the BFSD2.
4. Evaluate the range of conditions in which the BFSD2 can be operated.

To determine whether statistically significant fluxes were occurring at the test locations (Objective 1), 12 seawater samples were collected at 7-hour intervals using the BFSD2. The water samples were analyzed for metals including cadmium, copper, manganese, nickel, lead, zinc and silica. Sediment samples, when collected, were analyzed for grain size, total solids, total organic carbon (TOC), acid volatile sulfide (AVS), simultaneously extracted metals (SEM), and total metals. Although the sediments might have been contaminated with other constituents, only the flux of the listed metals was evaluated during the demonstrations.

Other metals including antimony, arsenic, selenium, silver, thallium, and iron also were analyzed in the seawater samples collected during the three blank chamber tests. These data will be used at future dates when establishing baseline performance for these metals.

Sample concentrations were corrected for dilution introduced by the sampling process, and a regression curve was generated for each analyte based on the concentration data. Flux rates, with regression coefficients, were compared to the composite flux rate and standard deviation determined for each metal during triplicate blank chamber tests. The measured flux rate for each metal was then evaluated to assess if a statistically significant flux had been measured when compared to the blank chamber (background) test. The BFSD2 was evaluated for repeatability (Objective 2) by analyzing the results of repeat deployments, 2 weeks apart, at the same Paleta Creek site. Demonstration data were also compared to data from the site during previous prototype BFSD tests in the same approximate location. Finally, repeatability was evaluated by comparing the results from three blank chamber deployments. The logistical and economic resources necessary (Objective 3) were evaluated by documenting costs associated with planning, scheduling, and executing the demonstration deployments, laboratory analysis, data management, and report preparation. Lastly, the range of conditions for operating the BFSD2 was evaluated (Objective 4) by describing the conditions under which the BFSD2 operated and the projected range of contaminants applicable to the technology.

The demonstration approach was to collect time series of water samples using the BFSD2 at two geographically different locations. At the San Diego Bay location (Paleta Creek), two deployments at the same site were made; at the Pearl Harbor location, one deployment at each of two geologically different sites were made (Middle Loch and Bishop Point). Comparison of the results of the two Paleta Creek demonstrations to one another was intended to evaluate repeatability of the technology. Comparison of the results from the two geographically different sites in Pearl Harbor was intended to demonstrate data differences and analysis/interpretation approaches. Comparison of the Pearl Harbor data as a whole with that from San Diego also demonstrated geological differences between continental shelf and mid-Pacific riff measurements. Three “blank test” deployments were also conducted, during which the BFSD2 was deployed in seawater with a sealed sampling chamber. Three time-series of samples were collected and a baseline was established for each analyte, which provided a statistical estimate of the lower limit of flux detection measurable with the BFSD2. The data also served as another measure of repeatability. Previous results obtained at the same location using the prototype BFSD also provided a general measure of trend repeatability. A rate of flux between the sediment and the water for each analyte for each deployment was calculated. The flux rate was calculated using knowledge of the volume of water enclosed within the BFSD2, the surface area of sediment isolated, the time the samples were collected, and the concentrations of the contaminants of interest in the individual sample. Because this technology has no equivalent, the BFSD was evaluated based on the internal QA/QC of the laboratory analysis and an analysis of the data.

4.2 PHYSICAL SETUP AND OPERATION

4.2.1 Physical Setup

Deployment preparations included BFSD2 maintenance, decontamination, and setup. Maintenance included inspection and repair because of leakage or corrosion, inspection of sealing surfaces, seals and O-rings, inspection and replacement of sacrificial zinc anodes, downloading and/or deleting unnecessary files in the memory-limited control and data acquisition subsystem, and inspection of any worn or other potentially failure prone areas.

Decontamination involves soaking and/or rinsing all surfaces contacting seawater samples in a series of fluids beginning with tap water, then de-ionized water, then a special detergent (“RBS”), then de-ionized water, then nitric acid, then 18 meg-ohm de-ionized water and, finally, filtered air. The collection bottles are disassembled and all component parts are soaked, 4 hours minimum in each fluid. A 25% concentration of ultra-pure nitric acid soaks Teflon® parts (bottles, lids, and sensor chamber) and a 10% concentration is used for all other parts (including acid-sensitive polycarbonate filter bodies). The synchronized rotary valves, tubes, and fittings remain assembled to the BFSD2 and are cleaned in place by flowing the series of decontamination fluids through them. The acquisition and control subsystem executes a special program that activates each valve position for specified time during which the decontamination fluids are drawn through by a vacuum system. Finally, the collection chamber, lid, diffuser, circulation pump, tubes, and fittings are physically scrubbed and rinsed in place with non-metallic brushes. All decontaminated surfaces are dried, reassembled, or otherwise sealed to isolate them from ambient, airborne contaminants.

BFSD2 setup includes various tasks performed before deployment. These tasks include the following:

1. Charging the gel-cell 24-Vdc battery
2. Replacing the 14 circulation subsystem C-cell batteries
3. Replacing the six acoustic release 9-Vdc batteries
4. Installing a new acoustic release subsystem burn-wire
5. Cleaning the plating anode and rigging the recovery float
6. Checking and refilling (if required) the compressed-oxygen supply tank

7. Checking the insertion light subsystem function and replacing its one battery (if required), installing the 12 sample collection bottles and evacuating them to less than 25 in-Hg
8. Setting up laptop computer files for post-deployment data uploading
9. Reviewing and modifying, as required, the deployment operational control programs
10. Downloading the predrop program into the acquisition and control subsystem

4.2.2 Deployment

Each BFSD deployment requires at least three people. One person is responsible for maneuvering, positioning, and securing the surface vessel. Deploying and retrieving the BFSD requires two more people. The checklists included in appendix D are the step-by-step procedures followed on deck to avoid oversights and mistakes. Ancillary tasks performed include collection of a sediment sample with a spring-loaded grab sampler and logging site Global Positioning System (GPS) coordinates. Figures 19 through 22 show typical deployment and recovery scenes.

4.2.3 Recovery

Recovery is initiated following an elapse time after the planned deployment greater than the operational program by at least 2 hours. This elapse time allows for accumulated processing delays that lengthen the overall autonomous time period. Once within approximately 100 yards of the deployment position, a coded acoustic signal is transmitted to the BFSD2 acoustic receiver from the deck unit. A 15-minute function time begins during which the burn-wire is consumed and the recovery buoy is released. The line attached to the buoy winches the BFSD2 and the attached coiled cables to the surface and aboard the vessel. Heavy sediment and other debris are washed off the BFSD2 before bringing it onboard. On deck, an inspection of collection bottle status is made as an immediate indicator of deployment performance. Turning the compressed-oxygen cylinder valve off and installing storage caps on the pH and oxygen sensors is also completed without delay. Other assessments that might be accomplished onboard include upload of logged data from the acquisition and control subsystem and processing of pH and oxygen sensor data as performance indicators. Spreadsheet templates are used to quickly generate graphs and charts of converted and processed data that display results for the entire operational deployment. Aboard a properly configured surface vessel such as SPAWAR Systems Center, San Diego’s (SSC San Diego’s) R/V ECOS during the San Diego Bay demonstration, sample handling such as acid preservation, labeling and sealing of 100-ml laboratory samples, and 25-ml splits for measurement of silica concentration was accomplished. Once off-loaded to shore, the BFSD2 must be thoroughly washed down with fresh water to remove all remaining debris, sediment, and seawater and minimize corrosion. As soon as practicable, a freshwater purge of the synchronous rotary valves and associated tubes and fittings is accomplished.

Figure 19. Deployment equipment (SSC San Diego dock).

Figure 20. Crane loading aboard workboat (Bishop Point, Pearl Harbor).

Figure 21. Deployment (Middle Loch, Pearl Harbor).

Figure 22. Recovery (Middle Loch, Pearl Harbor).

4.3 SAMPLING PROCEDURES

The sampling procedures followed for the BFSD2 demonstrations provided assurance that the overall project goals and objectives were met. Careful adherence to the procedures ensured that data collected were useful in evaluating the effectiveness of the BFSD2 for benthic flux measurements of trace metals.

4.3.1 Overview of Sampling Operations

Sampling operations at each demonstration location consisted of site deployments during which the BFSD2 collected seawater samples at timed intervals and a sediment confirmation sample collected following each site deployment. Three additional identical blank (background) deployments with the BFSD2 collection chamber sealed using a polycarbonate bottom plate were used to statistically establish system blank performance as a baseline for comparison to the sediment flux data.

4.3.1.1 BFSD2 Sampling. Samples were collected *in situ* in 12 250-ml Teflon® precleaned sampling bottles at preprogrammed time intervals. A description of the sampling technology can be found in section 2.1. Sampling was initiated by starting the acquisition and control subsystem program, which activated synchronous rotary valves connected to the sample bottles. In-line filters with 0.45-micron membrane filters passed only seawater with dissolved-phase contaminants at the time of collection. After each deployment, the samples were transferred to appropriate sample containers and acidified, if necessary. A baseline ambient water sample was collected as the number one BFSD2 sample during deployment. The sample was analyzed and used to establish the ambient concentration at time zero for each analyte. The total time required for the 12 sampling events including the time zero sample using 7-hour intervals was approximately 72 hours with consideration for accumulated data processing delays.

4.3.1.2 Sediment Sampling. A sediment sample was collected at the end of each different site deployment using a spring-loaded grab sampler. The sediment was containerized, capped, labeled, and sealed. The sediment samples were used in various analyses, including digestion and extraction processes to measure trace metal levels. Other measurements related to seawater data analysis and interpretation were conducted and are reported in a later section.

4.3.1.3 System Blank Samples. With the BFSD2 configured as described in section 2.1, three deployments using identical procedures were accomplished. The samples were collected and handled as in the demonstrations (see section 4.3.1.1 above) and shipped to the analytical laboratory for the analyses discussed in the following subsections.

4.3.1.4 Quality Control. Demonstration samples and blank samples included equipment blanks, trip blanks, and laboratory blanks to assess the performance of the equipment in the field.

4.3.1.5 Communications and Documentation. The SSC San Diego program manager communicated regularly with demonstration participants to coordinate all field activities associated with the demonstrations and to resolve any logistical, technical, or QA issues that arose as the demonstrations progressed. Successful implementation of the demonstrations required detailed coordination and constant communication among all participants. Field documentation was included in field logbooks, field data sheets, chain-of-custody forms, and kept in a bound logbook. Each page was sequentially numbered and labeled with the project name and number.

All photographs were logged by the digital camera and transferred to the computer file system. Those entries included the time, date, orientation, and subject of the photograph. Specific notes about each sample collected were written on sample field sheets and in the field logbook. Any deviations from the approved final demonstration plan were thoroughly documented in the field logbook and communicated to parties affected by the change. Original field sheets and chain-of-custody forms accompanied all samples shipped to the laboratory.

4.3.1.6 Field Sample Collection. Sampling personnel collected and prepared samples using the procedures described in the following subsections. All field activities conformed with the requirements of the Demonstration Plan and its attached Health and Safety Plan.

Sampling operations at each site consisted of a deployment of the BFSD to collect seawater samples at timed intervals, and collection of a sediment grab sample after deployments. The series of samples collected during three blank test deployments with the chamber sealed with a polycarbonate bottom were used to assess the background level from which statistically significant fluxes can be derived.

4.3.1.6.1 Field Blanks. One field blank for the San Diego Bay demonstration consisted of an additional 250-ml bottle filled with de-ionized water strapped to the flux chamber. This sample was used to assess the integrity of the sample bottle seals if anomalous data were obtained.

4.3.1.6.2 Equipment Blanks. These samples consist of running 250 ml of de-ionized water through the BFSD2 sampling subsystem before deployment. One equipment blank was collected for each site demonstration. The equipment blank was used as a quality control measure to ensure that the BFSD2 was properly decontaminated between deployments.

4.3.1.6.3 Trip Blank. One trip blank for the San Diego Bay demonstration was collected by placing a closed 250-ml sample of de-ionized water in a sample cooler at the beginning of the demonstration. The trip blank was used as a quality control measure, if necessary, to ensure that samples are not contaminated during sample storage and shipment to the laboratory.

4.3.1.6.4 Silica. Confirmatory silica analysis was used to ensure that the BFSD2 is functioning properly without any significant loss of collection chamber seal. Silica is a common component in constructing the hard parts of some planktonic organisms, and it typically fluxes out of sediments at a constant rate because of dissolution processes. By analyzing each of the samples collected using the BFSD for silica and plotting the concentration versus time data, a linear increase in silica concentration over time strongly suggests that there was a good seal of the chamber with the sediment. The first sample at time zero provides a value for silica in bottom waters at the start of the experiment. The silica analysis was performed using 25 ml of seawater removed from each sample collected before acid preservation.

4.3.1.6.5 BFSD2 System Blanks. Finally, a triple-duplicate deployment with the collection chamber sealed with a polycarbonate bottom (“blank test”) was conducted as an experiment blank at the SSC San Diego dock in San Diego Bay. The data collected during those deployments provided a baseline with which to compare the site-specific flux rates to document a statistically significant flux rate from both analytical and system variability in a seawater environment.

4.3.1.7 Laboratory Blanks. Laboratory blanks and laboratory QC checks assess the precision and accuracy of the analysis, demonstrate the absence of interferences and contamination from glassware and reagents, and ensure the comparability of data. Laboratory QC checks consist of laboratory duplicates, surrogates, MS/MSDs, and method blanks.

4.3.1.7.1 Method Blanks. Method blanks were used to verify that preparation of samples was contamination-free. Each batch of extracted and digested samples was accompanied by a blank that was analyzed in parallel with the rest of the samples, and carried through the entire preparation and analysis procedure. Method blanks may also be called calibration blanks. Calibration blanks are analyzed for seawater samples analyzed for metals or silica and for sediment samples analyzed for metals or SEM.

4.3.1.7.2 Precision. Analytical precision and method detection limits are determined by replicate storage, preparation, and analysis of standard seawater. Further verification of precision is achieved by splitting 1 in 20 field samples. Laboratory duplicates are analyzed during analysis of water samples analyzed for metals, water samples analyzed for alkalinity (if performed), sediment samples analyzed for metals or SEM.

4.3.1.7.3 Accuracy. 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 are analyzed by the method of standard additions, spiked samples are not used. MS and

MSD samples were used for analysis of water samples analyzed for metals, sediment samples analyzed for metals, sediment samples for AVS, and sediment samples for SEM.

4.3.1.8 Sample Storage, Packaging, and Shipping. The field team followed chain-of-custody procedures for each sample as it was collected following BFSD2 retrieval. An example chain-of-custody form can be found in appendix E. The following information was completed on the chain-of-custody form: project number, project name, sampler's name, station number, date, time, station location, number of containers, and analysis parameters.

Following retrieval and removal of the samples from the BFSD at the end of each single deployment, and until shipment to Battelle, all samples were stored in refrigerators or coolers and maintained with ice at a temperature of approximately 4°C. The custody of samples was maintained by standard operation procedures (SOP). Samples to be shipped to the confirmatory laboratory were packaged and shipped according to the sample packaging and shipment requirements SOP. Copies of these SOPs are available upon request.

4.4 ANALYTICAL PROCEDURES

4.4.1 Selection of Analytical Laboratory

The analytical laboratory selected to provide analytical services was Battelle Marine Sciences Laboratory (Battelle). Battelle was selected because of its experience with QA procedures, analytical result reporting requirements, and data quality parameters. Battelle is not affiliated with SSC San Diego or any of the demonstration team members.

4.4.2 Analytical Methods

Sample and data analysis are important elements in using samples collected by BFSD. Samples were analyzed for metals including cadmium, copper, lead, manganese, nickel, zinc, and silica. The marine sediment samples and seawater samples collected by BFSD2 were sent to Battelle for analysis. Table 1 lists the analytical methods. Other metals including antimony, arsenic, selenium, silver, thallium, and iron were also analyzed in the seawater samples collected during the three blank chamber tests. These data will be used in future projects to establish baseline data for the metals.

Table 2. Analytical methods.

Analyte	Seawater Sample (Analytical Method)	Sediment Sample (Analytical Method)
Cadmium	ICP-MS	GFAA
Copper	ICP-MS	XRF
Iron	GFAA	XRF

Table 2. Analytical methods. (continued)

Analyte	Seawater Sample (Analytical Method)	Sediment Sample (Analytical Method)
Manganese	ICP-MS	XRF
Nickel	ICP-MS	XRF
Lead	ICP-MS	XRF
Zinc	ICP-MS	XRF
Miscellaneous Metals—Antimony, Arsenic, Selenium, Silver, and Thallium	ICP-MS GFAA or XRF	NA
Silica[1]	NA	NA
Alkalinity	NA	NA
Grain Size	NA	NA
Total Solids	NA	NA
Total Organic Carbon	NA	NA
Acid Volatile Sulfide	NA	NA
Simultaneously Extracted Metals	NA	ICP-MS (EPA Method, 1638)

NA: Not applicable

ICP-MS: Inductively coupled plasma mass spectroscopy

XRF: X-ray fluorescence

GFAA: Graphite furnace atomic absorption

[1] Silica was analyzed in the field using a HACH DR2010 instrument to assure sample integrity and determine whether samples will be sent to the laboratory for full analysis.

4.4.2.1 Preconcentration. The preconcentration method used for this project was a tetrahydroborate-reductive precipitation as a preconcentration technique. Samples were first acidified with nitric acid to pH 1.8 for storage. Samples were then adjusted to pH 8 to 9 with high-purity ammonia solution and iron and palladium were added. A sodium tetrahydroborate solution was added before the solution was filtered through a 25-mm-diameter acid-washed, acid-resistant cellulose nitrate

0.45-micrometer membrane filter. Concentrated nitric and hydrochloric acids are added to the empty bottle to dissolve any precipitate adhering to the walls; the acid mixture was later transferred to the filter assembly. The filter was washed with water and the solution was diluted to 25 ml. The filter and its holder were rinsed with 3-ml aliquots of the nitric and hydrochloric acids and water between samples, and were used repeatedly. The combination of iron and palladium produced the rapid formation of a precipitate after the addition of sodium tetrahydroborate.

4.4.2.2 Inductively Coupled Plasma Mass Spectrometry. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis allows the simultaneous, multi-elemental determination of metals by measuring the element-emitted light by optical spectrometry. Element-specific atomic-line emission spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes.

4.4.2.3 Graphite Furnace Atomic Absorption. Graphite Furnace Atomic Absorption (GFAA) allows the individual analysis of iron, arsenic, lead, selenium, and thallium to provide lower detection limits. In the furnace, the sample is evaporated to dryness, charred, and atomized. A light beam from a hollow cathode lamp or an electrode-less discharge lamp is directed through the tube into a monochromator and onto a detector that measures the amount of light. Because the wavelength of a light beam is characteristic of a single metal, the light energy absorbed is a measure of that metal's concentration.

4.4.2.4 Silica. The seawater sample was allowed to react with molybdate under conditions that form the silicomolybdate, phosphomolybdate, and arsenomolybdate complexes. A reducing solution containing oxalic acid is then added that reduces the silicomolybdate complex to give a blue reduction compound and simultaneously decomposes any phosphomolybdate or arsenomolybdate so that interference from phosphate and arsenate are eliminated. The extinction of the resulting solution was measured using 25-cm cells. This method was performed using a Hach Model DR2010 Field Kit before sending samples to the laboratory.

4.4.2.5 Sediment Samples. Sediment sample analysis included methods to determine grain size, TOC, AVS, and total metals. The collected sediment samples were homogenized and split into subsamples before analysis. Sediment samples for total metals analysis were freeze-dried and ground before analysis. Total metals were then determined using X-ray fluorescence (XRF) or GFAA.

4.4.2.5.1 Grain Size. Grain size was measured by a combination of sieving, particle counters, and pipette analysis.

4.4.2.5.2 Total Organic Carbon (TOC). Total Organic Carbon (TOC) was measured on an automated carbon analyzer by measuring total carbon and inorganic carbon contents, with the difference providing the TOC values. Inorganic carbon from carbonates and bicarbonates were removed by acid treatment. The organic compounds were decomposed by pyrolysis in the presence of oxygen or air.

4.4.2.5.3 X-Ray Fluorescence. X-Ray fluorescence uses energy dispersive x-ray fluorescence spectroscopy to quantify elemental concentrations in sediment and tissue samples.

4.4.2.5.4 Acid Volatile Sulfide (AVS). Acid Volatile Sulfide (AVS) is operationally defined as the fraction of sulfide present in the sediment that is extracted with cold hydrochloric acid. Analysis of AVS is an indicator of potential metal toxicity in sediments. AVS was determined by photoionization detection (PID) following a step that converted the sulfide in the sample to hydrogen sulfide. During the first step, the sample was allowed to react with 1 N hydrochloric acid, the system was purged with purified inert gas, and produced hydrogen sulfide was trapped using a column immersed in liquid nitrogen. The PID method used gas chromatographic separation and photoionization detection; the area under the curve of the chromatograph was used to calculate sulfide concentration from the linear regression of the standard curve.

4.4.3 Data Reduction and Analysis

Correction of concentration for dilution, regression analysis, and flux rate concentrations were calculated using a custom spreadsheet template. See appendix C for a complete set of spreadsheets. Results from these complex computations require careful analysis and interpretation to reach valid conclusions. Various other site-specific data and information must be used in combination with computed flux results to fully interpret the data. The approach taken and the conclusions reached for the demonstrations of this report are presented in the next section.

5. PERFORMANCE ASSESSMENT

5.1 PERFORMANCE DATA

5.1.1 Blank Tests

The primary purpose for performing system blank tests was to establish BFSD2 minimum performance levels or detection limits for assessment of flux data obtained during later demonstration tests. Three replicate 70-hour blank tests were conducted using BFSD2 between 14–31 May 1998. The tests were conducted from the end of SSC San Diego Pier 159 at approximately 2 feet off the bottom, in seawater ranging from about 14 to 20 feet deep, depending on tidal flow.

As discussed earlier, the BFSD 2 collection chamber bottom was sealed with a polycarbonate plate and filled with ambient seawater at the start of each 70-hour test. Before each test routine, procedures were performed for decontamination of the sampling system. Equipment and source blanks were taken. After each test, the samples were handled in accordance with EPA Methods 1638 and 1669, and the routine chain of custody procedures were used in preparation and shipment to Battelle Marine Sciences Laboratory for analysis. Scripps Institute of Oceanography received and analyzed the silica samples.

Each test produced 12 250-ml sample bottles of seawater filtered *in situ* to 0.45 micron. Sample bottle one in each test was filled with ambient seawater taken from the water column as the BFSD2 was lowered to its test depth at about 15 feet below the surface. Sample bottle two in each test was filled with seawater from the sealed chamber at 6 minutes after start of the 70-hour test. The remaining 10 sample bottles were filled from the chamber at 7-hour intervals. The data, analysis, and graphs for each test were processed and compiled in Microsoft Excel spreadsheet, “BFSD2 Blank Tests.xls.” Appendix C provides copies of the spreadsheet results and includes data and graphs for the BFSD2 flow-through sensors.

Table 3 summarizes the blank test results.

Table 3. Blank test results.

Metal	**Blank Flux (µg/m^2/day)**			**Repeatability (µg/m^2/day)**		
	Test 1(12)	**Test 2 (6)**	**Test 3 (6)**	**Average Flux**	**+/- 95% C.L.**	**Std. Deviation**
Copper (Cu)	**25**	**-13**	**15**	**2.82**	**8.73**	**19.7**
Cadmium (Cd)	**-5.3**	**-0.8**	**-0.09**	**-0.52**	**0.75**	**2.8**
Lead (Pb)	**2.8**	**5**	**1**	**3.16**	**1.59**	**2.0**
Nickel (Ni)	**23**	**20**	**-6.7**	**10.28**	**7.34**	**16.4**
Manganese (Mn)	**-289**	**-249**	**-250**	**-264.85**	**7.49**	**22.8**
Zinc (Zn)	**-194**	**-13**	**200**	**-3.38**	**-68.61**	**197**
Silica (SiO_2)* **(*mg/m2/day)**	**-4**	**-3.3**	**1.4**	**-1.97**	**2.88**	**2.9**

5.1.1.1 Discussion of Blank Results. As expected, the blank results for most metals showed little or no time trend, indicating minimal source or loss of target analytes during the blank experiments. Figures 23 through 29 provide graphs of concentration versus time for each analyte for each blank test. With the exception of lead and manganese, replicate analysis indicates that none of the metal fluxes were significantly different from a zero flux condition at the 95% confidence level. Copper results for the three replicates showed both small positive and small negative flux rates. Replicate blanks for cadmium were all small and negative; however, the variability was sufficient that the mean as still not significantly different than zero. Results for lead indicated small positive flux rates with a mean value of 2.9 μg/m^2/day, which was different from the zero flux condition, suggesting a potential small source of lead in the experimental procedure. Nickel results indicated small positive and negative fluxes with no obvious uptake or sources of nickel from the system. Replicates for manganese showed substantial negative flux rates, indicating a significant loss of manganese because of some aspect of the experimental procedure. Results for zinc showed both positive and negative fluxes with no clear pattern of source or uptake.

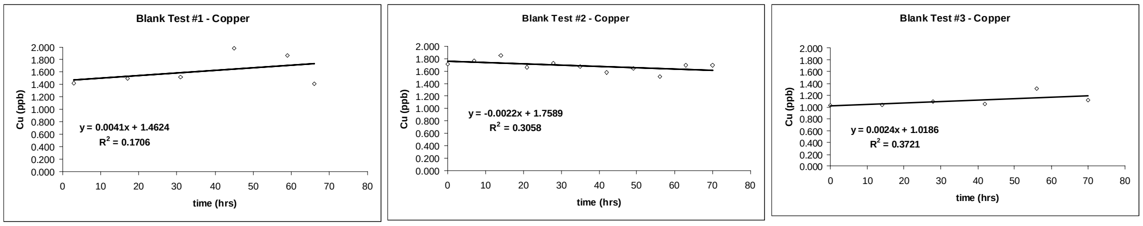


Figure 23. Blank performance for copper (Cu).

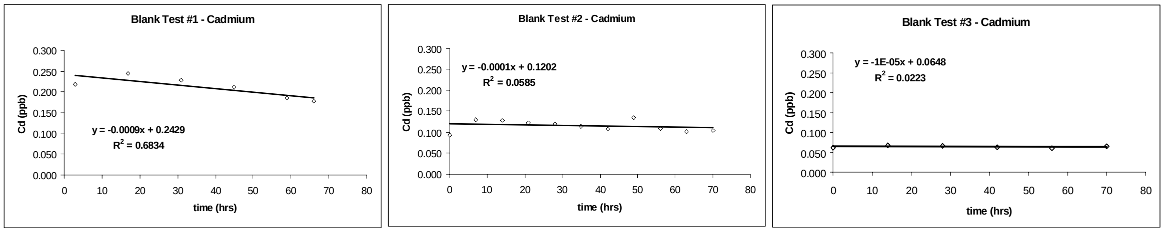


Figure 24. Blank performance for cadmium (Cd).

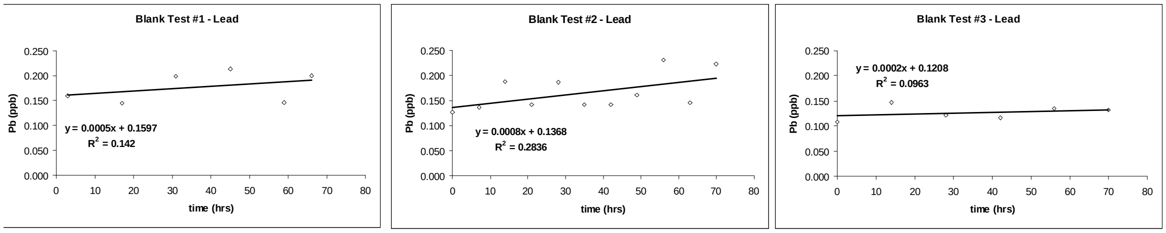


Figure 25. Blank performance for lead (Pb).

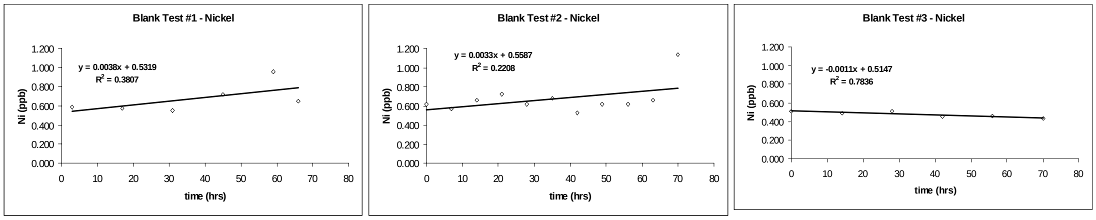


Figure 26. Blank performance for nickel (Ni).

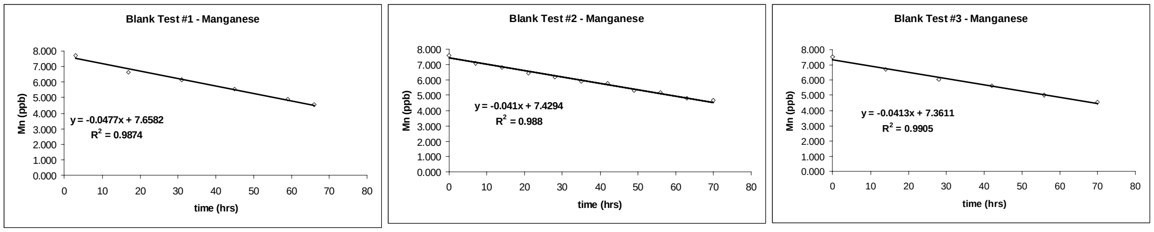


Figure 27. Blank performance for manganese (Mn).

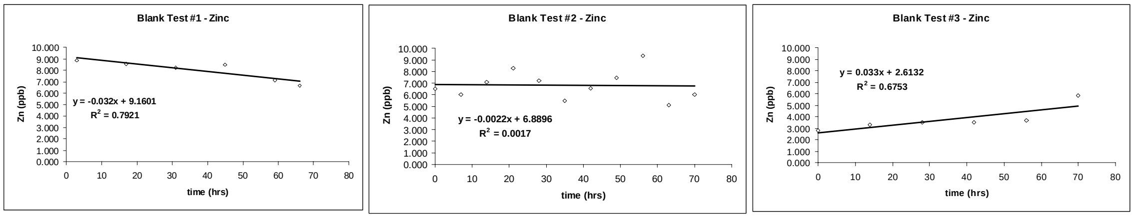


Figure 28. Blank performance for Zinc (Zn).

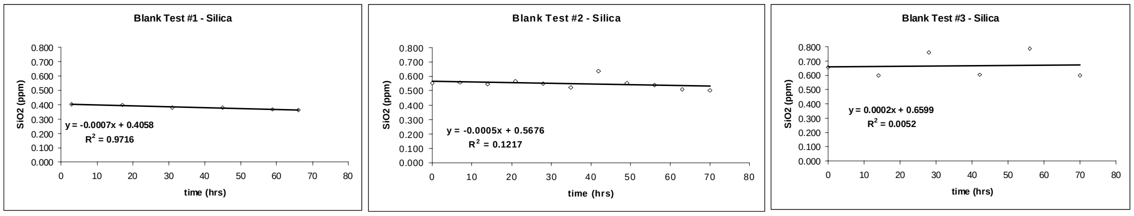


Figure 29. Blank performance for silica (SiO_4).

Scripps Institution of Oceanography analyzed silica concentrations, which are used to indicate chamber integrity and seal. The CA EPA request for an independent analysis of silica could not be reasonably obtained from Battelle. Subsequent silica analyses were conducted on-site with field analytical systems (i.e., the Hach Kit).

Results show a high, repeatable level of Manganese uptake by the BFSD2. Results from earlier prototype BFSD blank tests were not consistent with this result and warrants further investigation. However, because manganese is not generally viewed as a toxic metal, the resolution of this issue is less critical than for other metals.

The somewhat higher blank fluxes observed for zinc are consistent with previous results and are attributed to the ubiquitous nature of zinc and associated contamination during sampling and analysis. Because previously measured flux rates for zinc generally lie outside the range of these blanks, and because of the higher toxicity thresholds for zinc relative to other metals, this is not considered as a serious problem. However, as with all trace metals, zinc contamination must be carefully minimized during all phases of the experimental procedure.

5.1.1.2 Discussion of Blank Tests. Although the three blank tests were reasonably trouble-free and produced generally high quality data, many points deserve further discussion and explanation.

5.1.1.2.1 Sensors. The flow-through sensors for dissolved oxygen and pressure (figures 30 and 31) produced data that requires explanation. The “noisy” dissolved oxygen data were discovered as caused by restricted flow over the sensing element. Flow improvements resolved the problem before the Paleta Creek demonstrations (figure 35). The oxygen measurements during the blank test are not critical because there is little oxygen depletion when no sediment is present. Drift of the pressure sensor readings was more problematic, and resolution required troubleshooting at the factory after the Paleta Creek demonstrations.

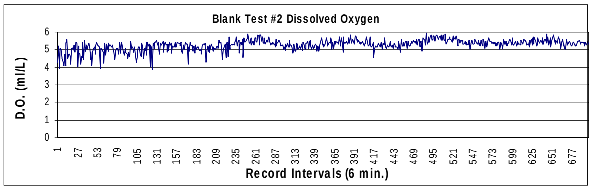


Figure 30. Blank test for dissolved oxygen

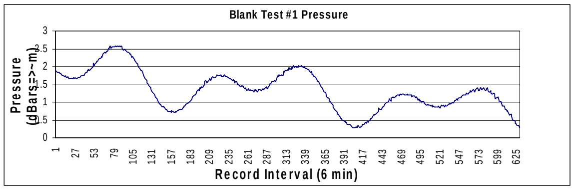


Figure 31. Blank test pressure.

5.1.1.2.2 Ambient Seawater Sample. Sample bottle one and later Paleta Creek demonstration analyses were not used in blank test analyses. Analytical laboratory results clearly indicate that the metal concentrations in the water collected in bottle one as the BFSD2 descended to the test depth were not consistent with concentrations in the chamber after it was closed and sealed at the surface before descending to the test depth. CA EPA certification evaluators agreed that the sample taken at 6 minutes after the start of the test was a better representation of replacement water entering the chamber. The unused concentration value is still shown (in bold) in the spreadsheet. A sensitivity analysis of the affect of this change on dilution correction calculations and subsequent flux results show it as insignificant. Consequently, an improved method was implemented to fill sample bottle one from more representative bottom water.

5.1.1.2.3 Sample Analysis. Not all samples were analyzed to minimize analytical costs. For Blank Test 1, only the six odd-numbered samples were analyzed (with further changes, see next paragraph); for Blank Test 2, all 12 samples were analyzed; for Blank Test 3, only the six even-numbered samples were analyzed. Additional trace metals beyond those identified for CA EPA certification evaluation were also analyzed for future applications.

Blank Test 1 suffered a “False Start” when an error in a software control loop shut the test down after 6 minutes, following the filling of sample bottle two. The error was corrected from the surface, and the test was restarted 3 hours later without raising the BFSD2 from the test depth. Sample bottle three filled immediately upon restart and sample bottle two was retained as representative of ambient conditions. To complete the set of six samples, sample bottle 12, with a 7-hour interval, was added to the other odd-numbered samples. The total duration for Blank Test 1 was 66 hours.

5.1.1.3 Blank Tests Assessment. It was concluded that the BFSD2 blank performance was statistically established and the values obtained were repeatable, precise, and accurate enough to allow valid measurement of *in situ* sediment flux rates.

5.1.2 San Diego Bay, Paleta Creek Demonstrations

Two 70-hour demonstrations of BFSD 2 were conducted at the heavily industrialized Paleta Creek entrance to San Diego Bay (figure 32). The quiescent, marina-like area is used for mooring support craft and receives periodic stormwater inflow from the Paleta Creek drainage basin. The site was selected because of known levels of trace metals in the sediments (as established in two previous prototype BFSD tests) and because of its convenient location for an initial field test and first demonstration of BFSD2. Two demonstrations were conducted 2 weeks apart (6–8 June 1998 and 18–22 June 1998) with the first demonstration being a full dress rehearsal for the second, formal demonstration. The locations for the tests were within 10 feet of one another and within the same proximity to two previous prototype BFSD deployments. The tests were conducted at a depth of about 18 ±3 feet, depending on tidal flow, and offshore about 30 feet from a quay wall. Deployment and retrieval was from the SSC San Diego research vessel R/V ECOS.

Figure 32. BFSD2 Paleta Creek deployment.

Before both tests, the BFSD 2 was cleaned and prepared using the same procedures used during the triplicate blank tests. Aboard R/V ECOS, after loading and connecting various equipment (laptop computer, TV monitor, light, cabling), a standard pre-deployment checklist was followed. Once moored at the site with the GPS location logged, the BFSD2 was lowered to within 2 feet of the bottom and a 15-minute test was started to stabilize the flow-through sensors and measure the ambient dissolved oxygen level. This test was run twice during the first demonstration to ensure repeatability. The ambient dissolved oxygen level is used to establish system control limits for maintaining a narrow range of dissolved oxygen in the collection chamber during the 70-hour test and for assessment of sediment oxygen uptake rates. As requested by CA EPA certification evaluators, a second, independent dissolved oxygen measurement was made outside the collection chamber during the second demonstration by attaching an additional instrument to the BFSD2 frame next to the collection chamber.

After entering the control limits into the 70-hour test program software and downloading it, the BFSD2 was raised for manual activation of the number one sample bottle valve. A new, higher mounting location for the valve was implemented following the blank tests to improve collection of representative ambient bottom water. With the BFSD2 partially submerged and the collection chamber approximately 3 feet below the surface, the valve was opened manually and the BFSD2 was immediately lowered back to approximately 2 feet from the bottom. After a short delay to arrange deck release lines, the BFSD2 was then allowed to free-fall to the bottom and insert its collection chamber into the sediment.

The landing and insertion were monitored using a video camera. Activation of the three insertion indicator lights was verified. The video camera, aided by a floodlight, also allowed a limited assessment of the site before initiating the 70-hour test. After starting the test, it also allowed confirmation of lid closure before complete detachment of lanyards and connections for autonomous operation. Both demonstration deployments were straightforward and without problems. The R/V ECOS returned to SSC San Diego and left the BFSD2 in its autonomous operation mode.

Retrieval of the BFSD2 after the tests was routine except for malfunction of the commercial acoustic recovery system. Recovery was with a separate line stowed at the site. Acoustic receiver burn-wire modification, latch modification, and, most importantly, sandpaper cleaning of the ground electrode were later implemented. Once BFSD2 was washed down and on deck, the 12 250-ml sample bottles were removed for processing using EPA handling and chain-of-custody procedures. During the first demonstration, the samples were returned to SSC San Diego for splits (silica and metals). For the second demonstration, splits were made aboard R/V ECOS using pre-acidified 125-ml containers for metals samples and pre-cleaned 25-ml beakers for silica measurements. Silica measurements were made aboard R/V ECOS using a field-portable Hach model DR2010 instrument. The metals samples were packaged and shipped to Battelle Marine Sciences Laboratory for analysis of the six metals selected for CA EPA certification evaluation. All data and results for the two demonstrations were compiled in Microsoft Excel® spreadsheets titled “BFSD2 PCPD.xls” and “BFSD2 PCD.xls.” Appendix C provides copies of the spreadsheet results and includes data and graphs for the BFSD2 flow-through sensors.

Tables 4 and 5 summarize the two Paleta Creek demonstration results.

Table 4. BFSD2 Paleta Creek Pre-Demonstration (PCPD) results.

Metal	Flux	+/- 95% C.L.	Flux rate Confidence	Triplicate Blank Flux (μg/m^2/day)		Bulk Sediment	Overlying Water
	(μg/m^2/day)	(μg/m^2/day)	(%)	Average	+/- 95% C.L.	(μg/g)	(μg/L)
Copper (Cu)	-1.75	19.71	38.1%	2.82	8.73	165	1.54
Cadmium (Cd)	9.64	4.14	100.0%	-0.52	0.75	1.16	0.148
Lead (Pb)	11.06	7.94	100.0%	3.16	1.59	98.9	0.1561
Nickel (Ni)	25.24	4.62	100.0%	10.28	7.34	19.1	0.9262
Manganese (Mn)	71.33	701.54	80.7%	-264.85	7.49	405	28.12
Manganese (Mn)[1]	5763.99	23621.74	100.0%	-264.85	7.49	405	28.12
Zinc (Zn)	715.02	257.38	100.0%	-3.38	65.22	356	8.90
Other							
Oxygen (O_2)* (*ml/m^2/day)	-1050.87	86.25	na	na	na	na	5.2
Silica (SiO_2)* (*mg/m^2/day)	30.29	11.33	100%	-1.97	2.88	na	0.81

1. Mn flux calculated on the basis of first three samples due to non-linearity

Table 5. BFSD2 Paleta Creek Demonstration (PCD) results.

Metal	Flux	+/- 95% C.L.	Flux rate Confidence	Triplicate Blank Flux (μg/m^2/day)		Bulk Sediment	Overlying Water
	(μg/m^2/day)	(μg/m^2/day)	(%)	Average	+/- 95% C.L.	(μg/g)	(μg/L)
Copper (Cu)	-6.57	17.74	80.7%	2.82	8.73	165	1.46
Cadmium (Cd)	7.02	3.87	100.0%	-0.52	0.75	1.16	0.06897
Lead (Pb)	4.32	12.39	65.6%	3.16	1.59	98.9	0.07879
Nickel (Ni)	19.44	8.75	99.8%	10.28	7.34	19.1	0.8378
Manganese (Mn)	103.94	957.14	73.3%	-264.85	7.49	405	24.02
Manganese (Mn)[1]	4194.24	101841.32	99.9%	-264.85	7.49	405	24.02
Zinc (Zn)	574.26	274.14	100%	-3.38	-68.61	356	8.38
Other							
Oxygen (O_2)* (*ml/m^2/day)	-1341.12	160.18	na	na	na	na	4.7
Silica (SiO_2)* (*mg/m^2/day)	28.75	15.63	100%	-1.97	2.88	na	0.79

1. Mn flux calculated on the basis of first three samples due to non-linearity

Numbers in the Flux Rate Confidence column indicate the statistical confidence that the measured flux rate is different than the blank flux rate. Results from the blank study, bulk sediment analysis, and overlying water and oxygen uptake analysis are shown for comparison.

Figures 33 and 34 show graphical comparison of the results.

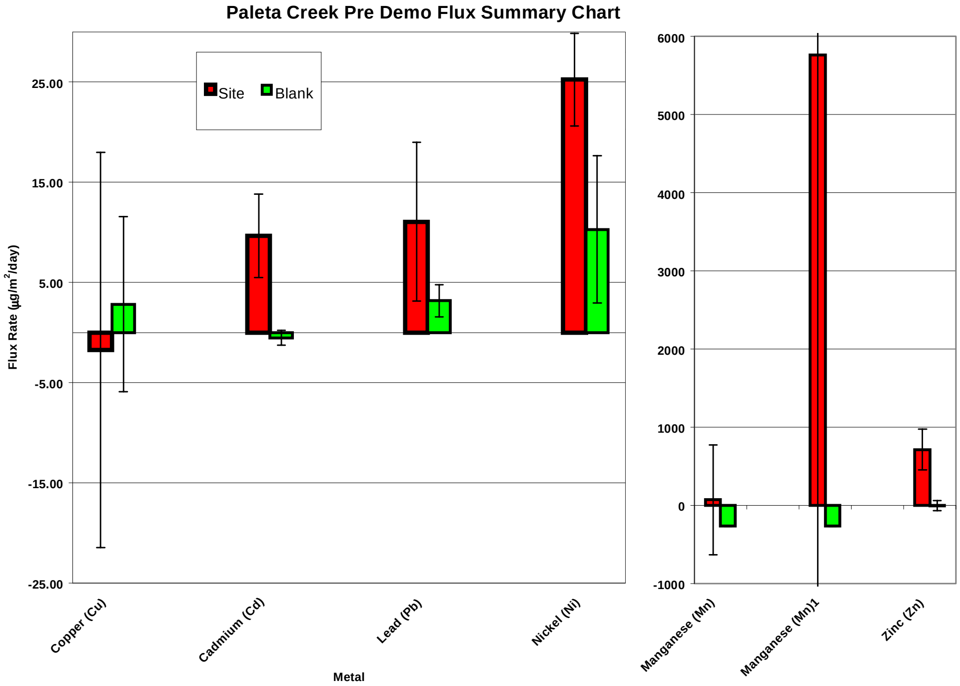


Figure 33. Paleta Creek Pre-Demonstration results.

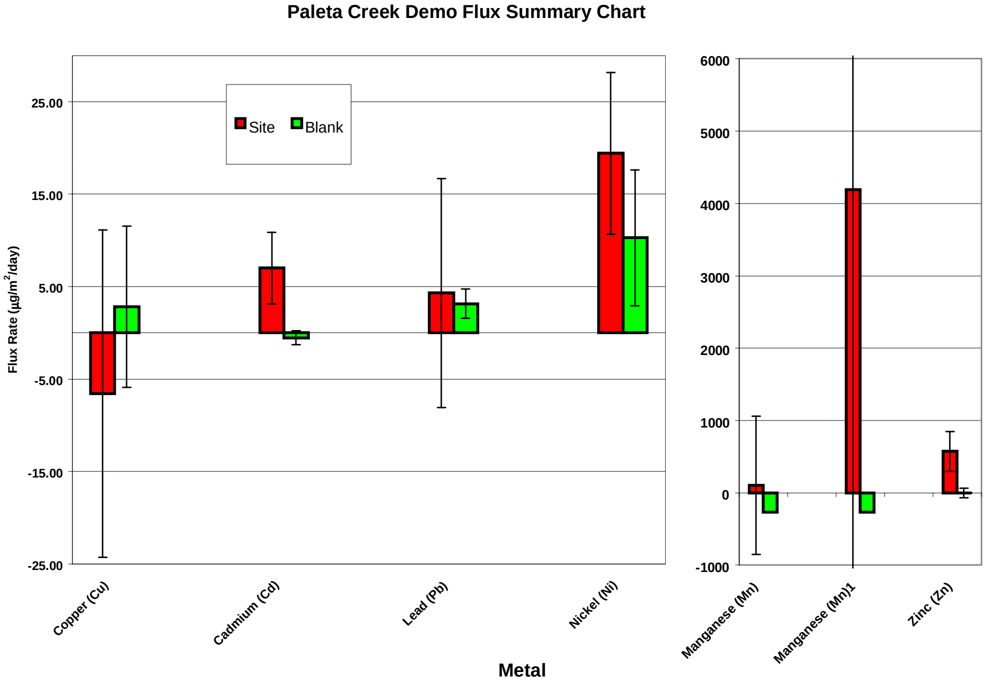


Figure 34. Paleta Creek Demonstration results.

5.1.2.1 Discussion of Paleta Creek Demonstrations Results. In general, BFSD2 results from the two Paleta Creek demonstrations were similar and consistent with previous prototype deployments at this location. Figures 35 and 36 are the sets of graphs of concentration versus time for each analyte in each of the demonstrations, compared with blank performance. The results for the Pre-Demonstration indicate that cadmium, lead, nickel, and zinc had fluxes out of the sediment that were highly significant when compared to the blank chamber results. Manganese[1] also had a positive outward flux, but the statistical confidence was somewhat lower. The flux of copper indicated a negative flux (sediment uptake) although the statistical confidence was only 65%.

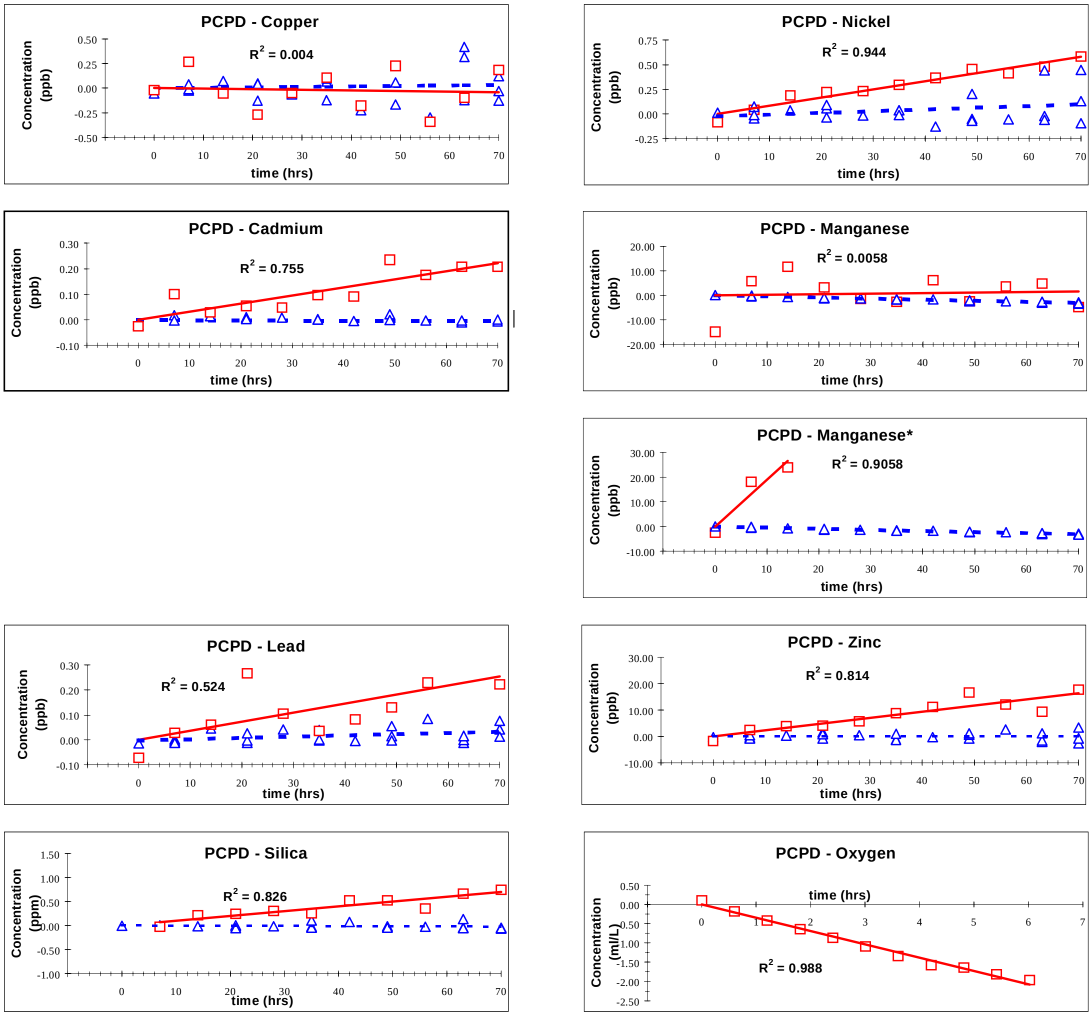


Figure 35. Paleta Creek Pre-Demonstration (concentration versus time).

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[1] Later identification of a “quenching”-like trend in the manganese flux during Pearl Harbor demonstrations led to a re-analysis of the above results. The tables reflect a second set of values for manganese based on the initial monotonically increasing data. Please refer to section 5.1.3.1 for an explanation of the affect.

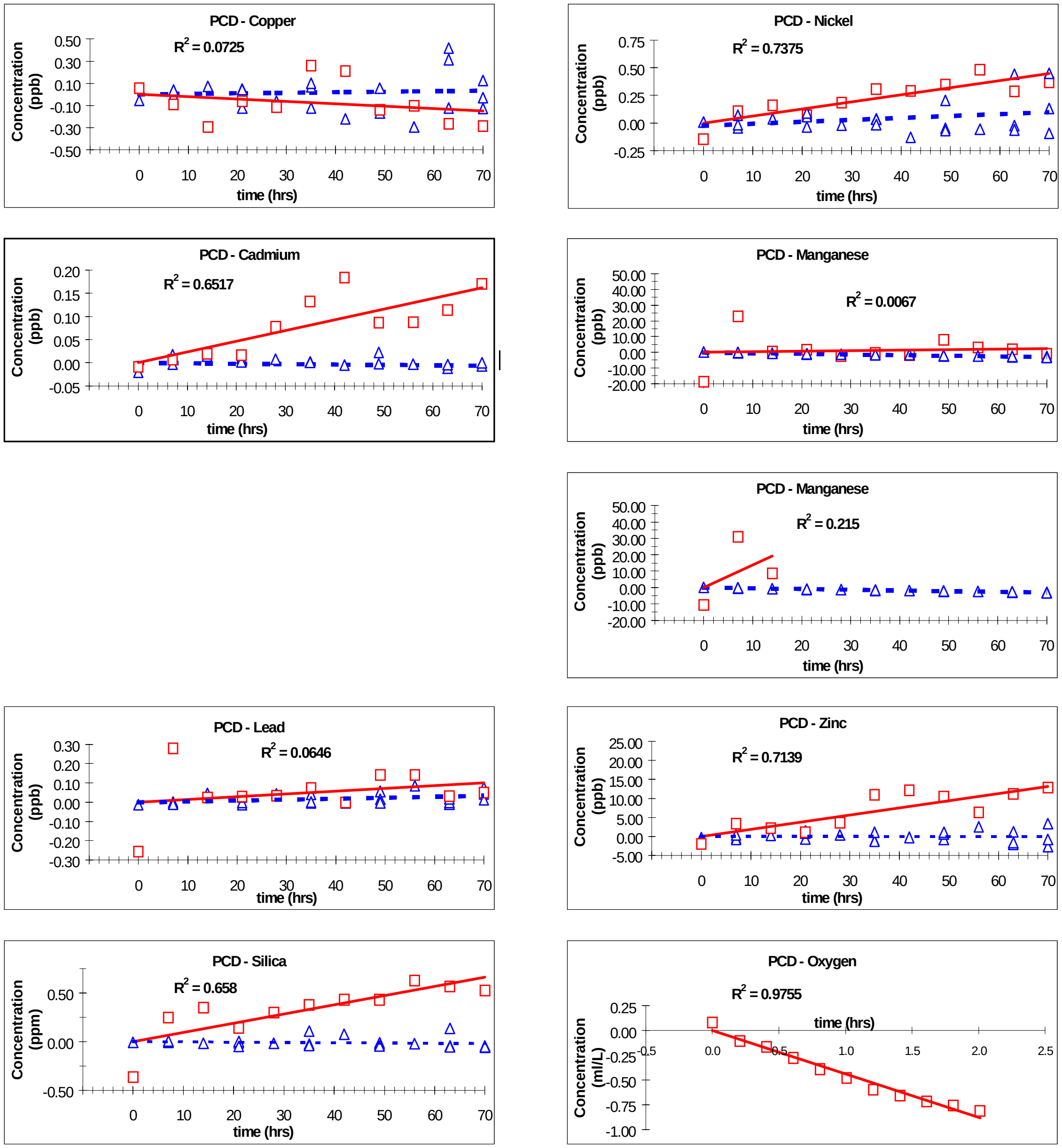

Figure 36. Paleta Creek Demonstration (concentration versus time).

Results for the formal demonstration were similar to those of the pre-demonstration with the exception of lead. Cadmium, nickel, and zinc all had fluxes out of the sediment that were highly significant when compared to the blank results. The magnitude of the cadmium, nickel, and zinc fluxes for the demonstration were similar, though slightly lower, than those observed for the Pre-Demonstration. Manganese[2] again had a positive outward flux but a lower statistical

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[2] See footnote #1 on previous page

confidence. As with the Pre-Demonstration, the flux of copper was negative (sediment uptake) although the statistical confidence was <0.1%.

5.1.2.1.1 Flux Measurements. As tables 4 and 5, and figures 33 through 37 show, cadmium, lead, nickel, manganese, and zinc had positive flux rates that were statistically different from blank test results. The relative magnitude of the flux rates were also consistent for demonstrations and earlier prototype work at the site. In other words, zinc had a larger flux rate than manganese, manganese was larger than nickel, nickel was larger than lead, and lead and cadmium were very close to the same magnitude. The magnitude of the flux rates for the formal demonstration were generally similar though somewhat less (except manganese) than those of the pre-demonstration test 2 weeks earlier; however, the differences are not statistically significant. A correlation with sediment oxygen uptake is evident and might explain the slight downward shift of fluxes. The flux rate for manganese is likely more positive than measured when corrected by the large, repeatable negative flux measured in the blank tests. Copper results indicate a slightly negative flux (sediment uptake) that has been observed in previous work. This may be attributed to pore water chemistry involving sulfide binding, complexation with organic matter, or elevated water column concentrations associated with hull leachate sources as discussed extensively in earlier reports. The oxygen uptake measured during both deployments is consistent and indicates continuous consumption of dissolved oxygen, which can be attributed to oxidation of organic matter and biological uptake at the sediment water interface.

5.1.2.2 Discussion of Paleta Creek Demonstrations Tests. Important aspects of the demonstrations including performance indicators and deployment problems are discussed in the following subsections.

5.1.2.2.1 Performance Indicators. Several methods were used to evaluate system performance of the BFSD2 during and after the demonstrations. To assure a proper seal of the chamber, the following were monitored: an underwater video camera, insertion light indicators connected to pressure sensors on the sealing flange, and silica, pH, and oxygen levels within the chamber for expected trends. Landing and insertion were monitored with the video camera and landing lights indicated a good seal. After starting the test, the video camera also confirmed lid closure of the chamber.

A linear increase in silica during the deployments was used as another indicator of proper system performance and chamber seal. The results (figures 35 and 36) show that silica concentration increased linearly, and that the silica flux rates were consistent and repeatable for the two deployments, indicating proper system performance and chamber seal. Oxygen variations in the chamber were monitored to ensure maintenance of ambient oxygen levels, a proper chamber seal, and to evaluate sediment oxygen uptake. The rate of oxygen consumption (sediment uptake) during the deployments, also shown in figures 35 and 36, was sufficient to cause repeated cycling of the BFSD2 oxygen recharge subsystem. Figure 37 provides graphs of the oxygen sensor data for the two deployments, showing the operation of the control system. The control limits selected allowed the dissolved oxygen to remain within approximately 1 ml/L of the ambient level and still yield data to assess the sediment uptake rate. The multiple cycles for both recharge and uptake were consistent and repeatable.

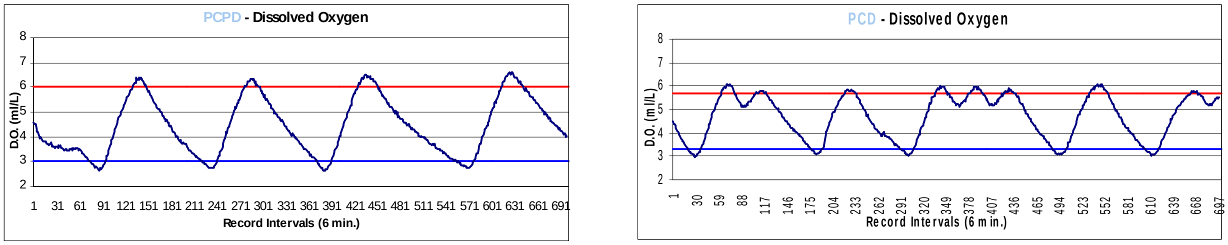


Figure 37. Paleta Creek Demonstration (oxygen control results).

As requested by CA EPA certification evaluators, an independent dissolved oxygen measurement of ambient bottom water at the BFSD2 test site was made during the formal demonstration deployment. The measurement instrument was battery-power-limited and operated for only the first 39 hours of the deployment. During that period, cyclic changes of approximately 0.5 ml/L occurred about the ambient level of approximately 5 ml/L. Thus, oxygen results reconfirm that a proper chamber seal was achieved and that oxygen levels within the chamber were maintained close to the ambient level and with similar, though slightly larger, variability to that observed outside the chamber.

In the properly sealed BFSD 2 chamber, the pH will generally show a decreasing trend as the breakdown of organic matter at the sediment water interface drives CO_2 into the chamber water. This decreasing trend was observed during both deployments (figure 38). Some small fluctuations from the expected steady decline in chamber pH were seen. While the exact cause of these fluctuations is not known, many factors including photosynthetic activity and sediment and pore water oxidation chemistry can account for the minor reversals. In the absence of other evidence of a breech in chamber seal, these small fluctuations were attributed to natural variations.

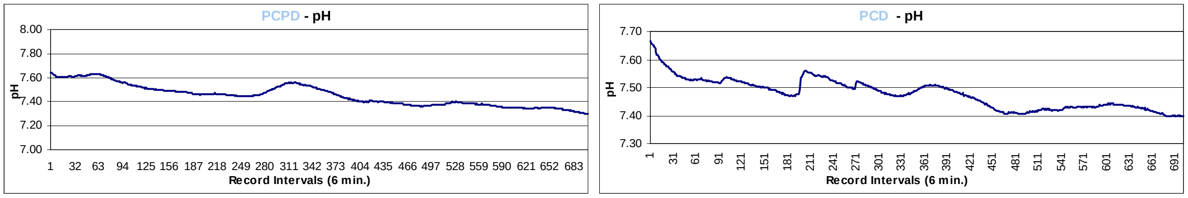


Figure 38. Paleta Creek Demonstration (pH results).

5.1.2.2.2 Deployment and Recovery Problems. Two minor problems were encountered during the demonstrations. The first was failure of the commercial acoustic recovery system to function. During the Pre-Demonstration, the failure was attributed to one too many burn-wire strands, which led to excessive time for functioning. One strand was removed for the next test; however, the release latch mechanism was corroded and failed to release the buoy after the burn-wire had properly functioned. The latch was subsequently modified and is an inspection point as part of the pre-deployment checklist procedure. Most importantly, abrasive cleaning of the ground (plating) electrode with sandpaper must be performed after every use.

The second problem was the concentration of metals in the water collected from the open chamber as it descended to the bottom was not consistent with concentrations in the chamber shortly after it reached the bottom. The values from laboratory analysis of the water in sample bottle one (which filled during descent, after manual operation of its valve near the surface) and from water in sample bottle number two (filled from the chamber 6 minutes after lid closure) were inconsistent. As with the blank tests, the concentration values from the second sample bottle were considered more representative of makeup water entering the chamber and were used in dilution correction calculations. As with the blank tests, a sensitivity analysis indicated an insignificant affect on flux results. A more acceptable method for collecting representative bottom water was later implemented and test deployed before the Pearl Harbor demonstrations.

5.1.2.3 Discussion Of Data Interpretation. To understand the significance of the measured flux rates in Paleta Creek from a water quality standpoint, the potential loading and subsequent increase in metals concentrations within the overlying water must be estimated. A simplified analysis is presented here to show how BFSD2 data can be used for this purpose.

The Paleta Creek study area where the demonstrations were performed is bordered by land on three sides, and open to San Diego Bay only to the southwest. The bounded area has a surface area of about 62400 m^2. The average depth of the area is about 7 m and, thus, the overall volume is about 436800 m^3. The tidal range in San Diego Bay averages about 1.4 m. A simple estimate of the residence time can be obtained based on complete tidal flushing as

$$\tau_{res} = \frac{V_{pc}}{V_{tp}} = \frac{D_{pc}}{H_t N_t} = \frac{7}{1.4 \times 2} = 2.5\, days$$

where τ_{res} is the residence time, V_{pc} is the volume of the Paleta Creek study area, V_{tp} is the tidal prism volume for the area, D_{pc} is the depth of the study area, H_t is the tidal range, and N_t is the number of tides per day.

In steady-state conditions, the residence time can be related to the overlying water concentration by the relation,

$$\tau_{res} = \frac{m_{ow}}{\dot{m}_{sed}}$$

where m_{ow} is the mass of a given metal in the Paleta Creek study area overlying water, and m_{sed} is the loading from the sediment.

The overlying water concentration can thus be estimated from the flux rates as

$$c_{ow} = \frac{m_{ow}}{V_{pc}} = \frac{\tau_{res}\dot{m}_{sed}}{V_{pc}} = \frac{\tau_{res} F_{sed} A_{pc}}{V_{pc}} = \frac{\tau_{res} F_{sed}}{D_{pc}}$$

where F_{sed} is the sediment flux rate measured by the BFSD, and A_{pc} is the surface area of the sediment in the Paleta Creek study area. Using this relation, the estimated overlying water concentrations for each of the metals from each of the surveys can be estimated as table 6 shows.

Table 6. Estimated sediment flux contribution to overlying water concentrations for the Paleta Creek study area.

Metal	PCPD Flux	PCD Flux	τ_{res}	D_{pc}	C_{ow} PCPD	C_{ow} PCD	C_{ow} meas.	PCPD % of meas.	PCD % of meas.
	$\mu g/m^2/day$	$\mu g/m^2/day$	days	m	ug/l	ug/l	ug/l		
Copper (Cu)	-2	-7	2.5	7	-	-	2.41	-	-
Cadmium (Cd)	10	7	2.5	7	0.0036	0.0025	0.0786	4.54%	3.2%
Lead (Pb)	11	4	2.5	7	0.0039	0.0014	0.182	2.16%	0.8%
Nickel (Ni)	25	19	2.5	7	0.0089	0.0068	1.02	0.88%	0.7%
Manganese (Mn)	73	105	2.5	7	0.0261	0.0375	21.0	0.12%	0.2%
Zinc (Zn)	716	575	2.5	7	0.2557	0.2054	8.91	2.87%	2.3%
Silica (SiO_2)	30*	30	2.5	7	0.011 **	0.011 **	0.79 **	1.35%	1.4%

*$mg/m^2/day$ **mg/l

Note: C_{ow} measured is the overlying water concentration that was measured during the PCD study. The percent of measured column indicates the fraction of the overlying water concentration that can be explained by the sediment flux.

Comparing the estimated overlying water concentration to the measured concentration indicates that the contribution caused by sediment fluxes ranges from a high of 4.5% for cadmium to a low of about 0.2% for manganese. In practice, these estimates could be used to evaluate the potential benefit of a sediment removal or capping action compared to a no-action scenario. The simple model employed here neglects many factors such as tidal flushing efficiency of the study area and scavenging of metals near the sediment–water interface that could influence the estimated concentrations. If the tidal flushing is not complete (which is realistic), then the residence time and estimated contribution from the sediments would increase. A typical flushing efficiency is about 50%, which would increase the estimated C_{ow} by a factor of 2. Colloid and particle scavenging near the sediment water interface would tend to reduce the sediment flux contribution although the magnitude of this process is not well-known.

5.1.3 Pearl Harbor, Hawaii, Demonstrations

During February 1999, two 70-hour BFSD2 demonstrations were conducted at two different sites in Pearl Harbor, Oahu, Hawaii. The BFSD2 deployments were conducted as part of a combined demonstration with integrated sediment investigation technologies and included site screening before both BFSD2 deployments.

The first test was conducted 5–8 February 1999 within the Naval Inactive Ship Mooring Facility (NISMF) at Middle Loch, where approximately 70 moored ships await disposition (disposal, sale, temporary storage, etc.). The area is quiet and approximately 26 feet deep with murky water and fine-grained sediment overlain with an easily disturbed 1- to 2-foot flocculent layer. Reports of sediment depths over 100 feet were not confirmed, but are believable. Some benthic organisms were found in the sediment during screening. All work at the site was accomplished from an open-deck, 35-foot Navy workboat operated by enlisted personnel (figure 39). A portable generator powered the video monitor, underwater light, and laptop computer during deployment; however, for recovery, all electrical connections were made after reaching the shore facility.

Figure 39. BFSD2 Pearl Harbor Middle Loch Demonstration.

The second test was conducted 11–14 February 1999 within the area known as Alpha Docks, Marine Diving and Salvage Unit One (MDSU-1) located at Bishop Point on the entrance channel to the harbor (figure 40). Again, historical remedial investigation (RI) and screening data indicated elevated levels of trace metals present in the sediment. This area is an active industrial location and included several U.S. Navy housing barges that are moved about by tugboats. The area has a depth of approximately 25 feet with generally clear water and medium- to fine-grained sediments. Tidal currents are enough to minimize any flocculent layer. Some benthic organisms were found during sediment screening. The U.S. Navy workboat was used for deployment, but because of proximity to the quay wall, recovery was accomplished from shore using an 80-foot crane.

Figure 40. BFSD2 Pearl Harbor Bishop Point Demonstration.

Before both tests, the BFSD2 was cleaned and prepared using the same procedures used during triplicate blank tests as well as other deployments and demonstrations. For the first deployment at NISMF, Middle Loch cleaning was accomplished at SSC San Diego before loading the BFSD2 into its re-usable shipping container (figures 41 and 42). The shipping container, designed for compatibility with commercial air cargo carriers includes compartments, shelving, and storage bays sufficient for shipment of BFSD2 and all materials and supplies required for extended field operations. Shipping weight was approximately 1450 pounds. For safety reasons, the compressed oxygen cylinder was vented to less than 250 psi and no hazardous materials (i.e., nitric acid for cleaning and sample preservation) were air-shipped. The container proved convenient for on-site access and minimized working space requirements. After arrival and unpacking, system checks and oxygen bottle refilling operations preceded. Nitric acid was secured from the local U.S. Navy environmental laboratory.

Figure 41. BFSD2 container (front view).

Figure 42. BFSD2 container (back view).

Aboard the U.S. Navy workboat, after loading and connecting various equipment (laptop computer, TV monitor and light, and cabling) to the portable generator, a standard pre-deployment checklist was followed. At the site, after tying off, lowering the bow platform and logging the GPS location, the BFSD2 was lowered by hand-winch to near the bottom and either slowly lowered into the sediment (to minimize disturbance and maintain video coverage, as at Middle Loch) or released from about 2 feet for free-fall (to ensure insertion when video coverage can be maintained: as at Bishop Point). Activation of the battery-powered insertion lights by switches mounted on the chamber at the 3-inch level was verified and used to establish adequate sediment insertion. Once on the bottom a 15-minute program was started to stabilize the flow-through sensors and measure the ambient dissolved oxygen level. After entering the dissolved oxygen control limits into the 70-hour test program, downloading and verifying it, the test was started after visibility conditions for lid closure were confirmed. After starting the program, lid closure (which also activates #1 sample bottle) was viewed and commands for circulation pump activation (at 10 minutes) and sample valve activation (at 16 minutes) for sample bottle number two was monitored before disconnecting for autonomous operations. The disconnected cables were plugged, coiled, and cast overboard in a direction away from the BFSD2. Both demonstration deployments were straightforward and without problems.

For both tests, the BFSD2 was returned to the shore facility for all data recovery. After freshwater washdown and cleanup, the 12 250-ml sample bottles were removed for processing using EPA handling and chain-of-custody procedures. Pre-acidified 125-ml containers were filled and capped, labeled, logged, and refrigerated for subsequent analytical laboratory metals analysis. The remaining sample volume was used to measure silica concentrations with the field portable Hach model DR2010 Instrument. The silica concentrations plotted against time and the BFSD2 pH and dissolved oxygen sensor data, also plotted against time, were reviewed for any possible sample compromise before shipment to the analytical laboratory. Tables 7 and 8 summarize the results of the Pearl Harbor Middle Loch and Bishop Point demonstrations.

Table 7. BFSD2 results from the Pearl Harbor Middle Loch (PHML) demonstration.

Metal	Flux ($\mu g/m^2/day$)	+/- 95% C.L. ($\mu g/m^2/day$)	Flux rate Confidence (%)	Triplicate Blank Flux ($\mu g/m^2/day$) Average	Triplicate Blank Flux ($\mu g/m^2/day$) +/- 95% C.L.	Bulk Sediment ($\mu g/g$)	Overlying Water ($\mu g/L$)
Copper (Cu)	14.79	3.46	99.9%	2.82	8.73	195	0.80
Cadmium (Cd)	1.80	0.31	100.0%	-0.52	0.75	0.2	0.02277
Lead (Pb)	-0.12	0.43	95.2%	3.16	1.59	34	0.03879
Nickel (Ni)	27.17	15.91	100.0%	10.28	7.34	214	0.9472
Manganese (Mn)	-468.18	683.35	97.9%	-264.85	7.49	1180	52.19
Manganese (Mn)[1]	2131.59	904.57	100.0%	-264.85	7.49	1180	52.19
Zinc (Zn)	49.74	17.25	93.5%	-3.38	65.22	314	2.28
Other							
Oxygen (O_2)* (*ml/m^2/day)	-1085.52	64.84	na	na	na	na	4.17
Silica (SiO_2)* (*mg/m^2/day)	65.03	42.43	100%	-1.97	2.88	na	1.19

1. Mn flux calculated on the basis of first five samples due to non-linearity

Table 8. BFSD2 results from the Pearl Harbor, Bishop Point (PHBP) demonstration.

Metal	Flux	+/- 95% C.L.	Flux rate Confidence	Triplicate Blank Flux (µg/m^2/day)		Bulk Sediment	Overlying Water
	(µg/m^2/day)	(µg/m^2/day)	(%)	Average	+/- 95% C.L.	(µg/g)	(µg/L)
Copper (Cu)	112.46	17.60	100.0%	2.82	8.73	241	0.36
Cadmium (Cd)	1.85	1.96	99.4%	-0.52	0.75	0.3	0.009
Lead (Pb)	0.71	1.11	78.7%	3.16	1.59	93	0.06519
Nickel (Ni)	21.04	15.41	96.3%	10.28	7.34	42.9	0.3934
Manganese (Mn)	223.33	284.79	100.0%	-264.85	7.49	324	1.78
Manganese (Mn)[1]	2177.45	192.60	100.0%	-264.85	7.49	324	1.78
Zinc (Zn)	191.18	54.07	100.0%	-3.38	65.22	304	1.43
Other							
Oxygen (O_2)* (*ml/m^2/day)	-567.12	54.96	na	na	na	na	6.5
Silica (SiO_2)* (*mg/m^2/day)	118.61	27.62	100%	-1.97	2.88	na	0.31

1. Mn flux calculated on the basis of first three samples due to non-linearity

Numbers in the Flux Rate Confidence column indicate the statistical confidence that the measured flux rate is different than the blank flux rate. Results from the blank study, bulk sediment analysis, overlying water, and oxygen uptake analysis are shown for comparison.

The results for Middle Loch indicate that copper, cadmium, and nickel had fluxes out of the sediment that were highly significant when compared to the blank chamber results. Zinc also had an outward flux, but the statistical confidence was somewhat lower. Lead had a negative flux (sediment uptake), but the statistical confidence was again somewhat lower. The flux of manganese was negative when calculated using all the samples, but was positive when using only the first five samples. After the first five samples, the manganese concentration in the chamber dropped dramatically. The reason for this drop is not known, but could be attributed to oxidation and subsequent precipitation or flocculation when the chamber water reached a high concentration. The initial manganese flux measured by the first five bottles is similar to fluxes measured at other sites (Note: A similar result was subsequently identified for the Paleta Creek demonstrations and re-analyzed also). The silica flux was out of the sediment and was highly significant when compared to blank results. Dissolved oxygen indicated a sediment uptake.

The results for Bishop Point were significantly different than those of Middle Loch, with the exception of cadmium, which was nearly identical. Copper, cadmium, manganese, and zinc had fluxes out of the sediment that were highly significant when compared to the blank chamber results and the magnitude of the copper and zinc fluxes were markedly higher than those observed for Middle Loch. The nickel flux, however, was somewhat less and with a reduced confidence. Lead fluxed outward at Bishop Point, but confidence is only marginal when compared to blank chamber results. As with Middle Loch, the manganese flux at Bishop Point was non-linear and the concentration in the chamber leveled off after the third sample. The manganese flux calculated using only the first three samples is similar to the flux estimated using the first five samples at Middle Loch and similar to that measured at other sites. The flux calculated using all the samples is low but still positive. The silica flux results were again highly significant compared to blank results and were higher than Middle Loch. The dissolved oxygen sediment uptake was about half that of Middle Loch. Figures 43 and 44 show the results.

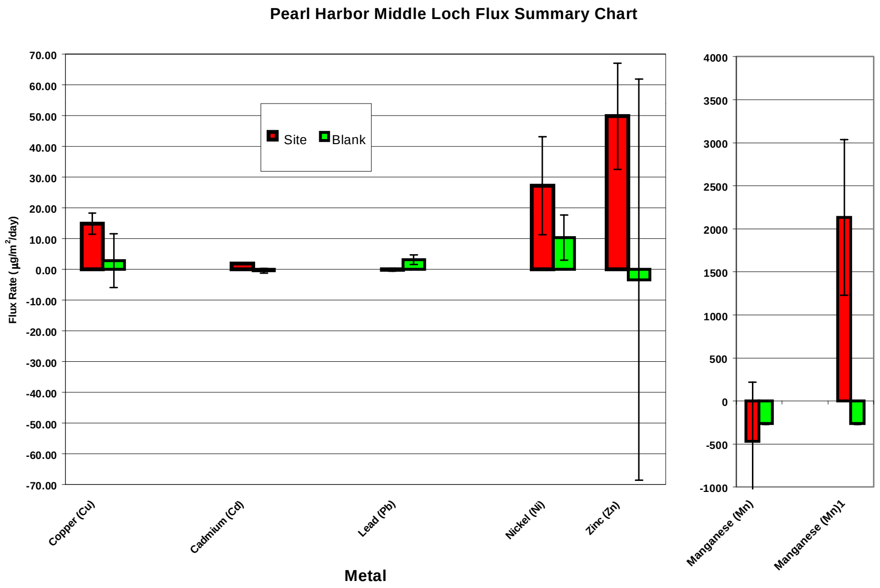


Figure 43. Pearl Harbor Middle Loch Demonstration results.

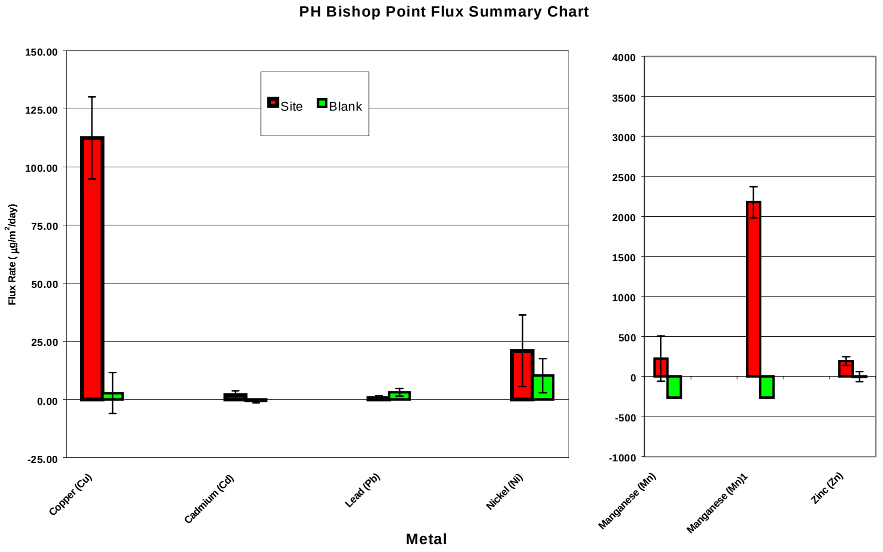


Figure 44. Pearl Harbor Bishop Point Demonstration results.

5.1.3.1 Discussion of Pearl Harbor Demonstration Results. In general, BFSD2 results from the two Pearl Harbor Demonstration locations were significantly different than one another. Figures 45 and 46 are the sets of graphs of concentration versus time for each analyte in each of the demonstrations compared with blank performance. The results for the Middle Loch Demonstration indicates that copper, cadmium, and nickel had fluxes out of the sediment that were highly significant when compared to the blank chamber results. Zinc also had an outward flux but the statistical confidence was somewhat lower. Lead had a negative flux (sediment uptake), but the statistical confidence was again somewhat lower. The flux of manganese was negative when calculated using all the samples, but was positive when using only the first five samples. After the first five samples, the manganese concentration in the chamber dropped dramatically. The reason for this drop is not known, but could be attributed to oxidation and subsequent precipitation or flocculation when the chamber water reached a high concentration. The initial manganese flux measured by the first five bottles is similar to fluxes measured at other sites (Note: A similar result was later identified for the Paleta Creek demonstrations and re-analyzed also.) The silica flux was out of the sediment and was highly significant when compared to blank results. Dissolved oxygen indicated a sediment uptake.

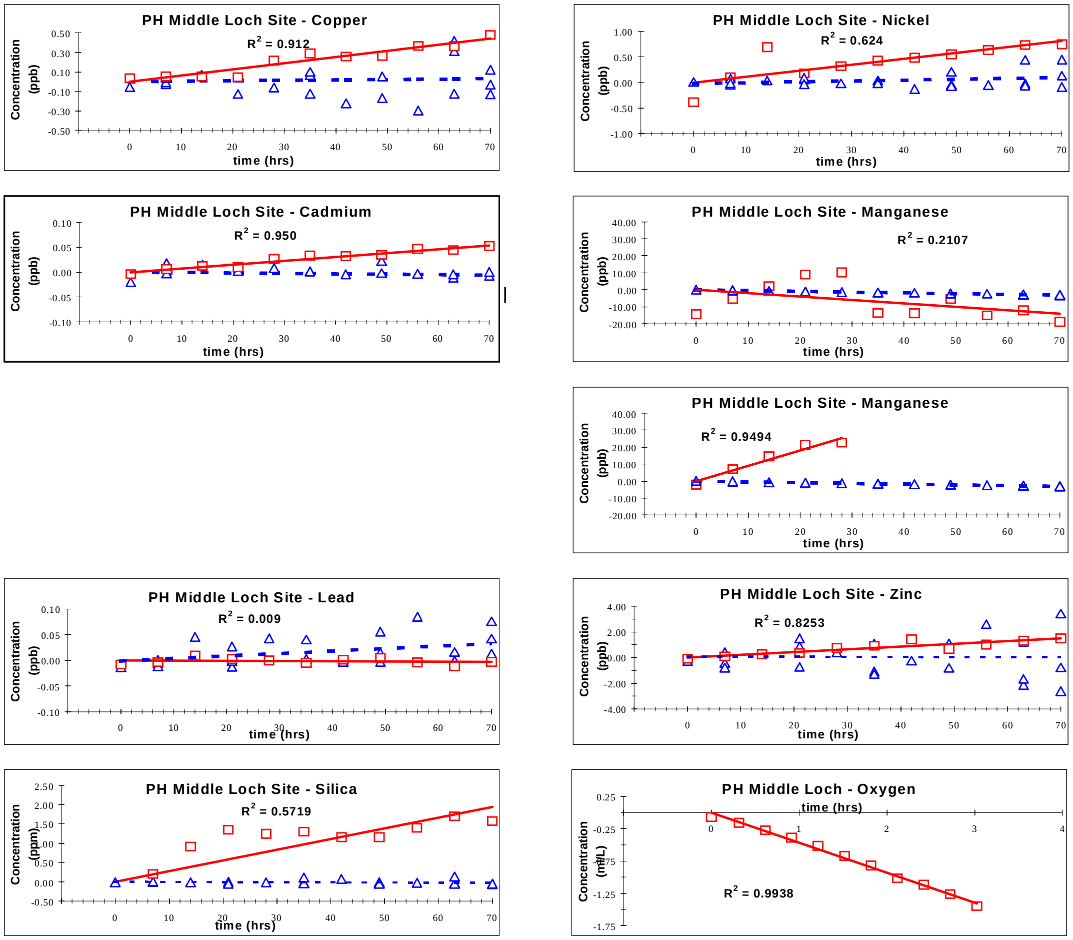


Figure 45. Pearl Harbor Middle Loch Demonstration (concentration versus time).

The results for Bishop Point were significantly different than those of Middle Loch, with the exception of cadmium, which was nearly identical. Copper, cadmium, manganese, and zinc had fluxes out of the sediment that were highly significant when compared to the blank chamber results and the magnitude of the copper and zinc fluxes were markedly higher than those observed for Middle Loch. The nickel flux, however, was somewhat less and with a reduced confidence. Lead fluxed outward at Bishop Point, but confidence is only marginal when compared to blank chamber results. As with Middle Loch, the manganese flux at Bishop Point was non-linear and the concentration in the chamber leveled off after the third sample. The manganese flux calculated using only the first three samples is similar to the flux estimated using the first five samples at Middle Loch and similar to that measured at other sites. The flux calculated using all the samples is low, but still positive. The silica flux results were again highly significant compared to blank results and were higher than Middle Loch. The dissolved oxygen sediment uptake was about half that of Middle Loch.

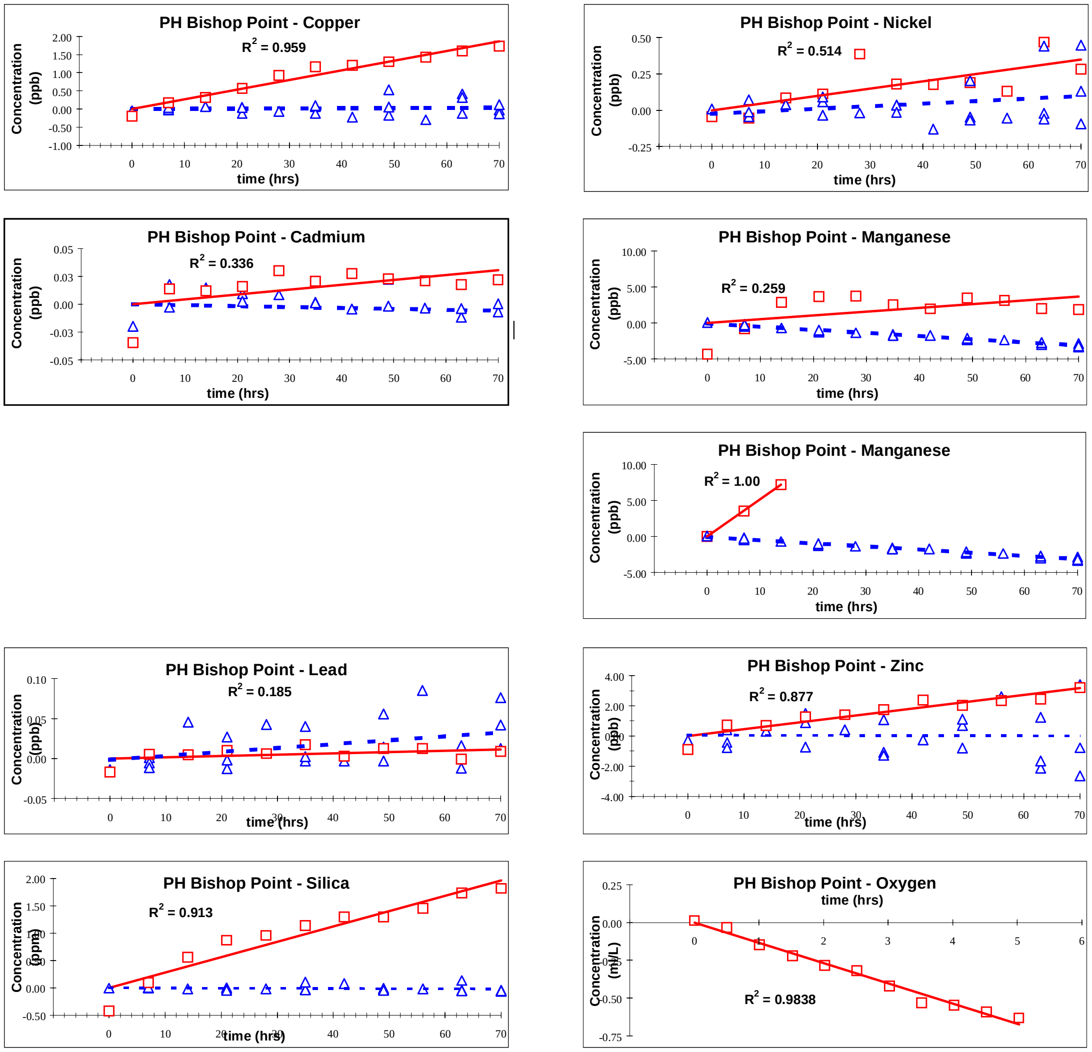


Figure 46. Pearl Harbor Bishop Point Demonstration (concentration versus time).

5.1.3.1.1 Flux Measurements. Flux measurements were made for the metals cadmium, copper, lead, nickel, manganese, and zinc. As tables 8 and 9 and figures 43 through 46 show, the BFSD2 results from the two Pearl Harbor demonstrations were significantly different from one another and from previous surveys.

Middle Loch fluxes were lower than those of Bishop Point, with the exception of Nickel (which was slightly higher). Of interest is that the manganese flux at Middle Loch was initially almost the same (during the first 28 hours) as that at Bishop Point during the first 14 hours and then both exhibited an abrupt downward change. Possible explanations for this observation include complex reduction-oxidation interactions, sulfide binding, complexation with organic matter, or elevated water column concentrations associated with hull leachate sources at the sediment interface. The concentration-time graphs for both manganese and silica at Middle Loch show similar “quenching” trends, which are also apparent to a lesser degree in comparable data from Bishop Point.

Bishop Point fluxes were all outward and larger in magnitude than Middle Loch (except nickel, as mentioned above). Copper, cadmium, manganese, and zinc had fluxes out of the sediment that were highly significant when compared to the blank chamber results and the magnitude of the copper and zinc fluxes were markedly higher than those observed for Middle Loch. The nickel flux, however, was somewhat less and with a reduced confidence. Lead fluxed outward at Bishop Point, but confidence is only marginal when compared to blank chamber results. With consideration for the more subtle manganese and silica “quenching” trends and the relatively lower oxygen uptake rate at Bishop Point, the fluxes appear to be less affected by possible interactions and are mobilizing from the sediment more linearly. The larger sediment grain sizes and size distribution at Bishop Point, as determined during site screening might also be contributing to the apparent linear mobility of the outward fluxing metals.

As with Middle Loch, the manganese flux at Bishop Point was non-linear and the concentration in the chamber leveled off after the third sample. The manganese flux calculated using only the first three samples is similar to the flux estimated using the first five samples at Middle Loch and similar to that measured at other sites. The flux calculated using all the samples is low, but still positive. The silica flux results were again highly significant compared to blank results and were higher at Bishop Point than Middle Loch. The dissolved oxygen sediment uptake at Bishop Point was about half that of Middle Loch.

5.1.3.2 Discussion of Pearl Harbor Demonstration Tests. Important aspects of the demonstrations including performance indicators and deployment problems are discussed the following subsections.

5.1.3.2.1 Performance Indicators. As discussed in section 5.1.2.2.1, several methods were used to ensure BFSD2 system performance during and after the demonstrations. In both deployments, the landing and insertion, monitored with the video camera and landing lights, indicated a good penetration, and after the test was started, the video camera also confirmed successful lid closure. At Middle Loch, the “soft” landing approach minimized disturbance of the flocculent layer and maintain maximum visibility in the already murky water. Penetration was about twice normal (approximately 6 inches) and all visibility was lost. Test start and lid activation was delayed (about 15 minutes) until the water cleared enough to confirm closure. At Bishop Point, a “free fall” landing approach was used from about 1 foot above the sediment without significant loss of visibility. The resulting outward-traveling small cloud of disturbed sediment clearly showed the “low bow-wave” design of the BFSD2 to function effectively. The color underwater video camera made viewing this performance possible.

A monotonic increase in silica during the demonstrations was used as another indicator of proper system performance and chamber seal. As figures 45 and 46 show, the silica concentration increased over the duration of the test, indicating proper system performance and chamber seal for both deployments. The flux magnitudes were high compared to previous mainland surveys, and may be explained by the tropical conditions (i.e., calciferous-rich). Bishop Point Silica results were reasonably linear, but Middle Loch silica flux was not. Following a rate of increase during the first 24 hours of almost twice that of Bishop Point, Middle Loch silica flux slowed significantly for the remainder of the test. The non-linearity in both silica and manganese fluxes suggest that as the concentrations in the chamber build, the fluxes may be altered by the presence of the chamber itself. This alteration could be attributed either to time/concentration dependent reactions within the chamber or changes in fluxes caused by changes in the gradient between the porewater and the overlying water trapped within the chamber.

The dissolved oxygen level in the chamber was monitored and recorded to ensure maintenance of ambient oxygen levels, proper chamber seal, and to evaluate sediment oxygen uptake. The rate of oxygen consumption (sediment uptake) during the deployments (figures 45 and 46) and was sufficient to cause repeated cycling of the BFSD2 oxygen control subsystem. Figure 47 shows graphs of the oxygen sensor data for the two deployments showing the operation of the control system. The control limits selected allowed the dissolved oxygen to remain within approximately 1 ml/L of the ambient level and still yield data to assess the sediment uptake rate. Functioning of the system in this manner ensured that chamber isolation of the water was maintained. The ambient oxygen level at Middle Loch was about one half that of Bishop Point and the sediment uptake rate was about twice that of Bishop Point. These conditions, when combined with the pH results discussed in the following subsections indicate Middle Loch has a higher level of organic decomposition. Again, this is reasonable when considering the differences between the sites.

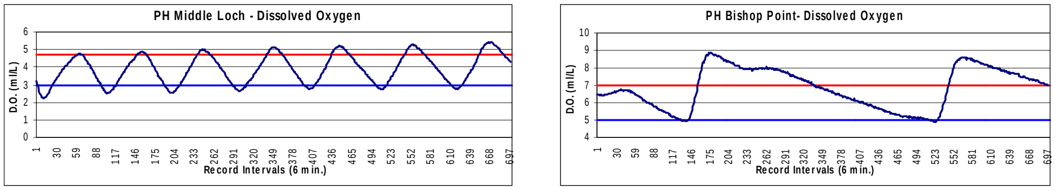


Figure 47. Pearl Harbor Demonstrations (oxygen control results).

The pH level in the chamber was monitored and recorded as another indicator of seal integrity. In a sealed BFSD2 chamber, the pH will generally show a decreasing trend as the breakdown of organic matter at the sediment water interface drives CO_2 into the chamber water. This decreasing trend was observed during both deployments (figure 48). As would be expected from results of oxygen uptake discussed above, the pH level dropped at a higher rate throughout the 70-hour test duration at Middle Loch.

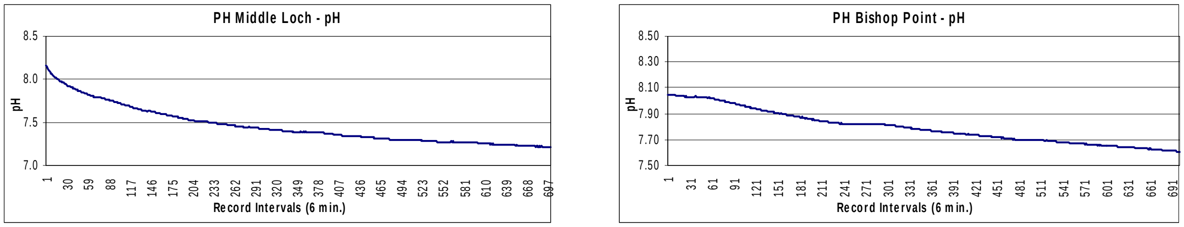


Figure 48. Pearl Harbor Demonstrations (pH results).

5.1.3.2.2 Deployment and Recovery Problems. One minor problem was encountered during recovery at the Middle Loch demonstration and no deployment problems were encountered at either site. At Middle Loch, the commercial acoustic recovery system failed to function following several transmissions of the coded signal. Diver assistance was required to deploy the marker buoy and routine recovery operations were then followed. Later analysis indicated absorption of the acoustic energy by the sediment because of the depth of BFSD2 insertion (almost covering the acoustic receiver window) and a near overhead aspect during transmission. Use of a standoff distance from the approximate location of the BFSD2 for future tests will minimize reoccurrence. Buoy activation was normal (within 8 minutes) after the Bishop Point deployment.

5.1.3.3 Discussion of Data Interpretation. Although the measurements from Pearl Harbor are limited to two locations, they provide significant insight into the importance of understanding contaminant mobility. One way to interpret the flux chamber measurements for Pearl Harbor is to evaluate them in the context of the exposure pathways defined in the RI study. In the RI study, sight-specific Biota-to-Sediment Accumulation Factors (BSAFs) were developed by comparing the tissue burdens of wild-caught organisms to the sediment concentrations found in the same region. In this approach, 100% of the tissue burden is attributed to sediment exposure. One of the primary pathways of sediment exposure is thought to be through remobilization of chemicals to the dissolved phase and later uptake by the organism. The results from the flux chamber measurements allow us to quantify and examine this important pathway.

As an example, we can consider the potential exposure for copper in sediments at the two sites. A cursory examination of the bulk sediment data in tables 7 and 8 indicate that the exposure levels at the two sites would be about the same, with a slightly lower level at Middle Loch than at Bishop Point. Thus, the predicted bioaccumulation for the two sites would also be similar. However, examination of the flux rates for copper at the two sites suggests a much different scenario. The flux rate of copper at Middle Loch was much lower than the flux rate measured at Bishop Point. This scenario indicates that the bulk sediment levels at the two sites do not necessarily reflect the exposure potential. This scenario is further supported by evaluation of the bulk sediment data on a scale normalized for iron content. This analysis indicates that while the levels of copper at Middle Loch fall along the ambient trend, the copper levels at Bishop Point have sources of copper beyond that available from background weathering (figure 49). The high oxygen uptake rates at Middle Loch also indicate the presence of reducing sediments that are likely to contain strong copper binding phases such as sulfides.

These results suggest consideration of a refined exposure model for organisms where the primary exposure is thought to be through the dissolved phase. For example, using the measured flux rates for copper, the contribution of the sediments to the water can be estimated. This would then be used to quantify the fraction of the biological exposure that could be attributed to this pathway. If this exposure mechanism cannot account for observed uptake or effects, then other pathways or sources must be considered.

Thus, the flux rate measurements at the two Pearl Harbor sites illustrate the usefulness of the system in identifying and quantifying exposure pathways between sediments and organisms. The flux results are also consistent with existing knowledge of sediment geochemistry. The results suggest that incorporation of flux measurements on a broader scale will help to improve ecological risk assessments by providing stronger links between bulk sediment chemistry and biological exposure.

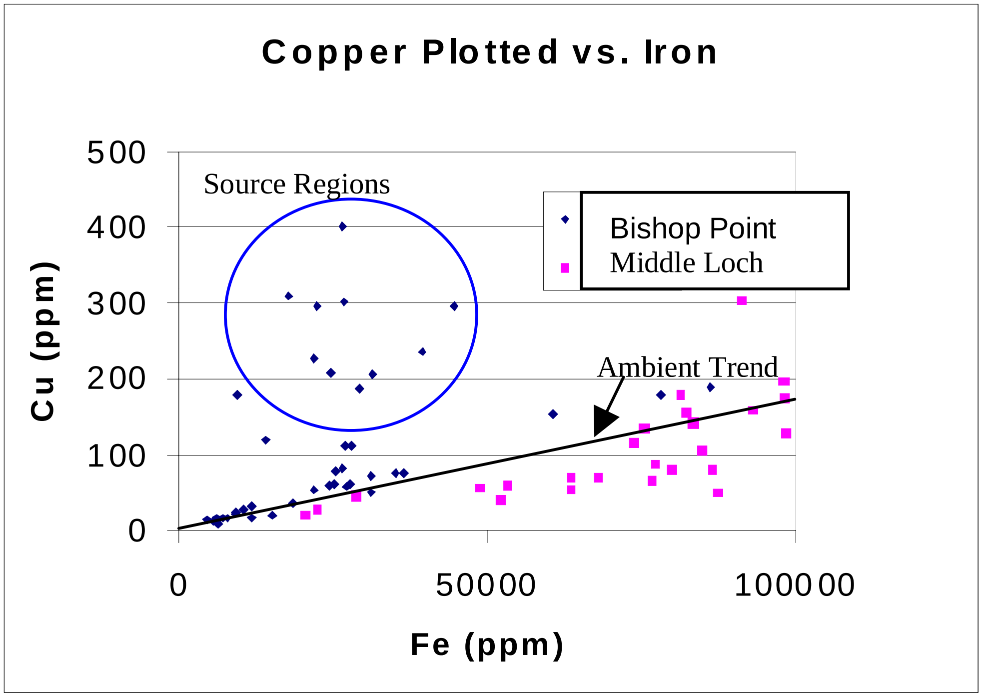


Figure 49. Pearl Harbor demonstration data with iron-normalized bulk sediment copper concentrations.

5.1.4 Paleta Creek and Pearl Harbor Demonstrations Data Assessment

BFSD2 performance assurance indicators show that: (1) a proper seal was achieved during both sets of demonstration deployments and chamber isolation of test water was maintained, (2) oxygen levels were maintained close to ambient levels, and (3) silica, oxygen, and pH trends varied as expected.

The two sets of deployments of BFSD2 at Paleta Creek and at Pearl Harbor, Hawaii, demonstrated consistent performance and the ability to measure trace metal mobility at distinctly different sites. Ease of operation and reliability were also demonstrated. It was further concluded that BFSD2 can provide accurate and repeatable measurements of the mobility of trace metal contaminants to and from shallow water marine sediments when certain prerequisite conditions are met. These sediment flux rates can be established with high confidence when the routine procedures, standard methods, and protocols demonstrated during this study are followed. The BFSD2 and its support equipment are mobile by air transport and field portable, and can be operated with a minimum of resources.

Comparison of measured sediment fluxes with blank-chamber fluxes provides a statistical benchmark for the significance of the measured flux rates. Where statistically significant fluxes are observed, evaluation of impacts on water quality can be performed, or comparisons can be made to bioaccumulation measurements to help identify exposure pathways. The resulting analysis will provide a significant new tool in evaluating potential cleanup options at contaminated sediment sites.

5.1.5 Technology Comparison

There are no directly comparable technologies to the BFSD for *in situ* contaminated sediment flux measurements. Current alternative approaches, such as bulk sediment analysis, have been discussed throughout this report. Alternate methods and associated costs are discussed in section 6.1.4. Site-specific considerations must be considered in determining which combination of technologies will provide the best information. Data analysis and interpretation is likewise dependent on site specific considerations as illustrated in this report.

6. COST ASSESSMENT

6.1 COST PERFORMANCE

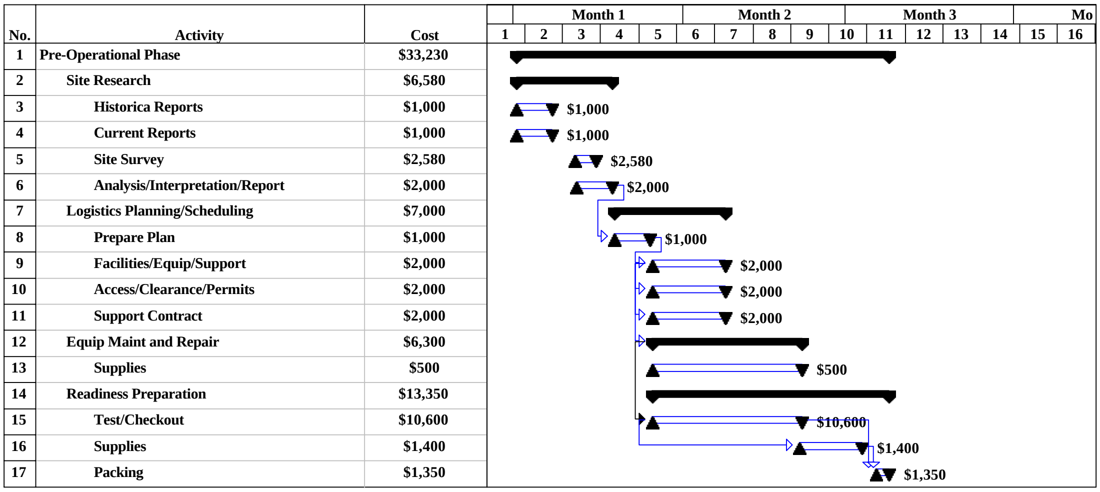
The expected operational costs for the Benthic Flux Sampling Device 2 (BFSD2) are largely driven by analytical laboratory costs. Although typical analytical laboratory prices have shown reductions, the detection level required to achieve meaningful BFSD2 flux measurements requires specialized equipment and highly skilled technicians available at limited sources. Other BFSD2 expected operational costs are driven primarily by labor, supplies, and transportation costs during the pre-operational, operational, and post-operational phases of deployment.

6.1.1 Pre-Operational Phase Costs

The costs incurred prior to field operations are derived from expenses involved with site research and applicability; logistics planning and scheduling; equipment maintenance and repair; and pre-deployment readiness preparations (supplies, packing, checkout). Table 9 and figure 50 include expected pre-operational phase costs and an associated schedule of activities.

Table 9. Expected pre-operational phase costs for BFSD2 deployment.

	Labor		**Non-Labor**		**Totals**
	Govt	Contr	Matls	Other	
Site Research	$5,580	$0	n/a	$1,000	**$6,580**
Logistics Plans	$7,000	$0	n/a	$0	**$7,000**
Maint and Repair	$1,600	$4,200	$500	$0	**$6,300**
Readiness Prep	$2,000	$10,850	$500	$0	**$13,350**
Totals	**$16,180**	**$15,050**	**1000**	**$1,000**	**$33,230**



No.	Activity	Cost
1	Pre-Operational Phase	$33,230
2	Site Research	$6,580
3	Historica Reports	$1,000
4	Current Reports	$1,000
5	Site Survey	$2,580
6	Analysis/Interpretation/Report	$2,000
7	Logistics Planning/Scheduling	$7,000
8	Prepare Plan	$1,000
9	Facilities/Equip/Support	$2,000
10	Access/Clearance/Permits	$2,000
11	Support Contract	$2,000
12	Equip Maint and Repair	$6,300
13	Supplies	$500
14	Readiness Preparation	$13,350
15	Test/Checkout	$10,600
16	Supplies	$1,400
17	Packing	$1,350

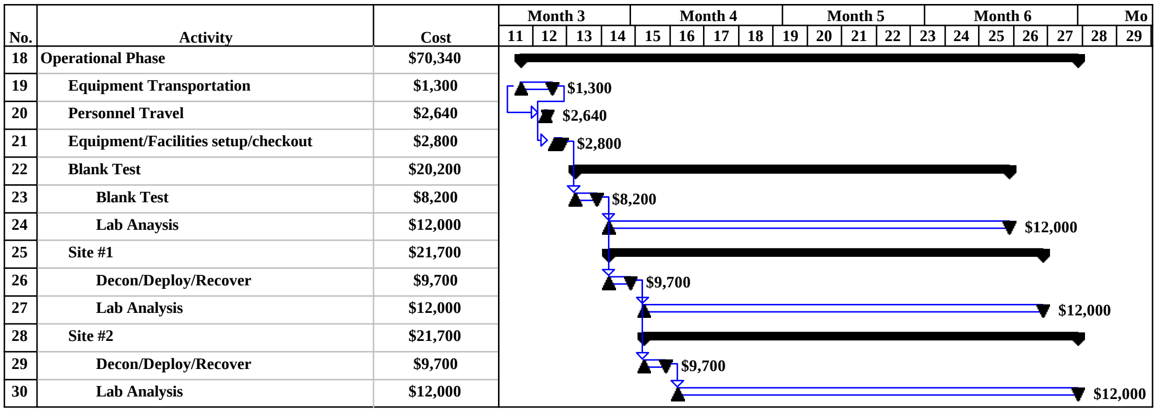
Figure 50. Expected pre-operational phase schedule for BFSD2 deployment.

6.1.2 Operational Phase Costs

The costs incurred for field operations are derived from expenses involved with equipment transportation; personnel travel and per diem; field facilities (shoreside work area, surface vessel, handling equipment); deployment, recovery, and turnaround on a 5-day cycle; and analytical laboratory costs for one blank test and the required number of sites. Table 10 and figure 51 include expected operational phase costs and an associated schedule of activities.

Table 10. Expected operational phase costs for BFSD2 deployment.

	Labor		Non-Labor			Totals
	Govt	Contr	Matls	Lab	Other	
Equip Trans	$100	$200	$0	n/a	$1,000	**$1,300**
Travel	$800	$600	$0	n/a	$1,240	**$2,640**
Equip/Facilities	$1,600	$1,200	$0	$0	$0	**$2,800**
Blank Test	$4,000	$3,000	$0	$12,000	$1,200	**$20,200**
Site #1	$4,000	$3,000	$0	$12,000	$2,700	**$21,700**
Site #2	$4,000	$3,000	$0	$12,000	$2,700	**$21,700**
Totals	**$14,500**	**$11,000**	**$0**	**$36,000**	**$8,840**	**$70,340**



No.	Activity	Cost
18	Operational Phase	$70,340
19	Equipment Transportation	$1,300
20	Personnel Travel	$2,640
21	Equipment/Facilities setup/checkout	$2,800
22	Blank Test	$20,200
23	Blank Test	$8,200
24	Lab Anaysis	$12,000
25	Site #1	$21,700
26	Decon/Deploy/Recover	$9,700
27	Lab Analysis	$12,000
28	Site #2	$21,700
29	Decon/Deploy/Recover	$9,700
30	Lab Analysis	$12,000

Figure 51. Expected operational phase schedule for BFSD2 deployment.

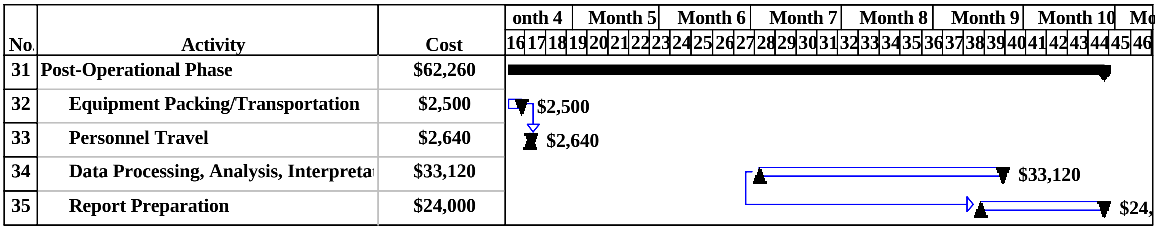
The operational phase costs for one site, which includes the costs for transportation, setup, and a blank test are $48,640, of which 49% is for analysis of the samples. Each additional site adds $21,700 to the total, of which 55% is for analysis of the samples. The operational phase schedule is likewise strongly driven by the standard 60-day laboratory analysis time, which can be shortened to 30-days or less, at additional cost. The 5-day operations period for a BFSD2 72-hour deployment, recovery and turnaround cycle fits conveniently with a standard workweek schedule. An accelerated schedule that shortens turnaround time and includes weekend work periods can achieve two deployments per week.

6.1.3 Post-Operational Phase Costs

The costs incurred following completion of site operations are derived from expenses involved with equipment packing and transportation; personnel travel; data processing, analysis, and interpretation; and report preparation. Table 11 and figure 52 include expected post-operational phase costs and an associated schedule of activities.

Table 11. Expected post-operational phase costs for BFSD2 deployment.

	Labor		Non-Labor			Totals
	Govt	Contr	Matls	Lab	Other	
Equip Pkg/Trans	$0	$1,500	$0	n/a	$1,000	**$2,500**
Travel	$800	$600	$0	n/a	$1,240	**$2,640**
Data Review	$20,000	$13,000	$0	$0	$0	**$33,000**
Report Prep	$24,000	$0	$0	n/a	$0	**$24,000**
Totals	**$44,800**	**$15,100**	**$0**	**$0**	**$2,240**	**$62,140**



No.	Activity	Cost
31	Post-Operational Phase	$62,260
32	Equipment Packing/Transportation	$2,500
33	Personnel Travel	$2,640
34	Data Processing, Analysis, Interpretat	$33,120
35	Report Preparation	$24,000

Figure 52. Expected post-operational phases schedule for BFSD2 deployment.

The post-operational phase costs are largely the labor costs to process, analyze, interpret, and report BFSD2 deployment results. The costs are approximately the same regardless of the number of deployments as long as the sites have generally common geophysical and geochemical characteristics. The schedule is driven by the inactive period of time while awaiting results from laboratory analysis of the samples.

6.1.4 Alternative Methods

Alternative sample collection methods to BFSD2's *in situ* collection and filtering of samples from the sediment–water diffusive interface are available. As with BFSD2, samples collected with alternative methods will require equivalent specialized laboratory analyses to determine contaminant flux rates. Those costs would be equivalent. Thus, a direct comparison focusing on the method of sample collection is useful. Available alternate methods fall into two approaches, *ex situ* and *in situ*. Either of the approaches introduce error sources not present with BFSD2 and minimizing the affects of the error sources increases costs and complexity. Sample integrity becomes a significant factor.

These issues aside, *ex situ* approaches can be as much as 50% cheaper for the field work, but this advantage quickly disappears with sediment processing costs. Alternative *in situ* approaches, where applicable, may yield even greater savings than 50% for the field work, but careful consideration of the factors discussed below may discourage their use.

Both alternative approaches involve isolation of sediment pore water. With either approach, the primary source of error is the oxidation of anoxic pore water, which can significantly alter the aqueous phase trace metals. To prevent oxidation, samples must be processed and handled in an inert atmosphere, typically nitrogen or argon. *Ex situ* methods typically first collect sediment samples that then require additional processing to extract pore water—requiring an inert atmosphere. Centrifuging or squeezing the sediment are accepted practices, but they too introduce error sources including solid-solution interactions. Sectioning samples before extraction to resolve sample depth for gradient determinations also adds cost and introduces errors. In addition, ex situ samplers must be rugged enough for field use yet provide isolation of the sediment sample from metal components. This requirement is particularly difficult for dredging and grab sampling equipment, however, coring equipment can include non-metallic sleeves. Alternative in situ methods collect pore water samples at the sediment interface using either suction filtration techniques or dialysis. *In situ* filtration techniques are limited to coarse grain sediments and do not offer depth resolution. Dialysis techniques incur minimum error sources, but suffer sample collection times as long as 20 days and produce small sample volumes. Periodic sample collection comparable to BFSD2 could require months, which, in turn, raises many additional issues.

7. REGULATORY ISSUES

7.1 APPROACH TO REGULATORY COMPLIANCE AND ACCEPTANCE

Regulatory acceptance has been a fundamental part of this project from the start and was included in the initial execution plan. The approach included application to the California Environmental Protection Agency (CA EPA), Department of Toxic Substances Control (DTSC) program known as “Cal Cert.” A formal “Services Agreement” was signed with the State of California and funded for technology evaluation and certification services. In addition, CA EPA membership in the Interstate Technology and Regulatory Cooperation (ITRC) group of the Western Governors Association (WGA) and the resulting multi-state recognition of certified technologies by at least the 26 member states’ environmental protection agencies promotes recognition and acceptance of the BFSD2. Recognition and acceptance by the U.S. Environmental Protection Agency (US EPA), and private sector, Native American, and foreign interests, are also promoted by their active participation in the ITRC. US EPA, state, local, and private environmental professionals, and CA EPA evaluators attended field demonstrations, which included technology briefings and displays. Finally, certification by CA EPA includes public notifications and listings officially distributed to a various recipients.

The Cal Cert application involved CA EPA review of the technology including background publications, reports, test and evaluation data, and an SSC San Diego site visit for technical discussions and equipment inspection. Because of the unique nature of the BFSD2 technology, a DTSC-wide search for a qualified lead technology evaluator was necessary to locate and secure the services needed for this project. Following acceptance of the Cal Cert application, a performance claim (section 7.1.1) was made by SSC San Diego and included in the Scope of Work (SOW) of the formal CA EPA, DTSC Services Agreement (section 7.1.2).

The demonstrations performed for this project were important elements in the Cal Cert process. CA EPA evaluators reviewed the site selections, the test plans, and attended the field demonstrations. The CA EPA evaluations accomplished independent measurements, data review, and analyses. Appendix E is the formal Cal Cert certificate and publicly released report.

7.1.1 Cal Cert Performance Claim

After acceptance of the Cal Cert application, SSC San Diego made the following performance claim:

PERFORMANCE CLAIM

for

BENTHIC FLUX SAMPLING DEVICE

for

CALIFORNIA EPA CERTIFICATION

The Benthic Flux Sampling Device (BFSD) is an automated, in situ, water-sampling device designed to collect data to quantify the flux of contaminants across the sediment-water interface in marine and aquatic environments. An isolated volume of water over approximately 0.2 square meters of sediment is enclosed in a chamber; discrete water samples are collected periodically over a deployment period of up to four days, preserved at the end of the deployment, and delivered to an analytical laboratory for analysis. With knowledge of the sediment surface area, the volume of water, the time the samples are collected, and the concentrations of constituents in the samples, a flux, expressed in mass per unit area per time, can be derived. The method, and resulting data, are valid when the BFSD standard operating procedures, the laboratory quality assurance and control procedures, and the internal quality assurance checks, such as silica flux, oxygen and pH stability, and statistical tests, have been met. The BFSD is capable of:

1. Deployment from a small surface craft using light duty handling equipment;
2. Operation in a marine environment at depths to 50 meters and bottom currents to 2 knots;
3. Remote real-time video imaging of the bottom site prior to autonomous operations;
4. Programmable, microprocessor-controlled autonomous operation for up to 96 hours;
5. Placement (bottom landing) with minimal disturbance of bottom sediments;
6. Isolation and maintenance of homogenous conditions in approximately 30 liter volume of bottom water for the period of sample collection;
7. Maintenance of oxygen content in the sample chamber within one milliliter per liter (ml/L) of initial conditions;
8. Collection of up to twelve 250 milliliter water samples from the chamber at selected intervals;
9. Measurement and storage of sample chamber depth, dissolved oxygen, pH, conductivity/salinity, and temperature data at selected intervals throughout deployment;
10. Recovery using a portable acoustic signal device to activate a tethered marker buoy; Quantification of flux rates for Cadmium, Copper, Nickel, Lead, Silver, and Zinc based on a least-squares, linear regression of concentrations from 6 to 12 samples;

11. Identification of statistically significant flux rates based on comparison of flux rates measured at the site to flux rates measured in a “blank” BFSD chamber;

13. Blank BFSD chamber performance meeting the following performance standards:

Metal	Blank Flux (ug/m2/day)	+/- 95% Confidence Interval
Arsenic	-5.16	2.10
Cadmium	-.0.52	0.75
Copper	2.82	8.73
Nickel	10.28	7.34
Lead	3.16	1.59
Silver	0.64	0.68
Zinc	-3.38	65.22

14. Verification of blank BFSD performance for each study based on site specific measurements;

15. Verification of proper flux chamber seal and sample collection based on silica concentrations within the chamber during the measurement period;

16. Identification of environmentally significant fluxes on the basis of comparisons/relations such as:
    a. Other known contaminant sources
    b. Hydrodynamic flushing rates of the basin
    c. Remobilization due to other mechanisms such as sediment resuspension
    d. Fluxes measured prior to placement of a containment system such as a cap
    e. Fluxes measured prior to removal of contaminated sediments
    f. Bioaccumulation in marine organisms at the site
    g. Mass balance analysis of input and loss rates for sediment contaminants.

7.1.2 Cal Cert Scope of Work

“In consideration of Applicant's obligations herein, DTSC shall provide professional staff to process a hazardous waste environmental technology certification application. The Scope of Work, Exhibit A, which is attached hereto and incorporated herein by this reference, more specifically sets out the work that will be performed pursuant to this agreement.

EXHIBIT A:

SCOPE OF WORK

Technology Evaluation and Certification Services for Certification of the Department of the Navy Space and Naval Warfare Systems Center, San Diego, Benthic Flux Sampling Device technology

Department of Toxic Substances Control (DTSC) shall perform the following work pursuant to the Agreement between Department of the Navy, Space and Naval Warfare Systems Center., San Diego (SSC San Diego) and DTSC:

1. Negotiate Technology Evaluation and Certification Services Agreement for the certification of the Benthic Flux Sampling Device (BFSD) technology developed by the SSC SD.
2. Review the data and other information submitted by SSC SD.
3. Perform an evaluation of the specific performance claims SSC SD for the equipment, operational procedures, and quality of manufacture for which certification has been requested.
4. Evaluate the efficacy of the BFSD as an automated, in situ water sampling device for collecting data to quantify the metal fluxes of contaminants across the sediment-water interface in marine and adequate environments in bays and estuary environments.
5. Perform an evaluation of the minimal operational standards the technology shall meet to ensure that the technology may be operated properly to insure accurate measurements of metal flux in ocean sediments.
6. Determine the conditions to be placed on the certification including quality assurance protocols and monitoring requirements to assure continued performance of the technology while certification is in effect.
7. Draft a technical evaluation report which summarizes information reviewed and the conclusions reached.
8. Draft DTSC’s proposed decision.
9. Provide for peer review within the DTSC, other interested agencies (both internal and external to the State), and other parties, as deemed appropriate.
10. Provide SSC SD Project Manager the opportunity to comment on and reply to any conclusions, conditions, etc., prior to publishing each proposed decision in the California Regulatory Notice Register.
11. Develop DTSC's proposed decision and publish the proposed decision in the California Regulatory Notice Register.
12. Respond to any comments regarding the proposed decisions.
13. Finalize the Technology Evaluation Report
14. Develop and publish DTSC’s final decision in the California Regulatory Notice Register.

8. TECHNOLOGY IMPLEMENTATION

8.1 DoD NEED

Sediments in many U.S. bays and harbors are contaminated with potentially harmful metal and organic compounds. Contamination occurred directly through disposal of shipyard and shipboard waste, and indirectly through urban runoff and groundwater exchange with land sites. Federal, state, and local regulatory agencies are adopting strict sediment quality criteria. These regulations represent a significant compliance issue for the DoD relative to discharge practices, dredging operations, and clean-up techniques. Previous studies indicate that biological uptake, accumulation, and toxicity result primarily from the fraction of the toxicant pool that is readily solubilized. In surface sediments, the production of this soluble fraction will, in most cases, cause it to migrate through the pore water and across the sediment-water interface. Contaminated sediments at DoD sites pose a potential human health and ecological risk. Source control programs will not eliminate sediment contamination immediately because of the slow degradation and cycling processes that control many pollutants in these systems

For these reasons, benthic toxicant fluxes can provide a unique *in situ* indicator of bioavailability and, hence, an estimate of the potential for risk to human health or environmental harm. Using direct measurements, DoD can reduce the escalating costs of compliance and remediation of contaminated sediments by determining if the contamination poses a significant risk for remobilization. Quantifying the mobility of these in-place contaminants is an essential requirement for deciding the proper method of remediation. The complexity of marine sediment systems makes it very difficult to predict contaminant mobility by indirect methods. There is currently no other satisfactory direct means of quantifying the mobility of contaminants from marine sediments except the Benthic Flux Sampling Device (BFSD2 and its prototype version).

8.2 TRANSITION

Technology transition of the BFSD2 is well underway. It consists of commercialization, regulatory acceptance, product improvement, and performance extension elements.

8.2.1 Commercialization

BFSD2 is a commercialized version of the prototype BFSD. The prototype BFSD was used during the Research, Development, Test and Evaluation (RDTE) phase of the program and was followed by fabrication of BFSD2 during the later Acquisition phase. A Technical Data Package (TDP) and procurement package were generated to support a fixed-price, competitive contract solicitation for fabrication of a commercialized version of the prototype BFSD, called BFSD2. The winner, Ocean Sensors, Inc., in San Diego, used commercial off-the-shelf (COTS) and replaceable/ repairable assemblies in meeting the TDP requirements.

8.2.1.1 Cooperative Research and Development Agreement. A Cooperative Research and Development Agreement (CRADA) was negotiated with Ocean Sensors, Inc.; however, it was not formalized and consummated. The company suggested, and SSC San Diego agreed, that a formal CRADA would not promote its goals for producing additional systems for other customers in response to market demand. No conflicting intellectual property issues were identified with their strategy and the company is currently awaiting new orders.

8.2.2 Regulatory Acceptance

See Approach to Regulatory Compliance and Acceptance, section 7.1.

8.2.3 Product Improvement

Both incremental and continuing product improvements have been included in technology implementation. New methods, processes, and procedures applicable to the BFSD2 were evaluated for use as a result of problems, constraints, or other drawbacks identified during operations.

8.2.3.1 Incremental Product Improvements. Incremental improvements were implemented during the project, such as reconfiguring the circulation pump for improved flow rate control; reconfiguring for *in situ* sample filtration using vacuum-filled collection bottles; installation of a insertion sensor subsystem to ensure minimum sediment penetration; installation of a subsystem to inject sodium bromide into the collection chamber as a conservative tracer to facilitate more accurate volume determination. Care was taken to ensure that such improvements did not invalidate ongoing certification efforts.

8.2.3.2 Continuing Product Improvements. Continuing improvements were implemented during the project, such as: method, timing, and location for collection of a suitable ambient water sample; numerous computational spreadsheet data reduction, processing and display improvements; numerous improvements for turnaround cleaning and preparation; and processes and procedures to improve maintenance and minimize corrosion. Again, we were careful to ensure that such improvements did not invalidate ongoing certification efforts.

8.2.4 Performance Extension

Current BFSD2 performance has been formally demonstrated and evaluated for *in situ* measurement of the mobility of metals (only) in contaminated sediments. DoD needs include capability to measure *in situ* mobility of organic contaminants in sediments. As with the current project, work with the prototype BFSD has shown extension of the technology to organics as possible. A separate RDT&E project will be performed to implement this capability in BFSD2 and a extension of this project to demonstrate and certify the performance.

9. LESSONS LEARNED

9.1 FLEXIBILITY

This project has been relatively straightforward and trouble-free. As with any multi-faceted program that involves a complex new technology, flexibility must be maintained to accommodate emergent issues. Plans and schedules must flex to allow for changes. This project suffered delayed funding at several points, but plans were flexible enough to allow work-around efforts that ultimately recovered schedule losses. Technical approaches must flex to allow for changes. This project benefited from many incremental and continuing product improvements that were accommodated within the technical approach without invalidating demonstration results.

9.2 MOTHER NATURE

Earlier studies had forecast contaminated sediments are non-homogeneous and subject to influences involving benthic organisms, complex marine geochemistry, and other factors. The demonstration results made this fact clear. Accommodation of differences between blank measurements made a few days apart and site measurements made a few feet apart were necessary.

9.3 STATISTICS

With consideration for the very low levels of contaminants measured (parts per *billion* and lower!), metrics involving statistical methods were needed to explain results. Accommodation for results in terms of probabilities and confidence levels must be made to tease out the true meaning of some flux measurements. Throughout, consistent and repeatable materials, processes, and procedures were necessary to minimize their influence on true results.

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APPENDIX A
POINTS OF CONTACT

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APPENDIX B

DATA ARCHIVING AND DEMONSTRATION PLAN

All documents except field and engineering notes are archived as electronic files. Steno-pads with field and engineering notes, as well as hard copies of many of the documents listed are kept in SSC San Diego Code D3604 file cabinets. The files below are stored on SSC San Diego Code D36's Local Area Network Share Drive. Backup tapes are routinely made of all files and are available from the LAN Administrator. The files include:

1. Microsoft Word:
    - Draft and Final Demonstration Plans
    - Draft and Final Reports
    - Individual Demonstration Test Reports
    - *Ex Situ, In Situ,* Test and Checkout Reports
    - Protocols and Procedures
    - Official Correspondence
    - Narrative and Contract Data Requirements Reports
    - CA EPA Certification Agreement

2. Microsoft Excel:
    - Battelle Marine Sciences Analytical Data
    - Computational Spreadsheet Workbooks
    - *Ex Situ, In Situ,* Test and Checkout Data
    - Financial Data

3. Microsoft Power Point:
    - Proposal Viewgraph Presentation
    - In Progress Review Viewgraph Presentations
    - SERDP/ESTCP Viewgraph Presentation

4. Microsoft Project:
    - Program Execution Schedule
    - Individual Demonstration Schedules, Budgets, Tasking
    - *Ex Situ, In Situ*, Test and Checkout Schedules

4. Qualcomm Eudora Pro:
    - all emails (with attachments)

5. MicroGraphics Picture Publisher:
    - Photographic Images
    - Composite Display Poster

APPENDIX C

SPREADSHEET PRODUCTS FOR EACH DEMONSTRATION

APPENDIX D

STANDARD PROCEDURES AND CHECKLISTS

BFSD 2

ON DECK FINAL CHECKLIST

1. Establish Laptop communications and verify "Sensor Check/Br$^-$ Injection" program file is loaded.
2. Oxygen Tank - Turn Valve ON
3. Br$^-$ Injection Valve OPEN (in-line position)
4. Sensor Caps - Slide CTD back and REMOVE O2 & pH storage solution caps (reinstall CTD)
5. Vacuum Check - Assure bottles #2- #12 have >25 in-Hg
6. INSTALL Check Valve plugs in bottles #2 - #12 (hand tight + ½ turn)
7. Check each insertion lever movement and light function
8. Check Camera FOV – Coverage of Insertion lights, lid closure, collection chamber & Br$^-$Injection vent bubbles
9. Open & latch lid - set rotary latch for ½ turn
10. Evacuate Bottle #1 to >25 in-Hg and install check valve plug
11. Rig release hasp and proceed to water entry

BFSD 2

IN WATER FINAL PROCEDURE/CHECKLIST

1. Lift BFSD, remove wheels and suspend over water
2. Submerge fully, stop and inspect for evidence of leakage
3. Lower to within view of bottom and inspect surface for adequate landing and seal potential
4. Execute bottom landing/chamber insertion by either
    a. Slowly descending and assuring insertion light function with minimum loss of visibility, or
    b. Rapidly descending and assuring insertion light function with possible impaired visibility.

IMPORTANT – Surface vessel must be able to hold position (+/- ~50 feet) for next 30 minutes (max). Overboard cables must not be allowed to tighten and disturb BFSD insertion.

5. Run "Sensor Check/Br^- Injection" program and visually verify lid closure followed by vent bubbles (Br^- Injection). Verify commands for CTD, pump and sensor operation by evidence of laptop computer data. After ~10 minutes, upload data, paste into Excel template and establish ambient O_2 level and control values.
6. Modify final test program with selected O2 control limits and download to CTD - verify all loops
7. Run final test program and if surface vessel position hold allows, verify operation from laptop data.
8. Important – *First* close Laptop communications interface and *then* disconnect cables
9. Install and tape watertight connectors, bundle cables and cast overboard - clear of BFSD location
10. Record location, weather conditions, etc, and secure for departure

BFSD 2

SHORESIDE DEPLOYMENT PREPARATIONS

1. Batteries checked/replaced/refreshed:
   - a. Gel cell charged to 24 Vdc @ 25 ma rate
   - b. 14 new D-Cells - pump
   - c. 6 new 9 Vdc batts - acoustic receiver
   - d. 1 new D-Cell - landing lights
   - e. CTD checked for 10+ Vdc
2. All components cleaned:
   - a. Sample bottles cleaned, assembled and vacuum checked (with slow leakers identified for early positions)
   - b. Pneumatic syringe cleaned and loaded w/52 ml Br concentrate
   - c. Valves/tubing fully rinsed and dried
   - d. Chamber cleaned (and "bagged" if req'd)
3. Check loops confirm all subsystems operational
4. Rotary valves in "start" position
5. Bottles installed and >25 in-Hg applied (any slow leakers in early positions).
6. O_2 pressure checked and adequate for deployment
7. Pneumatic syringe installed
8. Acoustic Receiver prepared:
   - a. Ground plate sanded/buffed clean of deposits
   - b. Switch in "ON" position
   - c. Burn wire (with one wire removed) installed
   - d. Function test performed
9. Sensors Calibrated
10. Laptop Status
    - a. Loops designed & checked
    - b. File structure set up (Operations: Loops Library/Data)
    - c. Template functions adjusted for calibrations

BFSD 2

DEPLOYMENT EQUIPMENT LIST

1. Cables
   - one 75’ primary underwater 3-cable set (Comm, Video, light)
   - three Pigtail cables for Laptop comm, TV/VCR, Light
   - Underwater connector plugs
2. Computer Case
   - Laptop computer
   - AC Power supply
   - Log book
   - Check lists, cheat sheets, etc
   - Floppy drive w/data discs
   - Mouse w/pad
3. TV/VCR, controller, VHS Tape(s)
4. Video camera power supply
5. Tool box
6. Extension cord/power strip
7. Hand vacuum pump

BFSD 2

RETRIEVAL/RECOVERY CHECKLIST

1. Stand off from deployment location > 100’ and transmit coded sonar pulse using EdgeTech deck unit (2 series of pulses). Allow 15 min (max) for buoy to deploy and reach surface.
2. Prepare deck hoist equipment and attach to buoy line
3. Raise to a visible depth and inspect/clear any fouling.
4. Raise above surface, open and secure lid, and wash down over water. Clear cables and haul onboard
5. Haul over deck, install pneumatic wheels, and lower to deck
6. Turn Oxygen tank valve “off”
7. Verify system is shut down (ie, pump off). Inspect for damage, leakage, and/or other abnormalities
8. Inspect and note bottle fill conditions, Br^- syringe injection condition, and measure “scum” line location
9. Slide CTD back and install pH and O_2 storage caps
10. Disconnect “comm” cable plug and upload data to prepared file location. Record copy of data to floppy disc.
11. Remove and label sample bottles one at a time, capping inlet port immediately upon removal of Teflon® fill tube.
12. Disconnect cables and plug open connectors. Secure cables.
13. Thoroughly wash down with fresh water and flush valves/tubing with fresh/DI water without delay

BFSD 2

SAMPLE BOTTLE CLEANING AND PREPARATION

1. Disassembly for cleaning (after sample removed)
   a. By hand, unscrew and remove lid from bottle. Avoid gripping and turning filter holder. Set bottle aside.
   b. By hand, unscrew filter holder halves. Avoid gripping and turning bottle lid. Using tweezers, remove membrane filter and store in marked Petre dish (if required). Remove orange O-ring and, using blunt object, dislodge and remove black filter support. Set lid/lower filter holder, O-ring, and support assembly aside.
   c. Using crescent wrench, unscrew and remove plug from top of check valve (if still there), then unscrew and remove spring retainer from top of check valve. Remove spring and valve plunger. Set parts aside.
   d. Using crescent wrench, unscrew and remove tubing plug from upper filter holder/tee assembly. Set parts aside.
2. Cleaning
   a. Rinse all parts in tap water to remove loose material.
   b. Rinse all parts thoroughly in deionized water.
   c. Soak all parts in 4% RBS solution for 4 hours minimum (24 hours preferred)
   d. Rinse all parts in deionized water
   e. Soak sample bottles and Teflon® tubing plugs in 25% nitric acid solution for 4 hours minimum (24 hours preferred)
   f. Soak upper and lower filter holder assemblies, orange O-rings, and black filter supports in 10% nitric acid for 4 hrs (24 hours is OK but NOT preferred).
   g. Rinse all parts in deionized water followed by thorough rinsing with 18-meg-ohm water.
   h. Set all parts in vented hood and allow to thoroughly air dry (overnight is preferred).
3. Assembly and preservation
   a. Assemble in the reverse the order of step 1. above, with the following additions:

- Apply a very thin layer of silicon grease to the check valve O-ring. Using the attached spring, lower the assembly into the check valve body and fully rotate it several times against the mating seat. Secure the spring with the retainer and tighten with a crescent wrench.
- Snap a black filter support into the lower filter holder/lid assembly. Using tweezers, secure a membrane filter and position it on top of the filter support. Position an orange O-ring on top of the membrane filter and hand-tighten the upper filter holder assembly in place. Securely tighten the assembly taking care not to grip and/or rotate the lid.
- Assemble a tube plug and tighten with a crescent wrench.
- Install a Teflon® gasket into the sample bottle lid (if used) and securely tighten the lid assembly to the sample bottle. Avoid gripping and/or turning the filter holder.
- Using a hand vacuum pump, evacuate the finished assemble to 25 in-Hg and set aside for 4 hours minimum (24 hours is preferred).
- If no leakage occurs, sample bottles may be used. If slight leakage occurs on a few, they may be labeled and used early in sample sequence. Leakage may be resolved by further tightening of sample bottle lid. Any leakage resolution requiring disassembly shall include cleaning as above.

APPENDIX E

California EPA, Technology Evaluation and Certification Program Certificate and Official Public Report

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

DEPARTMENT OF TOXIC SUBSTANCES CONTROL

Notice of Intent to Certify

Hazardous Waste Environmental Technologies

The California Environmental Protection Agency, Department of Toxic Substances Control (DTSC) intends to certify the following company's hazardous waste environmental technology listed below:

Applicant: Space and Naval Warfare Systems Center, San Diego, CA 92512-5001

Technology: Benthic Flux Sampling Device.

Health and Safety Code, section 25200.1.5, authorizes DTSC to certify the performance of hazardous waste environmental technologies. The purpose of the certification program is to provide an in-depth, independent review of technologies to facilitate regulatory and end-user acceptance. Only technologies determined not to pose a significant potential hazard to the public health and safety or to the environment when used under specified operating conditions may be certified.

DTSC makes no express or implied warranties as to the performance of the manufacturer's product or equipment. The end-user is solely responsible for complying with all applicable federal, state, and local regulatory requirements. Certification does not limit DTSC's authority to take any action necessary for protection of public health and the environment.

By accepting certification, the manufacturer assumes, for the duration of certification, responsibility for maintaining the quality of the manufactured equipment and materials at a level equal to or better than was provided to obtain certification and agrees to be subject to quality monitoring by DTSC as required by the statute under which certification is granted.

DTSC's proposed decision to certify is subject to public review and comment. Written comments must be received by DTSC no later than 30 days after publication of this notice. All comments will be considered and appropriate changes will be made prior to publishing DTSC's final decision.

Additional information supporting DTSC's proposed decision, including the September 1, 1999 draft report, *"Quantifying In Situ Contaminant Mobility in Marine Sediments"* prepared by Space and Naval and Warfare Systems Center, San Diego, which describes the Navy's field testing procedures and results, is available for review at, and comments should be mailed to:

California Environmental Protection Agency
Department of Toxic Substances Control
Office of Pollution Prevention and Technology Development
P.O. Box 806
301 Capitol Mall, 1st Floor
Sacramento, California 95812-0806
Attn.: Dr. Bruce La Belle (916) 322-3670

A description of the technology to be certified, the proposed certification statement and the certification limitations for the technology of the company listed above follow. DTSC emphasizes that this is a proposed certification for public comment, and not the final certification.

30-DAY PUBLIC NOTICE

HAZARDOUS WASTE ENVIRONMENTAL TECHNOLOGIES

PROPOSED TECHNOLOGY CERTIFICATION

Technology: Benthic Flux Sampling Device

Manufacturer: U.S. Department of Navy
Space and Naval Warfare Systems Center,
53560 Hull Street
San Diego, CA 92512-5001

Technology Description

The Benthic Flux Sampling Device (BFSD) is a benthic lander for in-situ measurements of metal contaminant fluxes from or into shallow marine sediments. The BFSD was designed and developed by the U.S. Navy Space and Naval Warfare Systems Center, San Diego (Navy) to further characterize metal contamination problems in bays, harbors and coastal waters resulting from a variety of sources, including ships, shoreside facilities, municipal outfalls, spills and non-point source runoff. The Navy has received a U.S. Patent (#5473952) for the BFSD.

The technology provides a means to assess contaminant mobility by directly measuring and quantifying the contaminant flux across the sediment-water interface. Other techniques for estimating fluxes across the sediment-water interface rely on measurement of sediment pore water concentrations as a basis for calculating a diffusive flux. In contrast, the BFSD collects samples over time to allow a direct determination of the total flux, which may also include exchanges between sediment pore water and the overlying water from biological or other non-diffusive processes.

The BFSD collects seawater samples periodically at timed intervals from a chamber of known volume which encloses a known surface area of sediment. After a laboratory has analyzed the samples, and with knowledge of the time intervals between samples, a flux rate between the sediment and water in mass per surface area per unit time (micrograms per square meter per day [mg/m2/day]) can be calculated. A minimum deployment over three tidal cycles or 72 hours is typically used to perform a flux rate measurement which incorporates overall tidal effects. This time period is intended to balance the need to determine an overall net flux with the recognition that the presence of a benthic lander may affect the benthic environment.

The BFSD consists of an open-bottomed chamber mounted in a modified pyramid-shaped tubular framework with associated sampling gear, sensors, control system, power supply, and deployment and retrieval equipment. The entire device is approximately 1.2 by 1.2 meters from leg to leg and weighs approximately 175 pounds. The lower part of the framework contains the chamber, sampling valves, sampling bottles, and batteries. The upper frame includes a release that is acoustically burn-wire triggered. The BFSD is designed for use in coastal and inland waters to maximum depths of 50 meters. A small boat or vessel equipped with winch and cable may be used to deploy and retrieve the BFSD. Maximum deployment time is approximately four days based on available battery capacity.

The chamber is a bottomless box, approximately 40 centimeters (cm) square by 18 cm tall, with a volume of approximately 30.0 liters. The volume was chosen to allow for a maximum overall dilution of less than 10 percent due to sampling withdrawal into 11 samples of 250 milliliters (ml) each. The chamber is constructed of clear polycarbonate to avoid disrupting any exchanges that may be biologically driven and, thus, light sensitive. To prevent stagnation in the corners of the chamber, triangular blocks of polycarbonate occupy the 90-degree angles. The top of the chamber is hinged at one edge so that it may be left open during deployment, allowing the chamber to fill with water while minimizing sediment disturbance. Once the chamber is in place, the computer control system closes the lid. A gasket around the perimeter of the chamber ensures a positive seal between the chamber and the lid. Exact alignment is not required, because the lid is slightly larger than the sealing perimeter of the gasket and pivots on two sets of hinges. The lid is held closed by four permanent magnets situated along the chamber perimeter. The bottom of the chamber forms a knife-edge. Pressure-compensated switches mounted on the bottom surface of three sides of a flange circling the chamber at 7.6 cm above the base activate a series of three lights visible with a video camera mounted on the upper frame. Illumination of the lights indicates a uniform minimum sediment penetration depth has been achieved and a good probability that a positive seal between the chamber and the sediment has been achieved.

During the deployment or sample collection period, the seawater in the flux chamber is continuously mixed and monitored for key parameters: conductivity, temperature, pressure, salinity, pH, and dissolved oxygen. Water enclosed in the flux chamber is continuously pumped through a recirculation loop including a flow-through sensor system. Mixing is accomplished as recirculated water is returned to chamber through a helical diffuser mounted vertically on the central axis of the chamber such that the hydrodynamics inside the chamber simulate near bottom currents outside the chamber.

The acquisition and control unit is an Ocean Sensors Model OS200 conductivity temperature depth (CTD) instrument, modified to allow control of the BFSD. It consists of a data logger that acquires and stores data from sensors, and a control unit that regulates sampling and other functions of the BFSD. The data logger collects data from a suite of sensors housed in the CTD and connected to the chamber through a flow-through loop. A small constant-volume pump maintains circulation in the flow-through system to the sensors and is also used to mix the contents of the chamber. The control unit closes the lid, activates the flow-through/mixing pump, activates dissolved oxygen control valves, and controls activation of the synchronized parallel rotary sampling valves.

Discrete samples are obtained using a vacuum collection approach consisting of sample containers, fill lines, in-line filters (with 0.45 micron membrane filters), check valves, and synchronized parallel rotary valves connected to the chamber fill line. Off-the-shelf 250ml Teflon collection bottles are modified to allow filling through the cap. Sampling containers of any volume, material (e.g., glass Teflon, polycarbonate), or shape may be used, provided the cap can be modified to accept the fill line connection, the bottle walls are strong enough to withstand the pressure at the sampling depth, and the cap seal is airtight and watertight at the sampling depth pressure. All valves, fittings, and tubes are made of Teflon or other nonmetallic materials to minimize potential metal contamination of samples and to facilitate cleaning. Samples are drawn from the chamber through a 4-mm Teflon tube connected to the rotary valves and into the sampling bottles. Sampling is initiated by the control system when it activates the valves at preprogrammed intervals. Seawater samples are drawn through the sampling system by a vacuum of 25 inches of mercury (minimum) which is applied to all sample bottles through check valves mounted in the bottle lids. The check valves are then sealed. Water enters each sample bottle when the rotary valves are activated at timed intervals or when the lid closes and opens a valve attached to its hinge. Filtered seawater flows into each bottle until pressure is equalized, normally yielding at least 240ml.

An oxygen control subsystem prevents anoxic conditions from occurring within the chamber. Based on the oxygen sensor data, the system automatically adds oxygen through a 15-meter long diffusion coil in the flux chamber. The system maintains the dissolved oxygen levels in the chamber within a user-selected window about the measured bottom water oxygen level. This is done because fluxes of metal contaminants are sensitive to redox conditions and most contaminant fluxes are not large enough to be measured in chambers without oxygen regulation; the isolated volume of seawater will become anoxic before significant contaminant fluxes have occurred.

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A deployment cable and release line are used to lower the BFSD to its intended depth. Following either rapid or slow descent to the bottom, the minimum depth of collection chamber insertion is sensed by pressure-compensated switches, which activate lights mounted on the chamber frame used for video monitoring and inspection of the sampling site. Recovery is accomplished by transmitting a coded acoustic signal to the frame-mounted receiver which in turn releases the marker buoy. The line attached to the buoy is used to lift the BFSD aboard the vessel. Stored sensor data is uploaded before detaching the cables.

A more detailed description of the BFSD and its components, including the sampling chamber, acquisition and control system, sampling subsystem, circulation subsystem, and oxygen control subsystem, is given in the September 1, 1999 draft report, "*Quantifying In Situ Contaminant Mobility in Marine Sediments*" prepared by Space and Naval Warfare Systems Center, San Diego (September 1, 1999 Draft Report).

Analytical Methods

Cleaning. Prior to each deployment, the BFSD sample collection system is cleaned and decontaminated. A sequential process of flowing cleaning fluids through the sampling subsystem using vacuum; of soaking disassembled parts (collection bottles and other parts) in prepared solutions; of physically brushing and rinsing the collection and sensor chambers and the circulation subsystem with prepared solutions is followed. A nitric acid soak/rinse is used, a final rinse is carried out with 18 meg-ohm/cm de-ionized water, then all paths of contamination are sealed/closed until deployment.

Performance Indicators. A series of performance indicators is used to evaluate the data obtained during operational deployments. One performance indicator is the chemistry time-series data for silica. Silica, a common nutrient used in constructing the hard parts of some planktonic organisms, typically shows a continuous flux out of the sediments due to degradation processes. The linear increase in silica concentration with time in the collected sample bottles is therefore used as an internal check for problems such as a poor chamber seal at the lid or sediment surface. A field analytical test set (Hach Model DR2010) is used to assess the silica concentrations immediately following retrieval and before sending collected samples to the analytical laboratory. Also, with a good chamber seal the ongoing bacterial degradation of organic material in the sediment consumes oxygen (which must be regulated by the BFSD) and generates carbon dioxide. This gradually lowers the chamber pH. Although the expected relationships of these performance indicators aid in determining normal or successful deployments, natural variability is always present to cloud these relationships. Variations in the pore water reactions at the various sites lead to differences in the observed fluxes of oxygen, silica, and the metals. One major factor contributing to the large variations in fluxes may be burrowing activity. Enhanced biological irrigation (pumping of the overlying seawater through sediment burrows by infaunal organisms) increases the surface area of the sediment-water interface and flow rates across the interface, and may also increase the observed fluxes. The organisms responsible for this biological pumping will also affect oxygen uptake rates and may make interpretation of the analytical results more difficult.

Blank Tests. As part of the performance verification, blank tests were performed by filling the BFSD with seawater and holding it in isolation from the surrounding water and sediments while samples were collected in the same manner as with sediment flux experiments. These tests were run in triplicate (triplicate blank test) to determine the lower limit of resolution for flux determinations of various metals. A polycarbonate panel was sealed across the bottom of the chamber, and the BFSD was filled with sea water as it was lowered to within several meters of the sediment surface. A standard operational program identical to the demonstration deployments was run for 70 hours. The blank test results are discussed further under the Evaluation Approach and the Field Activities and Test Results sections, below.

Computations. Fluxes are computed from the trace metal concentrations in each sample bottle using a linear regression of concentration versus time after the concentrations are corrected for dilution effects. These dilution effects result from the intake of bottom water from outside the chamber to replace the water removed for each collected sample. An interactive computational spreadsheet processes most data. Analytical laboratory results, sensor and other measured data, performance indicator results and blank test results are entered into the spreadsheet template and processed. A series of tables, charts and graphs are computed and displayed, including statistical confidence and other data and figures that summarize the results.

Analytical Method. Trace metal analyses of collected seawater for arsenic, cadmium, copper, manganese, nickel, lead, silver, and zinc in seawater, are performed by inductively coupled plasma mass spectroscopy. For the Navy field studies, Battelle Marine Science Laboratories performed the analyses using their Standard Operating Procedure, MSL-1-022-01, “Determination of Elements in Aqueous and Digestate Samples by ICP-MS.” Prior to analysis, samples are preconcentrated using a published tetrahydroborate reductive precipitation technique.

Basis for Certification

Evaluation Approach

The evaluation of the BFSD was designed to provide the data necessary to draw conclusions on the technology’s performance. Key data regarding the technology’s performance were collected during field studies performed as part of the evaluation. Additionally, the critical operating parameters and conditions related to the technology’s performance, reliability and safety were to be identified. The evaluation included a review of supporting documents and information submitted by the Navy which describes their technology and its intended operation and maintenance. The Navy had previously performed tests on a prototype BFSD (Prototype BFSD), which was designed and modified as part of their technology development and proof-of-concept efforts. DTSC reviewed these previous Navy studies to provide background on the technology and to help identify key parameters for the field studies.

The Navy conducted two field studies specifically for the certification evaluation, using the current version of the BFSD, as described in the technology description, above. These included two deployments at the Paleta Creek area of San Diego Bay, California and two deployments at the Middle Loch and Bishop Point areas of Pearl Harbor, Hawaii. The Navy conducted an additional field demonstration during the certification evaluation at the Alameda Naval Air Station, California which was also reviewed. The Department of Toxic Substances Control (DTSC) reviewed the work plans prior to the demonstrations and agreed with proposed field test objectives and procedures, and data quality objectives. DTSC staff also provided oversight and were present to observe many, but not all, of the field test activities. Following the completion of the field tests, the Navy submitted their reports providing the data collected and an analysis of the results. Detailed data submitted for the Alameda NAS site included two flux measurements. Additionally, detailed laboratory reports including QA/QC results were requested and reviewed.

The field tests were intended to verify the performance of the BFSD in quantifying the rates of exchange of target metal contaminants at the sediment-water interface. Specifically, the objectives of the BFSD technology demonstrations were to: (1) Evaluate the data to determine if a statistically significant flux was occurring at the test locations; (2) Evaluate the BFSD performance for repeatability; and (3) Evaluate a range of conditions in which the BFSD can be operated.

To determine whether statistically significant fluxes were occurring at the test locations (Objective 1), 12 seawater samples were collected at 7-hour intervals using the BFSD. The water samples were analyzed for metals including cadmium, copper, manganese, nickel, lead, zinc and silica. Sediment samples, when collected, were analyzed for grain size, total solids, total organic carbon (TOC), acid volatile sulfide (AVS), simultaneously extracted metals (SEM), and total metals. Although the sediments may have been contaminated with other constituents, only the flux of the listed metals was evaluated during the demonstrations. Sample concentrations were corrected for dilution introduced by the sample collection process, and a regression curve was generated for each analyte based on the concentration data.

To determine whether calculated fluxes are due to fluxes into or from the sediment, or due to sorption or other interactions of the metals with the BFSD components, flux rates with regression coefficients were compared with the results for each metal obtained during triplicate “blank” BFSD tests (blank tests). These blank tests were performed by filling the chamber with seawater, sealing it, and suspending it above (but isolated from) the surrounding seawater and sediment surface. The data obtained during the blank tests provided a measurement of the repeatability of metal analyses and allowed a determination of any changes in metal concentrations in seawater over time which result from the BFSD itself. The measured sediment flux rate for each metal was then evaluated to determine if a statistically significant flux had been measured when compared with the blank chamber (background) tests.

The BFSD was evaluated for repeatability (Objective 2) by analyzing the results of repeat deployments, two weeks apart, at the same Paleta Creek site. Demonstration data was also compared with data from the site during Prototype BFSD tests in the same approximate location. Finally, repeatability was evaluated by comparing the results from three blank chamber deployments. Lastly, the range of conditions for operating the BFSD was evaluated (Objective 3) by describing the conditions under which the BFSD operated as claimed, and the projected range of contaminants applicable to the technology.

At the San Diego Bay location (Paleta Creek) two deployments at the same site were made; at the Pearl Harbor location, one deployment at each of two geologically different sites were made (Middle Loch and Bishop Point). Comparison of the results of the two Paleta Creek demonstrations to one another was intended to evaluate repeatability of the technology. Comparison of the results from the two geographically different sites in Pearl Harbor was intended to demonstrate data differences and analysis/interpretation approaches.

Three "blank test" deployments were conducted, during which the BFSD was deployed in seawater with a sealed sampling chamber. Three time series of samples were collected and a baseline was established for each analyte, which provided a statistical estimate of the lower limit of flux detection measurable with the BFSD. The data also served as another measure of repeatability. Previous results obtained at the same location using the Prototype BFSD also provided a general measure of trend repeatability. For each analyte, a rate of flux between the sediment and the water during each deployment was calculated using knowledge of the volume of water enclosed within the BFSD, the surface area of sediment isolated, the time the samples were collected, and the concentrations of the contaminants of interest in the individual samples.

At the Alameda NAS Seaplane Lagoon location the Navy measured metal contaminant fluxes in sediments at four locations in support of an ongoing site characterization study. In addition to the metal analytes mentioned above, the Navy’s target metal analytes at this site included arsenic, mercury and silver. OPPTD staff were present to observe deployment and retrieval procedures for two of the deployments. A summary of the results for the four Seaplane Lagoon site deployments was reviewed in addition to the detailed data for the flux measurements made at the SPL-7 and SPL-10 locations. Laboratory reports and QA/QC results for these four flux measurements were not included in the certification evaluation.

Following the completion of the field tests, the Navy prepared a draft report “Quantifying In Situ Contaminant Mobility in Marine Sediments,” September 1999, which describes the technology and discusses in detail the results of the San Diego and Pearl Harbor field tests. This report was reviewed by DTSC staff as part of the evaluation, and incorporates their comments. DTSC staff reviewed the raw data and the statistical analyses used by the Navy as the basis for the report, as well as the data obtained during the Alameda field tests.

Review of Previous Testing of the Technology.

Results of previous testing and initial technology development efforts performed by the Navy were reviewed as part of the certification evaluation. Initial development program tests included ex situ (laboratory) and in situ (field) trials of critical components, subsystems, and systems. System development tests were conducted at various locations within San Diego Bay during 1989-91. Full-scale system trials during June 1991 were conducted in Sinclair Inlet, WA, including ten deployments of the Prototype BFSD to characterize flux rates of contaminants from seven shipyard sites and three reference sites (no blank test was conducted). Collected samples were analyzed for the trace metals arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn). Following review of the data, an active oxygen control subsystem with sensor feedback was developed and added to the system, along with several other changes to improve operation reliability.

During 1993, four tests of the upgraded version of the Prototype BFSD were conducted at sites within in San Diego Bay: one at Paleta Creek (at its entrance to the bay within Naval Station San Diego); two at a commercial yacht harbor (Shelter Island); and one at a industrial shipping terminal (PACO Industries). The deployments were preceded by blank tests to determine the lower limits of flux that could be resolved with the Prototype BFSD. Results from these deployments showed significant sediment flux rates when compared to blank test results and clear differences between the sites as related to potential trace metal sources. Paleta Creek results showed the highest flux levels for Cd, Cu, Ni and Zn.

Seven more Prototype BFSD deployments in San Diego Bay in support of a sediment quality assessment at Naval Station San Diego were conducted during 1995. Paleta Creek was again included along with five other sites near piers and quay walls and one site outside the study area used as a reference. The work, preceded by a blank test, yielded results that were consistent with the results from the 1993 study and showed Cd, Ni, Zn and Mn all to have positive fluxes. Paleta Creek again showed the highest trace metal fluxes with levels which were generally consistent with those measured in 1993. Correlations between measured trace metal flux levels and complex marine chemistry processes were studied and informative trends were identified. For example in the complex oxidation-reduction (redox) marine environment, it was found that trace metal fluxes are consistent with oxidation of solid metal sulfides as a sediment source.

Field Activities and Test Results

Blank Tests. The primary purpose for carrying out system blank tests was to establish BFSD minimum performance levels, or detection limits, for assessment of flux data obtained during subsequent demonstration tests. Three replicate 70-hour blank tests were conducted using BFSD between May 14 and 31, 1998. The tests were conducted from the end of SSC, San Diego Pier 159 at approximately two feet off the bottom in seawater ranging from about 14 to 20 feet deep, depending on tidal flow. As expected, the blank results for most metals showed little or no time trend, indicating minimal source or loss of target analytes during the blank experiments. With the exception of lead and manganese, replicate analysis indicates that none of the metal fluxes were significantly different from a zero flux condition at the 95% confidence level. The BFSD blank performance was statistically established and the values obtained were repeatable, precise and accurate enough to allow valid measurement of in situ sediment flux rates.

Paleta Creek, Pearl Harbor, and Alameda NAS Demonstrations Data Assessment. The BFSD performance assurance indicators for the flux measurements made at the three different geographic locations show that: a proper seal was achieved during the deployments and chamber isolation of test water was maintained; oxygen levels were maintained close to ambient levels; and silica, oxygen and pH trends varied as expected. The flux measurements at these sites for the target metals, arsenic, cadmium, copper, lead, nickel and zinc, were determined to be statistically different from the blank, indicating actual fluxes of these metals from or into the sediments were occurring. Data for cadmium, copper, lead, nickel and zinc were obtained from all three field tests, while data for arsenic was obtained only from the tests at Alameda NAS. The results for arsenic, however, showed a high level of confidence (>99%) that the calculated fluxes at this site were statistically different from the blank flux. Additional details and discussion of the results for the San Diego and Pearl Harbor field tests are available in the Navy's report "Quantifying In Situ Contaminant Mobility in Marine Sediments," September 1999. Supporting data for the Alameda field tests are available in the project files.

QA/QC Review

As part of certification evaluation, the DTSC Hazardous Materials Laboratory reviewed the laboratory data packages for 10 selected trace metal analyses performed by Battelle Marine Science Laboratories (Battelle). Review was based on Battelle's Standard Operating Procedure (SOP), MSL-1-022-01, "Determination of Elements in Aqueous and Digestate Samples by ICP-MS." The review found that due to possible contamination of the method blanks, some Mn and one copper result should be rejected. Additionally, the review found certain results for Cr, Co, Pb, Sb, Ag and Sn associated with QA/QC results outside the control limits should be used with caution. All other metal results reviewed were found acceptable.

Conclusions

1. The deployments of BFSD at the Paleta Creek, Pearl Harbor, and Alameda NAS demonstrated consistent performance, reliability, and the ability to measure trace metal fluxes at distinctly different sites.

2. The BFSD can provide accurate and repeatable measurements of the mobility of trace metal contaminants to and from shallow water marine sediments when certain prerequisite conditions are met. Statistically significant sediment flux rates can be established when the routine procedures, standard methods and protocols demonstrated during this study are followed. Comparison of measured sediment fluxes with blank-chamber fluxes provides a statistical benchmark for the significance of the measured flux rates. Where statistically significant fluxes are observed, evaluation of impacts on water quality can be carried out, or comparisons can be made to bioaccumulation measurements to help identify exposure pathways.

3. Measurement of manganese flux rates is problematic. The flux rate measured over time does not appear to be linear, possibly due to precipitation chemistry occurring with manganese within the flux chamber. The validity of using the first several time series concentration measurements to determine the flux for manganese was not clearly established.

4. A statistical comparison of the field-measured flux rate to the blank-chamber flux rate is necessary to establish a confidence level (e.g., 80%) that the sediment flux is different from the background variability observed under a no-flux condition. Confidence levels less than 80% indicate that the flux may not be detectable and that the results should be used with caution.

5. The best-fit linear flux rate generally provides the best estimate of the flux from the data. The measured statistical variation in the flux should be reported in terms of the slope of the linear regression line and the 95% confidence limits of the slope.

6. The data obtained from use of this technology should be interpreted by persons who are technically qualified to assess sediment fluxes and who are familiar with the site-specific applicability of the BFSD.

Certification Statement

Under the authority of Health and Safety Code section 25200.1.5, the Benthic Flux Sampling Device (BFSD), an automated, in situ, water sampling device designed to collect data to quantify the flux of contaminants across the sediment-water interface in marine and aquatic environments, is hereby certified as a site characterization technology subject to the specific conditions including the limitations/disclaimer set forth in the Certification Notice as published in the California Regulatory Notice Register on June 30, 2000, Register No. 26-Z, Volume No. [xx-Z], pages [xxxx - xxxx].

The BFSD, an autonomous benthic chamber lander, encloses a volume of water in an open-bottom chamber over approximately 0.2 square meters of sediment; discrete water samples are collected periodically over a deployment period of up to four days, preserved at the end of the deployment, and delivered to an analytical laboratory for analysis. With knowledge of the sediment surface area, the volume of water, the time the samples are collected, and the concentrations of constituents in the samples, a flux, expressed in mass per unit area per time, can be derived. The method, and resulting data, are valid when the BFSD standard operating procedures, the laboratory quality assurance and control procedures, and the internal quality assurance checks, such as silica flux, oxygen and pH stability, and statistical tests, have been met. The BFSD is capable of:

1. Deployment from a small surface craft using light duty handling equipment;

2. Operation in a marine environment at depths to 20 meters and bottom currents to two knots;

3. Remote real-time video imaging of the bottom site prior to autonomous operations;

4. Programmable, microprocessor-controlled autonomous operation for up to 96 hours;

5. Placement (bottom landing) with minimal disturbance of bottom sediments;

6. Isolation and maintenance of homogenous conditions in approximately 30 liter volume of bottom water for the period of sample collection;

7. Maintenance of oxygen content in the sample chamber within two milliliters per liter (ml/L) of initial conditions;

8. Collection of up to twelve 250 milliliter water samples from the chamber at selected intervals;

9. Measurement and storage of sample chamber depth, dissolved oxygen, pH, conductivity/salinity, and temperature data at selected intervals throughout deployment;

10. Recovery using a portable acoustic signal device to activate a tethered marker buoy;

11. Quantification of flux rates for Arsenic, Cadmium, Copper, Nickel, Lead, and Zinc based on a least-squares, linear regression of concentrations from six to 12 samples;

12. Identification of statistically significant flux rates based on comparison of sediment flux rates measured at the site to flux rates measured in a “blank” BFSD chamber containing sea water isolated from the sediment;

13. Blank BFSD chamber performance meeting the following performance standards:

Metal	Blank Flux (ug/m2/day)	+/- 95% Confidence Interval
Arsenic	-5.16	2.10
Cadmium	-.0.52	0.75
Copper	2.82	8.73
Nickel	10.28	7.34
Lead	3.16	1.59
Zinc	-3.38	65.22

14. Verification of proper flux chamber seal and sample collection based on silica concentrations within the chamber during the measurement period;

15. Identification of environmentally significant fluxes on the basis of comparisons/relations such as:

   a. other known contaminant sources
   b. hydrodynamic flushing rates of the basin
   c. remobilization due to other mechanisms such as sediment resuspension
   d. fluxes measured prior to placement of a containment system such as a cap
   e. fluxes measured prior to removal of contaminated sediments
   f. bioaccumulation in marine organisms at the site
   g. mass balance analysis of input and loss rates for sediment

1. Limitation to Specific Metals and Operating Conditions. The certification of the BFSD is specific to flux measurements of arsenic, cadmium, copper, nickel, lead, and zinc under the specified operating conditions. The performance with other metals or under different operating conditions was not addressed as part of the certification evaluation.

2. Requirement for Blank Tests. Except where water quality conditions are equivalent to those where blank test performance has previously been verified for seawater in the BFSD isolated from the sediment, BFSD blank tests shall be performed in accordance with the Navy's procedures to determine the lower limit of resolution for metal flux measurements. Additionally, blank test performance shall be verified for each new BFSD manufactured.

3. Reporting of measured flux rates should include the slope of the best-fit linear regression line (the linear flux rate), the 95% confidence limits of the slope (the measured statistical variation in the flux) and, for statistical comparison purposes, corresponding results of the triplicate blank tests. The statistical confidence level that the field-measured flux rate is measurably different from the blank-chamber flux rate shall also be reported. Flux measurement results should be reported as non-detectable or otherwise flagged when there is a confidence level of less than 80% that the benthic flux measurement is different from the blank flux measurement.

4. Operational Procedures. Users of the BFSD should follow the operational and maintenance procedures developed by the Navy. The procedures for operation, maintenance, sample collection and analysis, and data assessment are set forth in the *September 1999 draft Report*.

5. Compliance with Worker Health and Safety Laws. Operation of the BFSD must be in compliance with applicable federal, state and local regulations relating to the protection of worker health and safety.

6. Personnel Training. The operator shall be properly trained on how to operate the BFSD safely and effectively.

7. Compliance with Applicable Federal, State, Local Regulations. The user shall comply with all applicable federal, state, and local regulatory requirements.

8. Continuous Quality Control/Quality Assurance and Monitoring by DTSC. By accepting this certification the applicant agrees, for the duration of the certification, that the BFSD and its operation and maintenance and other documentation shall be maintained at a quality equal to or

better than that in place at the time of certification. The applicant also agrees to be subject to monitoring by DTSC.

9. Modifications and Amendments at the Request of the Applicant. Modifications and amendments to this certification may be requested by the applicant and will be subject to approval by DTSC.
10. Certification Reference. The holder of a valid hazardous waste environmental technology certification is authorized to use the certification seal (California Registered Service Mark Number 046720) and shall cite the certification number and date of issuance in conjunction with the certification seal whenever it is used. When providing information on the certification to the user of the technology or another interested party, the holder of a hazardous waste environmental technology certification shall at a minimum provide the full text of the final certification decision as published in the California Regulatory Notice Register.

Regulatory Implications

There are currently no standards or approved procedures developed by regulatory agencies for use of benthic landers, such as the BFSD, for measurement of contaminant metal flux. Although some clean water standards have been set for seawater, only guidelines currently exist for sediments. The interpretation and application of metal flux measurements with the BFSD is very site-specific and does not lend itself readily to standardized processes. In many cases, BFSD results may be used as an additional factor in a "weight of evidence" approach for risk-based decisions involving regulator concurrence.

Duration of Certification

This certification will remain in effect for three years from the date of issuance, unless it is revoked for cause or unless a duration for certifications different from that specified in this certification is adopted in regulations.

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13. SUPPLEMENTARY NOTES

14. ABSTRACT

The primary objective of the Benthic Flux Sampling Device 2 demonstration was to perform deployments at contaminated sites in San Diego Bay, California, and Pearl Harbor, Hawaii, under the observation of California Environmental Protection Agency (EPA) certification evaluators. The demonstration evaluated the quality of water samples collected using the BFSD2, repeatability, logistical and economic resources necessary for BFSD2 operation, and the range of conditions in which BFSD2 operates. Other objectives included exposure of various user communities to the technology to encourage continued interest and applications.

15. SUBJECT TERMS

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contaminant	cleanup assessment

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