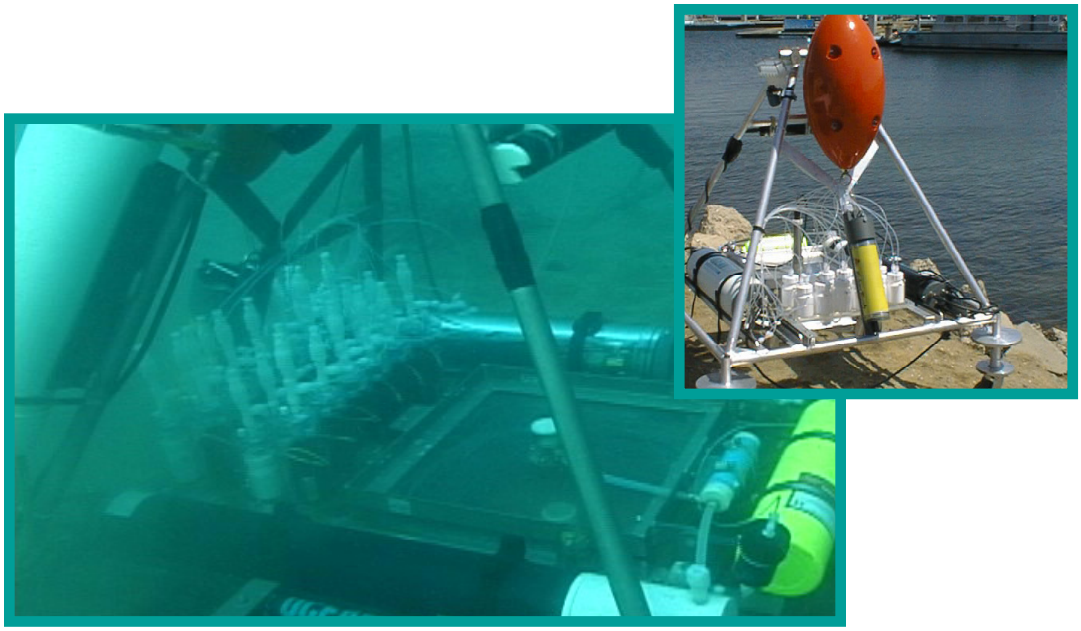
# ESTCP
# Cost and Performance Report

(ER-9712)



## Quantifying In Situ Metal and Organic Contaminant Mobility in Marine Sediments

January 2009

ENVIRONMENTAL SECURITY
TECHNOLOGY CERTIFICATION PROGRAM

U.S. Department of Defense

# COST & PERFORMANCE REPORT
ESTCP Project: ER-9712

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## ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| BFSD | Benthic Flux Sampling Device |
| BFSD2 | Benthic Flux Sampling Device 2 |
| CA Cert | California EPA's Technology Evaluation and Certification Program |
| CalEPA | California Environmental Protection Agency |
| CERCLA | Comprehensive Environmental Resource Conservation and Liability Act |
| DoD | Department of Defense |
| DTSC | Department of Toxic Substances Control |
| ESTCP | Environmental Security Technology Certification Program |
| ITRC | Interstate Technology and Regulatory Cooperation |
| MDSU-1 | Marine Diving and Salvage Unit One |
| ml | milliliters |
| ml/L | milliliters per liter |
| mm | millimeters |
| PAH | polynuclear aromatic hydrocarbons |
| PCB | polychlorinated biphenyl |
| PCPD | Paleta Creek Pre-Demonstration |
| SARA | Superfund Amendments and Reauthorization Act |
| SSC SD | Space and Naval Warfare Systems Center San Diego |
| USEPA | U.S. Environmental Protection Agency |

# ACKNOWLEDGEMENTS

This Cost and Performance Report is a companion to the "Quantifying In Situ Metal and Organic Contaminant Mobility in Marine Sediments – Final Report." The effort reported is centered on field demonstrations of the Benthic Flux Sampling Device (BFSD) and certification by California's Environmental Protection Agency (CalEPA's) Technology Evaluation and Certification Program (CA Cert). The technology evolved at Space and Naval Warfare Systems Center San Diego (SSC SD) during a period when the organization was known as NOSC, and later NRaD. The principal investigators during the prototype development phase were Dr. Bart Chadwick and Dr. Stephen Lieberman, with research and development sponsorship from Mr. Andy DelCollo of the Naval Facilities Engineering Command. The technical transfer phase was led by Mr. Tom Hampton and included Ms. Kim McCoy at Ocean Sensors, Inc., whose team fabricated a commercialized BFSD (BFSD2). Demonstration and validation efforts were sponsored by Dr. Jeff Marqusee through the Office of Under Secretary of Defense (Environmental Security), the Environmental Security Technology Certification Program (ESTCP). Mr. Bill Staack, Dr. Bruce Labelle, and Mr. John Wesnousky of the CalEPA led the CA Cert technical evaluation. Both the final technical report and this report are the work of Dr. Bart Chadwick and the author. The initial metals-only reports have been amended to include results of the project extensions for organics-contaminated sediments and combined metals/organics.

*Technical material contained in this report has been approved for public release.*

# 1.0 EXECUTIVE SUMMARY

Contaminants enter shallow coastal waters from many sources, including ships, shoreside facilities, municipal outfalls, spills, and nonpoint 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 (CERCLA), as amended by the Superfund Amendment and Reauthorization Act (SARA) of 1986, to assess and if necessary remove and remediate these sites and discharges in order 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, a determination of contaminant flux must be made.

This project addresses the DoD/Navy requirement for compliance, cleanup assessment, and remediation decisions using an innovative technology to directly quantify the mobility and bioavailability of contaminants in marine sediments. The environmental risks posed by these contaminants are determined largely by the degree to which they remobilize into the environment.

The project included demonstrations of the commercialized Benthic Flux Sampling Device (BFSD2) at sites in San Diego Bay (Paleta Creek) and Pearl Harbor (Middle Loch and Bishop Point). The demonstrations were used by evaluators from the CalEPA as part of their Technology Certification program process. The demonstrations were successful in showing accurate, precise, and repeatable results at both locations. The San Diego sites were used to emphasize repeatable performance, and the Pearl Harbor sites were used to emphasize the range of conditions for operation. Routine and standardized methods and procedures were used throughout the operations. The initial project, limited to metals contaminated sediments, was subsequently extended to organic contaminants.

Technical performance, schedule, and cost data were collected during the demonstrations that document the utility of the technology to measure, in situ, the mobility of contaminants in marine sediments effectively, efficiently, and in a timely manner. This new approach has no directly comparable technology in current use and thus represents an innovative and new resource to the environmental community.

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## 2.0 TECHNOLOGY DESCRIPTION

Variations in sediment chemical and physical properties make it impossible to rely on bulk sediment contaminant concentrations alone to predict contaminant mobility (or 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. Although fluxes can be calculated from measurements of contaminant pore water gradients and sediment physical properties, in some coastal areas pore water gradients are very steep and therefore difficult to measure. In addition, flux calculations based on pore water gradients only provide the diffusive component of a contaminant flux. Also of concern in coastal areas is that biological irrigation by infauna and wave or current induced flushing may 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 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.

A unique instrument for measurement of contaminant fluxes from marine sediments is the BFSD2, shown in Figure 1 with key components labeled.

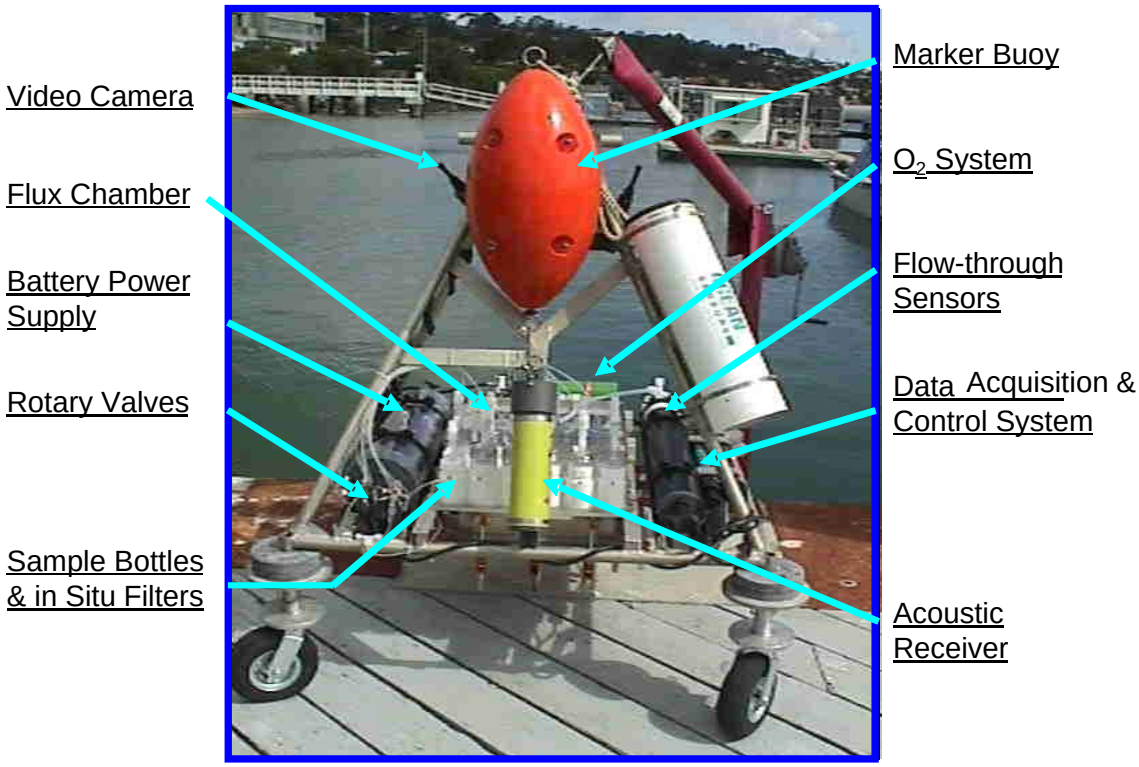


**Figure 1. Benthic Flux Sampling Device 2.**

The BFSD2 is the 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. It is an autonomous instrument for *in situ* measurement of toxicant flux rates from sediments. A flux out of or into the sediment is measured by isolating a volume of water above the sediment, drawing off samples from this volume over time, and analyzing these samples for increase or decrease in toxicant concentration. Increasing concentrations indicate that the toxicant is fluxing out of the sediment. Decreasing concentrations indicate that the toxicant is fluxing into the sediment. In Figure 1, the pyramid-shaped tubular frame, open-bottomed chamber, and associated sampling and control equipment are shown. At the top of the frame is an acoustically released buoy for BFSD2 recovery. At the bottom of the frame are the open-bottomed chamber and associated sampling gear, flow-through sensors, data acquisition and control unit, video camera system, power supply, and oxygen supply system. Figure 2 lists and illustrates the events occurring during a sampling period.

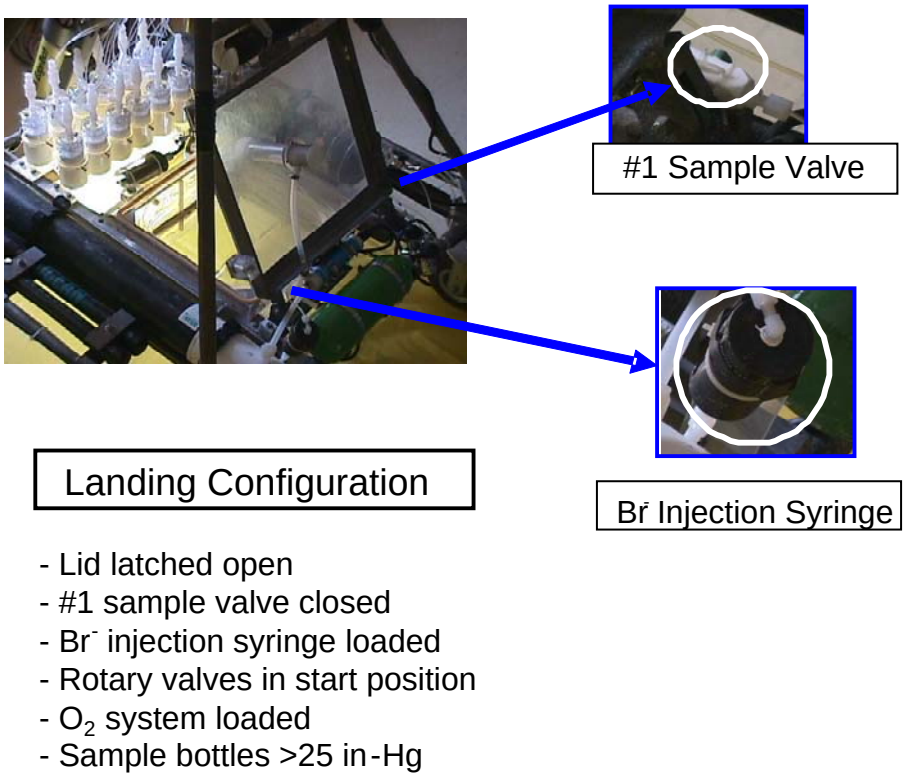


**Figure 2. BFSD2 Sampling Events.**

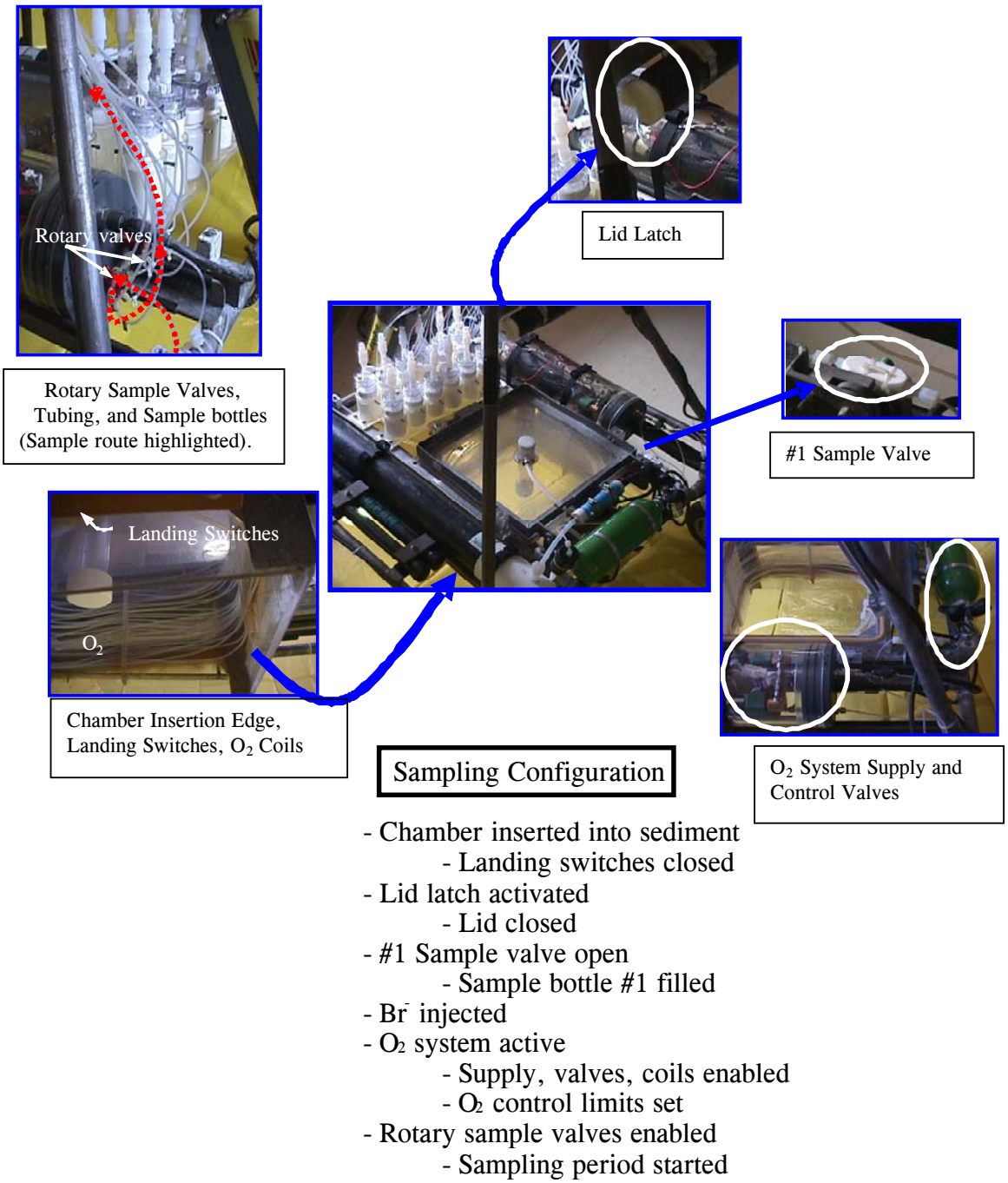


**Figure 2. BFSD2 Sampling Events** (continued)**.**

The BFSD2 is fundamentally a sample collection instrument. The methods established and resulting data are valid when the BFSD2 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:

- Deployment from a small surface craft using light duty handling equipment
- Operation in a marine environment at depths to 50 m and bottom currents to 2 knots
- Remote real-time video imaging of the bottom site prior to autonomous operations
- Programmable, microprocessor-controlled autonomous operation for up to 96 hours
- Placement (bottom landing) with minimal disturbance of bottom sediments
- Isolation and maintenance of homogenous conditions in approximately 30 L volume of bottom water for the period of sample collection
- Maintenance of oxygen content in the sample chamber within one milliliter per liter (ml/L) of initial conditions
- Collection of up to 12 250-ml water samples from the chamber at selected intervals
- Measurement and storage of sample chamber depth, dissolved oxygen, pH, conductivity/salinity, and temperature data at selected intervals throughout deployment
- Recovery using a portable acoustic signal device to activate a tethered marker buoy
- Quantification of flux rates for selected metals and organics based on a least-squares, linear regression of concentrations from six to 12 samples
- Identification of statistically significant flux rates based on comparison of rates measured in a "blank" BFSD chamber
- Verification of proper flux chamber seal and sample collection based on silica
- concentrations within the chamber during the measurement period
- Identification of environmentally significant fluxes on the basis of comparisons/relations such as:
    - Other known contaminant sources
    - Hhydrodynamic flushing rates of the basin
    - Remobilization due to other mechanisms such as sediment resuspension
    - Fluxes measured prior to placement of a containment system such as a cap
    - Fluxes measured prior to removal of contaminated sediments
    - Bioaccumulation in marine organisms at the site
    - Mass balance analysis of input and loss rates for sediment contaminants.

The primary advantage of the BFSD2 is that it provides a unique means of evaluating 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. At present, there is no other viable method for direct quantification of sediments as sources. At sites where it can be demonstrated that remobilization of contaminants is limited, significant cost savings may be achieved through reduction of cleanup costs. This 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 $100-1,000/cubic yard. A recent survey of Navy shoreside facilities indicated that, of the 31 facilities that responded, 29 reported the presence of 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. Limitations include deployment time, depth, and other physical conditions normally not factors for coastal measurements.

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# 3.0 DEMONSTRATION DESIGN

## 3.1 PERFORMANCE OBJECTIVES

The primary objective of the demonstrations of the BFSD2 was to perform deployments at contaminated sites in San Diego Bay, California, and Pearl Harbor, Hawaii, under the observation of CalEPA certification evaluators and other observers, including local, state, and federal regulators; remediation program managers; academia; industry and other DoD offices. Each site offered different validation opportunities: San Diego Bay was used to show instrument repeatability and comparison with historical trends, and Pearl Harbor was used to show site differences and geochemical trend analysis. The specific planned objectives of the demonstrations were to:

- Evaluate the quality of water samples collected using the BFSD2, specifically for determining if a statistically significant flux was occurring at the test locations in comparison to the blank flux results for the BFSD2
- Evaluate the BFSD2 for repeatability
- Evaluate the logistical and economic resources necessary to operate the BFSD2
- 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.

## 3.2 DEMONSTRATION SITE BACKGROUND

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

- The sites were known to have metals and organics-contaminated marine sediments and had been at least partially characterized. The sediment contaminant levels were anticipated to be high enough to demonstrate statistically significant fluxes at the sediment-water interface.
- Two metals deployments at the same Paleta Creek site would demonstrate repeatability; two metals deployments at geographically different Pearl Harbor sites would demonstrate characteristically different data and showcase analysis/interpretation results. One organics deployment at Paleta Creek and one at Bishop Point would demonstrate the extended performance.
- The contaminated sediments were located in shallow areas (less than 50 m deep) and readily accessible.
- Demonstration logistical support requirements would be demonstrated by deployments in Pearl Harbor.

- Data from prototype BFSD deployments conducted at the Paleta Creek site were available for use as reference data and for comparison with demonstration results.

## 3.3 DEMONSTRATION SITE CHARACTERISTICS

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 m. The tidal range from mean lower-low water to mean higher-high water is about 1.7 m. The maximum tidal velocity is about 0.05 to 0.1 m per second. Dissolved oxygen concentrations range from 4 to 8 ml/Ls; sea water 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 metals, tributyltin, polynuclear aromatic hydrocarbons (PAH), petroleum hydrocarbons, polychlorinated biphenyls (PCB), chlordane, dieldrin, and DDT.

The Paleta Creek site, Figure 3, is located in San Diego Bay in San Diego County adjacent to Naval Station San Diego on the western shore where Paleta Creek empties into the bay, slightly inland from the Navy Pier 8 and Mole Pier and north of Seventh Street.

**Figure 3. San Diego Bay, Paleta Creek Demonstration Site.**

Two metals demonstrations were conducted two weeks apart: June 6-8 and June 18-22, 1998. 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 about 18 +/- 3 ft depth, depending on tidal flow, and offshore about 30 ft from a quay wall. Deployment and retrieval was from the Space and Naval Warfare Systems Center San Diego (SSC SD) research vessel RV ECOS.

Pearl Harbor, Hawaii: Pearl Harbor, Figure 4, contains 21 $km^2$ of surface water area; the mean depth is 9.1 m. Tidal flow and circulation are weak and variable, with a mean tidal current velocity of 0.15 m per second and a maximum ebb flow of 0.3 m 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 mg/L. Pearl Harbor is most appropriately described as a high-nutrient estuary.

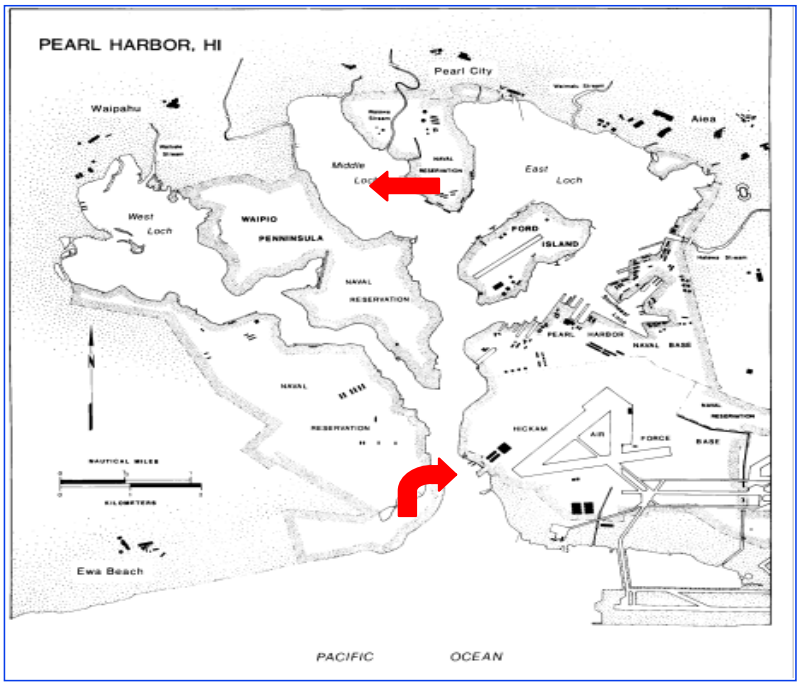


**Figure 4. Pearl Harbor, Middle Loch, and Bishop Point Demonstration Sites.**

Middle Loch is located in the northwestern end of Pearl Harbor, north and west of Ford Island, within the Pearl Harbor Naval Base. Sediments are fine grain silts and clays of basaltic origins and contain various concentrations of metals, toxic organic compounds, and hydrocarbon contaminants. Bishop Point is an active operational and industrial location on the entrance channel to the harbor. Sediments are coarser than Middle Loch as a result of stronger tidal flows and contain calcium (coral) components. These differences affect the mobility and availability of contaminants to flux as well as the chamber seal integrity with the sediment.

## 3.4 PHYSICAL SETUP AND OPERATION

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 shown in Figure 5, a deployment cable and release line is used to 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.

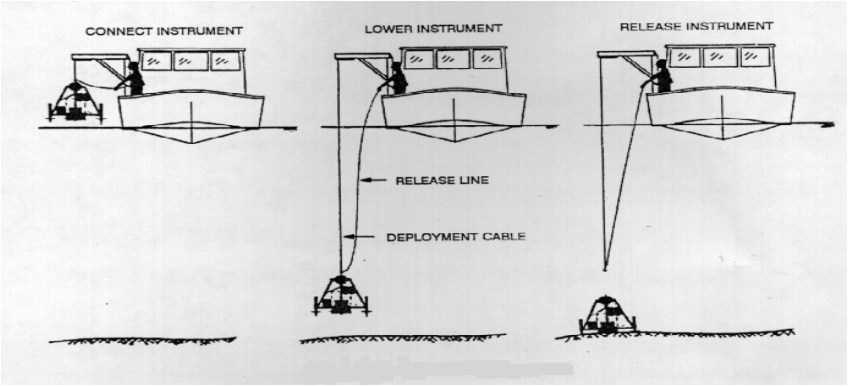


**Figure 5. Deployment.**

As shown in Figure 6, during recovery a coded acoustic signal is transmitted to a BFSD2-mounted receiver. This activates a burn-wire system and releases a marker buoy, which carries an attached recovery line to the surface. The line is used to lift the BFSD2 off the bottom and onto the surface vessel.

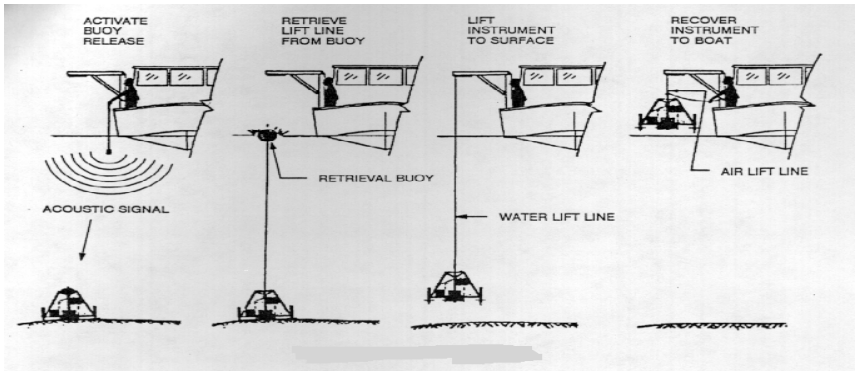


**Figure 6. Retrieval.**

## 3.5 SAMPLING PROCEDURES

Discrete samples are drawn from the collection chamber, Figure 7, using a vacuum collection approach consisting of sample bottles, fill lines, in-line filters (with 0.45 micron membrane filters for metals and 1.0 micron precombusted glass-fiber filters for organics), and check valves (Figure 8) connected to synchronized parallel rotary valves connected to the collection chamber. Samples are drawn from the chamber through a 4-mm Teflon tube connected to the rotary valves and into the sampling bottles (Teflon for metals and amber glass for organics). Sampling is

initiated by the control system when it activates the valves at preprogrammed intervals. Seawater is 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. Filtered seawater flows into each bottle until pressure is equalized, normally yielding at least 240 ml.

**Figure 7. Collection Chamber.**

**Figure 8. Sample Bottles.**

## 3.6 ANALYTICAL PROCEDURES

Oxygen Control: Over the course of a deployment, 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 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. An oxygen control system maintains the oxygen levels in the chamber within a user-selected window about the measured ambient 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. Oxygen is monitored using the oxygen sensor in the BFSD2 flow-through sensor system, and control valve (pressurize or vent) activation is incorporated into the control system software program.

During a typical deployment, after the flux chamber is initially submerged, the ambient oxygen level in the water is measured. The user then establishes a maximum and a minimum oxygen control limit, based on a user-specified range around the stable ambient level. Figure 9 shows a typical set of data. The control limits are entered into the operational control program and downloaded to the submerged BFSD2. During autonomous operations 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 10 shows a typical set of data obtained from a 72-hour deployment.

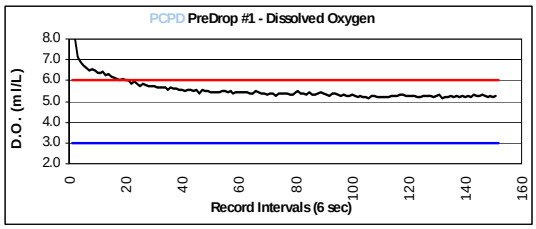


**Figure 9. Ambient Oxygen Data.**

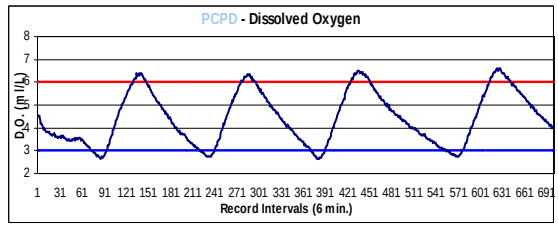


**Figure 10. Operational Oxygen Data.**

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. Figure 11 is an example of silica flux indicating an adequate chamber seal with the sediment.

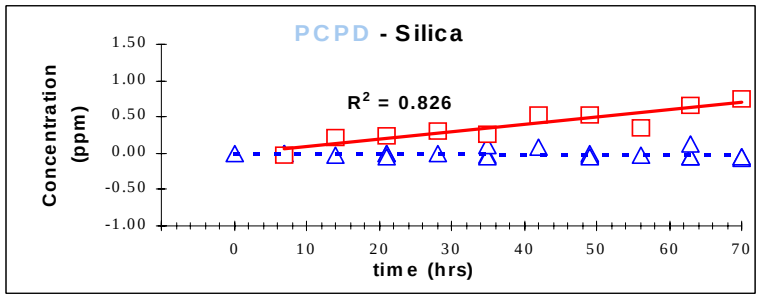


**Figure 11. Silica Flux for Good Chamber Seal.**

With a good chamber seal, the ongoing bacterial degradation of organic material in the sediment consumes oxygen and generates carbon dioxide, gradually lowering the chamber pH. Figure 12 is an example of this data for a good chamber seal with the sediment.

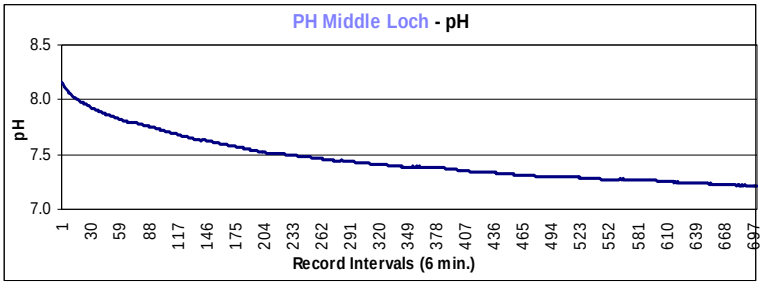


**Figure 12. pH data for Good Chamber Seal.**

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 other contaminants. 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 add to the complex interpretation of the analytical results.

Blank Tests: Prior to the BFSD2 demonstrations, separate triplicate blank tests were performed for both metals and for organics to determine the lower limit of resolution for flux determinations. 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 shown in Tables 1 and 2.

**Table 1. Blank Test Results Summary—Metals.**

| 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.[1] | 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 (SiO2)* (*mg/m$^2$/day) | -4 | -3.3 | 1.4 | -1.97 | 2.88 | 2.9 |

## Table 2. Blank Test Results Summary—Organics

| PAH | Blank Flux (ng/m$^2$/day) | | | Repeatability (ng/m$^2$/day) | | |
|---|---|---|---|---|---|---|
| | Test 1 | Test 2 | Test 3 | Average Flux | +/- 95% C.L. | Std. Deviation |
| 1. Naphthalene | -243.5 | -448.1 | -629.3 | -440 | 218.4 | 193.0 |
| 2. Acenaphthene | -32.4 | ND | ND | -32.4 | n/a | n/a |
| 3. Acenaphthylene | -350.2 | 141.0 | 275.9 | 22.2 | 372.9 | 329.5 |
| 4. Fluorene | 125.5 | -69.3 | -84.2 | -9 | 132.4 | 117.0 |
| 5. Phenanthrene | 89.0 | -39.8 | -16.3 | 11 | 77.6 | 68.6 |
| 6. Anthracene | 182.3 | 53.1 | -324.8 | -30 | 298 | 263 |
| 7. Fluoranthene | -421.5 | -1,539.0 | -1,308.9 | -1,089.8 | 667.8 | 590.1 |
| 8. Pyrene | 76.6 | -447.1 | -431.9 | -267.5 | 337.3 | 298.0 |
| 9. Benzo(a)anthracene | ND | ND | ND | n/a | n/a | n/a |
| 10. Chrysene | 23.9 | -61.9 | ND | -19.0 | 84.2 | 60.7 |
| 11. Benzo(b)fluoranthene | ND | ND | -134.3 | -134.3 | n/a | n/a |
| 12. Benzo(k)fluoranthene | ND | ND | -9.8 | -9.8 | n/a | n/a |
| 13. Benzo(a)pyrene | ND | ND | ND | n/a | n/a | n/a |
| 14. Indeno(1,2,3-c,d)pyrene | ND | ND | ND | n/a | n/a | n/a |
| 15. Dibenz(a,h)anthracene | ND | ND | ND | n/a | n/a | n/a |
| 16. Benzo(g,h,I)perylene | ND | 19.6 | ND | 19.6 | n/a | n/a |

| PCB | Blank Flux (ng/m$^2$/day) | | | Repeatability (ng/m$^2$/day) | | |
|---|---|---|---|---|---|---|
| | Test 1 | Test 2 | Test 3 | Average Flux | +/- 95% C.L. | Std. Deviation |
| (8) 2,4′-Dichlorobiphenyl | -66.6 | ND | 47.8 | -9.4 | 112.2 | 80.9 |
| (18) 2,2′,5-Trichlorobiphenyl | 205.2 | 23.3 | 27.0 | 85.2 | 117.6 | 104.0 |
| (28) 2,4,4′-Trichlorobiphenyl | -8.0 | ND | ND | -8.0 | n/a | n/a |
| (52) 2,2′,5,5′-Tetrachlorobiphenyl | ND | 7.9 | 89.9 | 49 | 80.4 | 58.0 |
| (66) 2,3′,4,4′- Tetrachlorobiphenyl | 53.6 | 16.6 | ND | 35 | 36.2 | 26.2 |
| (101) 2,2′,4,5,5′-Pentachlorobiphenyl | 57.8 | 57.4 | -3.5 | 37 | 40 | 35 |
| (118) 2,3′,4,4,5′-Pentachlorobiphenyl | ND | 2.7 | 2.3 | 2.5 | 0.3 | 0.2 |
| (153) 2,2′,4,4′,5,5′-Hexachlorobiphenyl | ND | ND | 9.5 | 9.5 | n/a | n/a |
| (180) 2,2′,3,4,4′,5,5′-Heptachlorobiphenyl | ND | -9.6 | ND | -9.6 | n/a | n/a |
| (206) 2,2′,3,3′,4,4′,5,5′,6′-Nonachlorobiphenyl | -2.8 | 247.0 | -17.0 | 75.7 | 168.0 | 148.5 |
| (209) 2,2′,3,3′,4,4′,5,5′,6,6′-Decachlorobiphenyl | -18.5 | ND | ND | -18.5 | n/a | n/a |

**Table 2. Blank Test Results Summary – Organics** (continued).

| Pesticide | Blank Flux (ng/m$^2$/day) | | | Repeatability (ng/m$^2$/day) | | |
|---|---|---|---|---|---|---|
| | Test 1 | Test 2 | Test 3 | Average Flux | +/- 95% C.L. | Std. Deviation |
| alpha-Chlordane | 7.0 | ND | ND | 7.0 | n/a | n/a |
| 2,4′-DDD | 7.0 | ND | ND | 7.0 | n/a | n/a |
| Methoxychlor | 25.7 | ND | ND | 25.7 | n/a | n/a |
| Endosulfan I | 48.8 | ND | ND | 48.8 | n/a | n/a |
| hexachlorobutadiene | ND | ND | 22.0 | 22.0 | n/a | n/a |
| Heptachlor | 304.5 | ND | ND | 304.5 | n/a | n/a |
| Heptachlor Epoxide | ND | ND | 8.8 | 8.8 | n/a | n/a |
| alpha-hexachlorocyclohexane | 3.3 | ND | ND | 3.3 | n/a | n/a |
| beta-hexachlorocyclohexane | 61.0 | ND | ND | 61.0 | n/a | n/a |
| lindane | 35.2 | 132.3 | 33.8 | 67.1 | 63.9 | 56.5 |
| trans-Nonachlor | 40.8 | ND | ND | 40.8 | n/a | n/a |

Computations: Fluxes are computed from the 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:

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

where [$C$] is the corrected concentration, [$s$] is the measured sample concentration, n is the sample number (1 through 12), $v$ 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 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.

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# 4.0 PERFORMANCE ASSESSMENT

## 4.1 PERFORMANCE DATA

One Paleta Creek organics demonstration was conducted March 2-5, 2001. The location for the test was within 100 ft of the previous metals deployments. The test was conducted at about 18 +/- 3 ft depth, depending on tidal flow, and offshore about 30 ft from a quay wall. Deployment and retrieval was from the SSC SD research vessel RV ECOS. Table 3 and Table 4 summarize the results of the two Paleta Creek demonstrations. Tables 5, 6, and 7 summarize the results of the organics deployment.

**Table 3. BFSD2 Metals Results from the Paleta Creek Pre-Demonstration.**

| Metals | Flux ($\mu g/m^2/day$) | +/- 95% C.L. ($\mu g/m^2/day$) | Flux Rate Confidence (%) | Triplicate Blank Flux ($\mu g/m^2/day$) | | Bulk Sediment ($\mu g/g$) | Overlying Water ($\mu g/L$) |
|---|---|---|---|---|---|---|---|
| | | | | Average | +/- 95% C.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] | 5,763.99 | 23,621.74 | 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 ($O_2$)* (*$ml/m^2/day$) | -1,050.87 | 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 nonlinearity.

## Table 4. BFSD2 Metals Results from the Paleta Creek Demonstration.

| Metals | Flux ($\mu g/m^2/day$) | +/- 95% C.L. ($\mu g/m^2/day$) | Flux Rate Confidence (%) | Triplicate Blank Flux ($\mu g/m^2/day$) | | Bulk Sediment ($\mu g/g$) | Overlying Water ($\mu g/L$) |
|---|---|---|---|---|---|---|---|
| | | | | Average | +/- 95% C.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] | 4,194.24 | 101,841.32 | 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 ($O_2$)* (*$ml/m^2/day$) | -1,341.12 | 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 nonlinearity

## Table 5. BFSD2 PAH Results from the Paleta Creek Demonstration.

| PAH | Flux ($ng/m^2/day$) | +/- 95% C.L. ($ng/m^2/day$) | Flux Rate Confidence (%) | Triplicate Blank Flux ($ng/m^2/day$) | | Bulk Sediment (ng/g) | Overlying Water (ng/L) |
|---|---|---|---|---|---|---|---|
| | | | | Average | +/- 95% C.L. | | |
| 1. Naphthalene | 459.20 | 429.58 | 94.5% | -440.30 | 458.38 | 13 | 6.7 |
| 2. Acenaphthene | 337.58 | 178.97 | 100.0% | -32.40 | 50.34 | 19 | 9.7 |
| 3. Acenaphthylene | 105.51 | 183.82 | 33.8% | 208.47 | 112.60 | 220 | 7.6 |
| 4. Fluorene | 173.17 | 149.76 | 100.0% | -76.74 | 28.38 | 34 | 2.3 |
| 5. Phenanthrene | 489.25 | 659.77 | 100.0% | 10.95 | 10.95 | 240 | 8.2 |
| 6. Anthracene | 569.42 | 260.29 | 100.0% | 117.68 | 64.62 | 470 | 5.3 |
| 7. Fluoranthene | 365.55 | 397.63 | 100.0% | -1,423.95 | 178.41 | 890 | 37 |
| 8. Pyrene | 951.97 | 755.67 | 100.0% | -439.51 | 70.73 | 740 | 13 |
| 14. Indeno(1,2,3-c,d)pyrene | -65.35 | 906.77 | NA | NA | NA | 470 | 1.4 |
| 16. Benzo(g,h,i) perylene | -46.63 | 263.97 | 67.7% | 20.15 | 65.15 | 400 | 1.4 |

**Table 6. BFSD2 PCB Results from the Paleta Creek Demonstration.**

| PCB | Flux ($ng/m^2/day$) | +/- 95% C.L. ($ng/m^2/day$) | Flux Rate Confidence (%) | Blank Flux ($ng/m^2/day$) | | Bulk Sediment (ng/g) | Overlying Water (ng/L) |
|---|---|---|---|---|---|---|---|
| | | | | Flux | +/- 95% C.L. | | |
| (18) 2,2′5,-Trichlorobiphenyl | 52.21 | 103.93 | 4% | 76.82 | 36.49 | 2.6 | ND |
| (28) 2,4,4′-Trichlorobiphenyl | 41.52 | 80.03 | 61% | -8.05 | 82.03 | 2.2 | 1.1 |
| (52) 2,2′,5,5′-Tetrachlorobiphenyl | 9.44 | 105.28 | 77% | 72.74 | 28.12 | 4.9 | 3 |
| (66) 2,3′,4,4′-Tetrachlorobiphenyl | -19.94 | 62.01 | 96% | 37.74 | 25.45 | 5.3 | ND |
| (101) 2,2′,4,5,5′-Pentachlorobiphenyl | 45.99 | 84.57 | 17% | 57.59 | 31.49 | 13 | ND |
| (118) 2,3′,4,4′,5-Pentachlorobiphenyl | -2.34 | 123.95 | 9% | 2.51 | 15.40 | 13 | ND |
| (153) 2.2′,4,4′,5,5′-Hexachlorobiphenyl | 22.26 | 78.55 | 43% | 9.45 | 11.71 | 23 | 0.11 |

**Table 7. BFSD2 Pesticide Results from the Paleta Creek Demonstration.**

| Pesticide | Flux ($ng/m^2/day$) | +/- 95% C.L. ($ng/m^2/day$) | Blank Flux ($ng/m^2/day$) | | Bulk Sediment (ng/g) | Overlying Water (ng/L) |
|---|---|---|---|---|---|---|
| | | | Flux | +/- 95% C.L. | | |
| 2,4′-DDT | 57.49 | 95.75 | NA | NA | 3.6 | 0.88 |
| 4,4′-DDT | 31.23 | 55.47 | NA | NA | 14 | ND |
| Dieldrin | -23.48 | 45.68 | NA | NA | 2 | ND |
| Hexachlorobenzene | 23.76 | 35.20 | NA | NA | 0.61 | ND |
| Mirex | 36.23 | 154.93 | NA | NA | ND | ND |

The first metals demonstration was conducted February 5-8, 1999, within the Naval Inactive Ship Mooring Facility at Middle Loch where approximately 70 moored ships await disposition (disposal, sale, temporary storage, etc.). The second metals demonstration was conducted February 11-14, 1999 within the area known as Alpha Docks, Marine Diving and Salvage Unit One (MDSU-1) located at Bishop Point. Tables 8 and 9 summarize the metals results of the Pearl Harbor Middle Loch and Bishop Point demonstrations.

**Table 8. BFSD2 Metals Results from Pearl Harbor Middle Loch (PHML).**

| Metals | Flux (µg/m$^2$/day) | +/- 95% C.L. (µg/m$^2$/day) | Flux Rate Confidence (%) | Triplicate Blank Flux (µg/m$^2$/day) | | Bulk Sediment (µg/g) | Overlying Water (µg/L) |
|---|---|---|---|---|---|---|---|
| | | | | Average | +/- 95% C.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 | 1,180 | 52.19 |
| Manganese (Mn)[1] | 2,131.59 | 904.57 | 100.0% | -264.85 | 7.49 | 1,180 | 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) | -1,085.52 | 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 nonlinearity.

**Table 9. BFSD2 Metals Results from Pearl Harbor, Bishop Point (PHBP).**

| Metals | Flux (µg/m$^2$/day) | +/- 95% C.L. (µg/m$^2$/day) | Flux Rate Confidence (%) | Triplicate Blank Flux (µg/m$^2$/day) | | Bulk Sediment (µg/g) | Overlying Water (µg/L) |
|---|---|---|---|---|---|---|---|
| | | | | Average | +/- 95% C.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] | 2,177.45 | 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 nonlinearity.

The metals results for Bishop Point were significantly different from those of Middle Loch, with the exception of Cadmium, which was nearly identical.

One Pearl Harbor organics demonstration was conducted September 8-10, 2001. The site is known as Alpha Docks, MDSU-1 located at Bishop Point. The location for the test was within

the immediate vicinity of the previous metals deployment. Tables 10, 11, and 12 summarize the results of the organics deployment.

**Table 10. BFSD2 PAH Results from the Bishop Point Demonstration.**

| PAH | Flux ($ng/m^2/day$) | +/- 95% C.L. ($ng/m^2/day$) | Flux Rate Confidence (%) | Triplicate Blank Flux ($ng/m^2/day$) | | Bulk Sediment (ng/g) | Overlying Water (ng/L) |
|---|---|---|---|---|---|---|---|
| | | | | Average | +/- 95% C.L. | | |
| 1. Naphthalene | -110.07 | 596.59 | 38.1% | -440.30 | 458.38 | 44 | 13 |
| 2. Acenaphthene | 2,680.41 | 10,124.62 | 51.2% | -32.40 | 50.34 | 1,800 | 37 |
| 3. Acenaphthylene | 627.85 | 1,483.64 | 82.7% | 208.47 | 112.60 | 1,200 | 5.6 |
| 4. Fluorene | 75.17 | 1,894.31 | 23.4% | -76.74 | 28.38 | 4,800 | 19 |
| 5. Phenanthrene | -552.72 | 1,305.06 | 98.2% | 10.95 | 10.95 | 54,000 | 32 |
| 6. Anthracene | 4,053.72 | 3,094.52 | 100.0% | 117.68 | 64.62 | 10,000 | 13 |
| 7. Fluoranthene | 4,435.81 | 10,157.65 | 97.4% | -1,423.95 | 178.41 | 270,000 | 52 |
| 8. Pyrene | 38.99 | 4,132.13 | 28.5% | -439.51 | 70.73 | 150,000 | 20 |
| 9. Benzo(a)anthracene | 75.00 | 306.84 | NA | NA | NA | 16,000 | Non-Detect |
| 10. Chrysene | 1,048.91 | 1,012.25 | 98.5% | 23.94 | 22.32 | 48,000 | 5.1 |
| 11. Benzo(b)fluoranthene | 919.99 | 375.56 | 99.8% | -134.30 | 297.91 | 36,000 | 6.2 |
| 12. Benzo(k)fluoranthene | 234.99 | 156.43 | 93.3% | -9.71 | 36.30 | 10,000 | 2.5 |
| 13. Benzo(a)pyrene | Non-Detect | NA | NA | NA | NA | 12,000 | Non-Detect |
| 14. Indeno(1,2,3-c,d)pyrene | 6.72 | 67.06 | NA | NA | NA | 7,400 | 1.6 |
| 15. Dibenz(a,h)anthracene | Non-Detect | NA | NA | NA | NA | 1,500 | 1.5 |
| 16. Benzo(g,h,i)perylene | 7.91 | 64.14 | 11.6% | 20.15 | 65.15 | 5,300 | 1.7 |

**Table 11. BFSD PCB Results from Bishop Point Demonstration.**

| PCB | Flux ($ng/m^2/day$) | +/- 95% C.L. ($ng/m^2/day$) | Flux Rate Confidence (%) | Blank Flux ($ng/m^2/day$) | | Bulk Sediment (ng/g) | Overlying Water (ng/L) |
|---|---|---|---|---|---|---|---|
| | | | | Flux | +/- 95% C.L. | | |
| (101) 2,2′,4,5,5′-Pentachlorobiphenyl | -2.62 | 93.70 | 4% | 57.59 | 31.49 | Non-Detect | 2.1 |

**Table 12. BFSD Pesticide Results from Bishop Point Demonstration.**

| Pesticide | Flux ($ng/m^2/day$) | +/- 95% C.L. ($ng/m^2/day$) | Blank Flux ($ng/m^2/day$) | | Bulk Sediment (ng/g) | Overlying Water (ng/L) |
|---|---|---|---|---|---|---|
| | | | Flux | +/- 95% C.L. | | |
| Mirex | 61.81 | 110.60 | NA | NA | Non-Detect | 1.00 |

One 72-hour test was conducted to demonstrate the ability of the BFSD2 to collect samples for both metals and PAH analysis in a single deployment. The MUDSU-1 facility at Bishop Point, Pearl Harbor, Hawaii, was selected because deployments for both metals and PAHs were made in the area. The combined demonstration was successfully conducted on December 9-12, 2002. A previous attempt was made in October 2003, but because of a technical malfunction and issues with the electronic control unit of the BFSD2, that deployment was unsuccessful.

Results for this test are shown in Table 13 and Table 14.

**Table 13. Metals Results from Combined Deployment.**

| Metals | 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 | +/- 95% C.L. |
| Arsenic (As) | 23.48 | 6.94 | 100.0% | -5.16 | 2.10 |
| Copper (Cu) | -71.30 | 39.43 | 100.0% | 2.82 | 8.73 |
| Cadmium (Cd) | 1.31 | 1.63 | 98.1% | -0.52 | 0.75 |
| Lead (Pb) | 17.40 | 24.63 | 99.0% | 3.16 | 1.59 |
| Nickel (Ni) | 59.18 | 55.96 | 100.0% | 10.28 | 7.34 |
| Manganese (Mn) | 427.65 | 238.42 | 100.0% | -264.85 | 7.49 |
| Manganese (Mn)[1] | 1,940.13 | 3,853.39 | 100.0% | -264.85 | 7.49 |
| Silver (Ag) | -0.36 | 0.88 | 86.1% | 0.64 | 0.68 |
| Zinc (Zn) | 374.36 | 133.74 | 100.0% | -3.38 | 65.22 |
| **Other** | | | | | |
| Oxygen ($O_2$)* (*$ml/m^2/day$) | -1,457.09 | 48.92 | na | na | na |
| Silica ($SiO_2$)* (*$mg/m^2/day$) | 0.00 | 0.00 | 48% | -1.97 | 2.88 |

[1] Mn flux calculated on the first three samples due to nonlinearity and to compare with metals-only demonstration

**Table 14. PAH Results for Combined Deployment.**

| PAH | Flux ($ng/m^2/day$) | +/- 95% C.L. ($ng/m^2/day$) | Flux Rate Confidence (%) | Triplicate Blank Flux ($ng/m^2/day$) | |
|---|---|---|---|---|---|
| | | | | Average | +/- 95% C.L. |
| 1. Naphthalene | 2,456.72 | 13,211.63 | 100.0% | -440.30 | 458.38 |
| 2. Acenaphthene | 9,222.27 | 6,867.34 | 100.0% | -32.40 | 50.34 |
| 3. Acenaphthylene | 778.37 | 880.29 | 100.0% | 208.47 | 112.60 |
| 4. Fluorene | 285.70 | 2,021.66 | 100.0% | -76.74 | 28.38 |
| 5. Phenanthrene | -3,555.98 | 7,892.27 | 100.0% | 10.95 | 10.95 |
| 6. Anthracene | 2,874.10 | 1,330.22 | 100.0% | 117.68 | 64.62 |
| 7. Fluoranthene | 19,696.65 | 3,869.67 | 100.0% | -1,423.95 | 178.41 |
| 8. Pyrene | 12,101.21 | 3,884.64 | 100.0% | -439.51 | 70.73 |
| 9. Benzo(a)anthracene | 760.90 | 668.14 | NA | NA | NA |
| 10. Chrysene | 1,949.20 | 1,370.02 | 100.0% | 23.94 | 22.32 |
| 11. Benzo(b)fluoranthene | 1,878.90 | 2,921.78 | 100.0% | -134.30 | 297.91 |
| 12. Benzo(k)fluoranthene | 1,890.41 | 1,526.34 | 100.0% | -9.71 | 36.30 |
| 13. Benzo(a)pyrene | 1,413.41 | 1,785.07 | NA | NA | NA |
| 14. Indeno(1,2,3-c,d)pyrene | 41.71 | 103.62 | NA | NA | NA |
| 15. Dibenz(a,h)anthracene | 34.46 | 85.60 | NA | NA | NA |
| 16. Benzo(g,h,i)perylene | 39.90 | 99.12 | 43.2% | 20.15 | 65.15 |

For the most part, flux rates for metals and organics behaved similarly at the Bishop Point site for the organics-only, metals-only and this combined demonstration of both organics and metals. Tables 15 and 16 show a side-by-side comparison of these demonstration flux results.

Copper and zinc are the only metals that showed a significant difference between sampling during the first metals only demo and the combined demo. Copper actually showed a reverse trend during the second test. Zinc flux rate was higher during the combined demo than during the first. However, cadmium, lead, nickel and manganese showed similar trends and lay within the 95% confidence intervals of the calculated slopes. Arsenic and silver were not reported during the first test and could not be compared here.

Flux rates for PAH were calculated for the first four samples taken in order to compare with the original Bishop Point organics test. Concentrations for PAH for both tests evened out or plateaued after the fourth sample was collected at about 22 hours. The "first four" flux rates are probably more realistic as that was measured before any interference or interaction with natural, in situ processes caused by the chamber itself. The only organic that was significantly different from the first test was Phenanthrene, which showed a negative flux or an absorption into sediments during the combined demo. All other organic compounds measured during the firat test showed similar flux rates when compared to the 95% confidence limits of the flux curves.

The cause for the organic concentrations leveling off is not immediately known. Low oxygen levels and anoxic conditions inside the chamber during the first test were blamed for the effect. However, adequate oxygen conditions were maintained during the second test with the same result. High bulk, sediment concentrations measured at Bishop Point may suggest a loading or saturation of PAH within the chamber after 22 hours, which would result in a dampening of the flux processes.

**Table 15. Comparison of Flux Rates from Metals-Only and Combined Demonstrations.**

| Metals | Combined Demo | | Metals Only Demo | |
|---|---|---|---|---|
| | Flux ($\mu g/m^2/day$) | +/- 95% C.L. ($\mu g/m^2/day$) | Flux ($\mu g/m^2/day$) | +/- 95% C.L. ($\mu g/m^2/day$) |
| Arsenic (As) | 23.48 | 6.94 | | |
| Copper (Cu) | -71.30 | 39.43 | 112.46 | 17.60 |
| Cadmium (Cd) | 1.31 | 1.63 | 1.85 | 1.96 |
| Lead (Pb) | 17.40 | 24.63 | 0.71 | 1.11 |
| Nickel (Ni) | 59.18 | 55.96 | 21.04 | 15.41 |
| Manganese (Mn) | 427.65 | 238.42 | 223.33 | 284.79 |
| Manganese (Mn)[1] | 1,940.13 | 3,853.39 | 2,177.45 | 192.60 |
| Silver (Ag) | -0.36 | 0.88 | | |
| Zinc (Zn) | 374.36 | 133.74 | 191.18 | 54.07 |

**Table 16. Comparison of Flux Rates from PAH-Only and Combined Demonstration.**

| PAH | Combined Demo | | PAH Only Demo | |
|---|---|---|---|---|
| | Flux ($ng/m^2/day$) | +/- 95% C.L. ($ng/m^2/day$) | Flux ($ng/m^2/day$) | +/- 95% C.L. ($ng/m^2/day$) |
| 1. Naphthalene | 2,456.72 | 13,211.63 | 1,848.00 | 4,406.00 |
| 2. Acenaphthene | 9,222.27 | 6,867.34 | 71,053.00 | 327,574.00 |
| 3. Acenaphthylene | 778.37 | 880.29 | 6,862.00 | 14,388.00 |
| 4. Fluorene | 285.70 | 2,021.66 | 10,387.00 | 110,972.00 |
| 5. Phenanthrene | -3,555.98 | 7,892.27 | 3,031.00 | 106,689.00 |
| 6. Anthracene | 2,874.10 | 1,330.22 | 26,955.00 | 27,293.00 |
| 7. Fluoranthene | 19,696.65 | 3,869.67 | 69,812.00 | 380,980.00 |
| 8. Pyrene | 12,101.21 | 3,884.64 | 24,512.00 | 190,722.00 |
| 9. Benzo(a)anthracene | 760.90 | 668.14 | Non-Detect | NA |
| 10. Chrysene | 1,949.20 | 1,370.02 | 8,792.74 | 10,650.17 |
| 11. Benzo(b)fluoranthene | 1,878.90 | 2,921.78 | 3,080.74 | 17,862.21 |
| 12. Benzo(k)fluoranthene | 1,890.04 | 1,526.34 | 977.52 | 3,135.53 |
| 13. Benzo(a)pyrene | 1,413.41 | 1,785.07 | Non-Detect | NA |
| 14. Indeno(1,2,3-c,d)pyrene | 41.71 | 103.62 | 122.97 | 7,141.99 |
| 15. Dibenz(a,h)anthracene | 34.46 | 85.60 | Non-Detect | NA |
| 16. Benzo(g,h,i)perylene | 39.90 | 99.12 | 33.19 | 5,249.47 |

Paleta Creek and Pearl Harbor Demonstrations 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 except for the Bishop Point organics test; and (3) silica, oxygen, and pH trends varied as expected. The samples collected were thus considered valid for laboratory analysis. The resulting flux calculations demonstrated statistically significant contamination mobility.

It was concluded that the two sets of deployments of BFSD2 at Paleta Creek and at Pearl Harbor demonstrated consistent performance and the ability to measure trace metal mobility at distinctly different sites. The subsequent single deployments at Paleta Creek and Pearl Harbor demonstrated continued consistent performance and the extended ability to measure trace levels of organic contaminants at these different sites. The applicable performance capabilities outlined in Section 2 and the demonstration objectives listed in Section 3 were met. Ease of operation and reliability were also demonstrated. It was further concluded that BFSD2 provides accurate and repeatable measurements of the mobility of metal and organic contaminants to and from shallow water marine sediments when the prerequisite performance assurance indicators mentioned above are met. These sediment flux rates can be established with high confidence when the routine procedures, standard methods, and protocols included in Appendix B and demonstrated during these studies are followed. The BFSD2 and its support equipment are mobile by air transport, field portable, and can be operated with a minimum of resources. One technician experienced with standard BFSD operational procedures and the part-time assistance of a deck hand plus a skilled small boat operator are required for BFSD2 operations. 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. The resulting analysis will provide a significant new tool in evaluating potential cleanup options at contaminated sediment sites.

The demonstration results discussed in this section met the objectives listed in Section 3. Both the technology demonstration team and the California EPA certification evaluators tasked with assessing the performance and results concluded that the applicable capabilities were met for metals. Official State of California Performance Certification for metals-contaminated sediment applications has been issued

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# 5.0 COST ASSESSMENT

The expected operational costs for the BFSD2, whether used for metals or organics or both, are largely driven by analytical laboratory costs. 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. The costs incurred for the reported demonstrations closely reflect the expected costs for operational deployments. Figures 13, 14, and 15 illustrate expected costs and schedules for the three phases of operations.

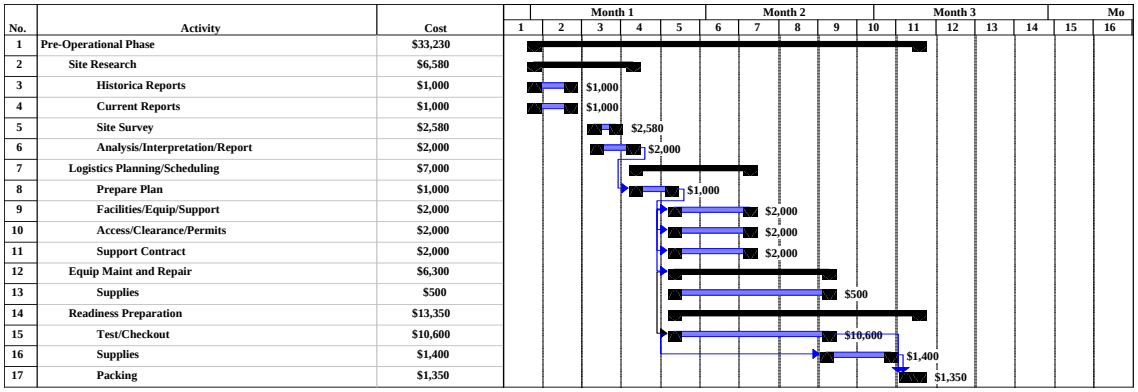


**Figure 13. Pre-Operational Phase Schedule and Cost.**

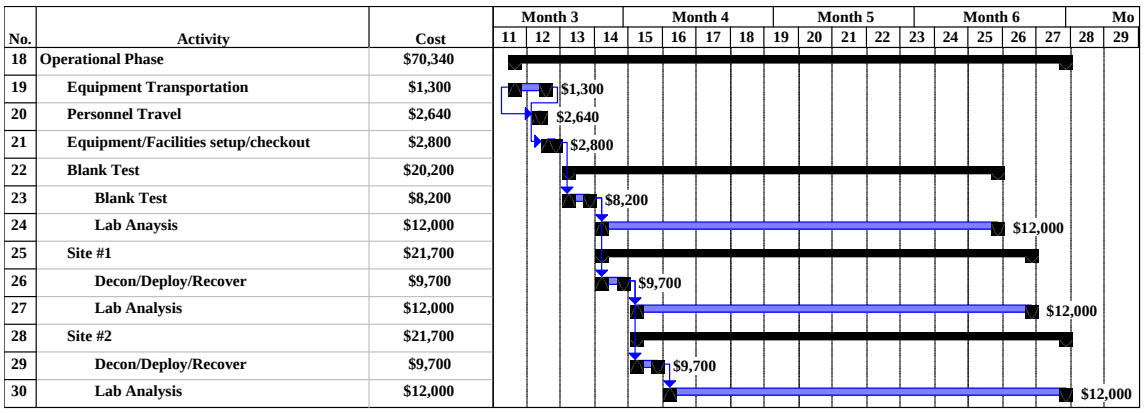


**Figure 14. Operational Phase Schedule and Cost.**

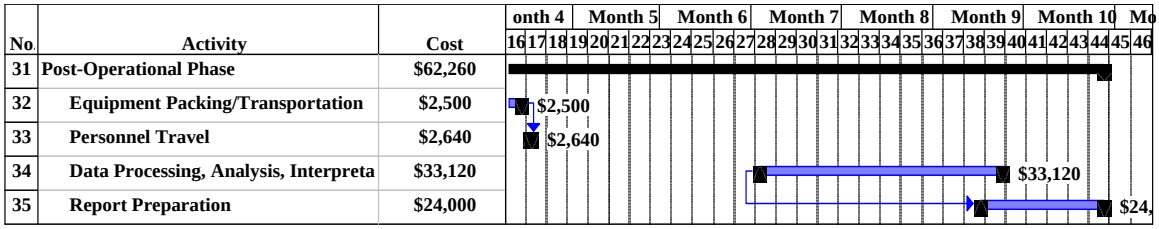


**Figure 15. Post-Operational Phase Schedule and Cost.**

With only marginal differences for metals or organics applications, the operational phase costs for one site, which includes the costs for transportation, setup, and one 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 work week schedule. An accelerated schedule, which shortens turnaround time and includes weekend work periods, can achieve two deployments per week.

The post-operational phase costs are largely the labor costs to process, analyze, interpret, and report the results of the BFSD2 deployments. The costs are approximately the same regardless of metals or organics and 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.

As discussed in Bufflax and Allen, 1995 (Key References), 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 using alternative methods require equivalent specialized laboratory analyses in order to determine contaminant flux rates. Analysis 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 introduces error sources not present with BFSD2. Minimizing the affects of the error sources increases costs and complexity. Sample integrity becomes a significant factor also. These issues aside, ex situ approaches can be as much as 50% cheaper for the field work, but this advantage quickly disappears with added sediment processing costs, especially for metals. 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, at least for metals.

Both alternative approaches involve isolation of sediment pore water. For metals, 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, normally nitrogen or argon. Ex situ methods typically first collect sediment samples, which 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 prior to 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 is particularly difficult for dredging and grab sampling equipment; however, coring equipment can include nonmetallic 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 additional issues.

# 6.0 IMPLEMENTATION ISSUES

## 6.1 COST OBSERVATIONS

The key factor affecting cost of BFSD2 deployment is analytical laboratory costs. While significantly different, the specialized metals and organics analysis costs for flux measurements have approximately the same cost and schedule. Lab costs are approximately 50% of overall costs and account for about the same proportion of the time required for a complete project. Lab costs are driven by the low detection limits necessary to achieve useful results. Other factors include labor, travel, and per diem costs. These costs can be minimized by careful planning to avoid unnecessary delays and by scheduling operations to make efficient use of the required BFSD2 operational scenario. The average cost per site drops steadily as the number of sites increases. This results from amortizing the costs for pre-deployment, blank test, and report preparation over a larger number of sites. Also, combining collection of both metals and organics samples in a single deployment offers significant cost and time savings.

## 6.2 PERFORMANCE OBSERVATIONS

Accurate, precise, and repeatable performance can be achieved with the BFSD2 when close adherence to established methods and procedures is followed. Use of the performance indicators to assess chamber performance prior to submitting samples for analysis reduces the chances of expending approximately 50% of overall time and money on compromised samples.

## 6.3 OTHER SIGNIFICANT OBSERVATIONS

As discussed above, BFSD2 cost and performance is relatively well established, but analysis and interpretation of flux results is not. The complex variations that influence and affect the mobility of contaminants at the sediment-water interface require careful consideration of all available information to reach useful conclusions. Experts in marine chemistry, biology, geology, and other related fields all have important contributions to make to the analyses. And as with current Ecological Risk Assessment methods, a weight of evidence approach, which considers as many factors as possible, is necessary to interpret the impact from measured fluxes.

## 6.4 REGULATORY AND OTHER ISSUES

Regulatory acceptance has been a fundamental element of this project from the start. The approach includes application to the CalEPA, Department of Toxic Substances Control (DTSC) Technology Evaluation and Certification Program known as “Cal Cert.” In addition, CalEPA membership in the Interstate Technology and Regulatory Cooperation (ITRC) group of the Western Governors Association and the resulting multistate 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 USEPA, as well as private sector, Native American, and foreign interests, is also promoted by their active participation in the ITRC. USEPA, state, local and private environmental professionals, as well as CalEPA evaluators, were in attendance at field demonstrations, which included technology briefings and displays. Finally, certification by the CalEPA includes public notifications and listings officially distributed to a wide range of recipients.

## 6.5 LESSONS LEARNED

Flexibility – As with any multifaceted program that involves a complex technology, flexibility must be maintained in order to accommodate any number of 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 workaround efforts, which ultimately recovered schedule losses. Technical approaches must flex to allow for changes. This project benefited from a number of incremental and continuing product improvements, which were accommodated within the technical approach without invalidating demonstration results. The project extension to demonstrate organics performance subsequent to the successful metals portion project resulted in efficient and low-risk success.

Mother Nature – It again became clear from demonstration results that contaminated sediments are nonhomogeneous and are subject to influences involving benthic organisms, complex marine geochemistry, and other factors. Accommodation of differences between blank measurements made a few days apart and site measurements made a few feet apart were necessary.

Statistics – With consideration for the very low levels of contaminants being measured (parts per trillion and lower!) metrics involving statistical methods were needed to put meaning to results. Accommodation for results in terms of probabilities and confidence levels must be made to tease out the true meaning of some flux measurements.

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# APPENDIX A

## POINTS OF CONTACT

| Point of Contact | Organization Address | Phone<br>Fax<br>E-Mail | Role in Project |
|---|---|---|---|
| Bradley Davidson | SPAWAR Systems Center, Pacific, Code 71750<br>53560 Hull Street<br>San Diego, California 92152 | Phone: 619-553-2804<br>Fax: 619-553-6305<br>E-Mail: bradley.davidson@navy.mil | Project Manager and Principal Investigator |
| Bart Chadwick, Ph.D. | SPAWAR Systems Center, Pacific, Code 71750<br>53560 Hull Street<br>San Diego, California 92152 | Phone: 619-553-5333<br>Fax: 619-553-6305<br>E-Mail: chadwick@spawar.navy.mil | Co-Investigator |
| Bill Staack, Esq., P.E. | Department of Toxic Substances Control<br>301 Capitol Mall, 1st Floor<br>Sacramento, California 95814 | Phone: 916-322-5591<br>Fax: 916-327-4494 or 445-2939<br>E-Mail: BStaack@DTSC.Ca.Gov | California EPA Certification |
| John Wesnousky | Department of Toxic Substance Control<br>California Environmental Protection Agency<br>301 Capitol Mall, 1st Floor<br>Sacramento, California 95814 | Phone: 916-322-2543<br>Fax: 916-327-4494<br>E-Mail: JWesnousky@DTSC.Ca.Gov | California EPA Certification |
| Peter Nakamura | Naval Facilities Command, Pacific Division<br>Honolulu, Hawaii | Phone: 808-474-4505<br>Fax: 808-474-4519<br>E-Mail: NakamuraPM@efdpac.navfac.navy.mil | Pearl Harbor Naval Complex |
| Kim McCoy | Ocean Sensors, Inc<br>4901 Morena Blvd, Suite 1001<br>San Diego, California 92117 | Phone: 619-274-9893<br>Fax: 619-274-9895<br>E-Mail: kmccoy@adnc.com | Commercialization |
| Andy DelCollo | Naval Facilities Command<br>Washington, DC | Phone: 202-685-9173<br>Fax: 202-685-1569<br>E-Mail: delcolloa@navfac.navy.mil | Development Sponsor |
| Jeff Marqusee, Ph.D. | Office of Under Secretary of Defense (Environmental Security)<br>Environmental Security Technology Certification Program (ESTCP)<br>Washington, D.C. | Phone: 703-696-2117<br>Fax: 703-696-2114<br>E-Mail: marqusj@acq.osd.mil | Demonstration and Validation Sponsor |

## APPENDIX B

## DATA REFERENCES

All documents except field and engineering notes are archived as electronic files. Stenopads with field and engineering notes as well as hard copies of many of the documents listed are kept in SSC SD Code D3604 file cabinets. The files below are stored on SSC SD, 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
    - Arthur D. Little Laboratory 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 Presentations

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

4. Qualcomm Eudora Pro:
    - All e-mails (with attachments)

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

ESTCP Program Office

901 North Stuart Street
Suite 303
Arlington, Virginia 22203

(703) 696-2117 (Phone)
(703) 696-2114 (Fax)

e-mail: estcp@estcp.org
www.estcp.org