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Quantifying In Situ Metal Contaminant Mobility in Marine Sediments

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LIST OF ACRONYMS

APDC	Ammonium pyrolidine dithiocarbamate
ASTM	American Society for Testing and Materials
AVS	Acid volatile sulfide
BFSD	Benthic Flux Sampling Device
CSCT	Consortium for Site Characterization Technology
CTD	Conductivity temperature depth
CVAF	Cold vapor atomic fluorescence
DQO	Data quality objectives
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
GC/MS	Gas chromatography mass spectrometer
GFAA	Graphite furnace atomic absorption
HAA	Hydride generation flame atomic absorption
ICPMS	Inductively coupled plasma mass spectrometry
ID	Identification
IDW	Investigation-derived waste
$\mu\text{g}/\text{m}^2/\text{day}$	micrograms per meter squared per day
MDL	Method detection limit
ml	Milliliters
ml/sec	Milliliters per second
mm	Millimeters
MS	Matrix spike
MSD	Matrix spike duplicate
OHSO	On-site health and safety officer
OSHA	Occupational Safety and Health Administration
PARCC	Precision, accuracy, representativeness, completeness, and comparability
PAH	Polynuclear aromatic hydrocarbons
PCB	Polychlorinated biphenyl
PFD	Personal floatation device
QA	Quality assurance
QAP	Quality Assurance Plan
QC	Quality control

LIST OF ACRONYMS (continued)

RPD	Relative percent difference
SARA	Superfund Amendments and Reauthorization Act
SEM	Simultaneously extracted metal
SOP	Standard operating procedure
SSC SD	Space and Naval Warfare Systems Center San Diego
TOC	Total organic carbon
USACE	United States Army Corps of Engineers
XRF	X-ray fluorescence

1.0 EXECUTIVE SUMMARY

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 DoD are contaminated with potentially harmful metal and organic compounds. The 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 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 California EPA 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.

Technical performance, schedule and cost data were collected during the demonstrations which 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 Benthic Flux Sampling Device 2 (BFSD2), shown in Figure 1 with key components labeled.

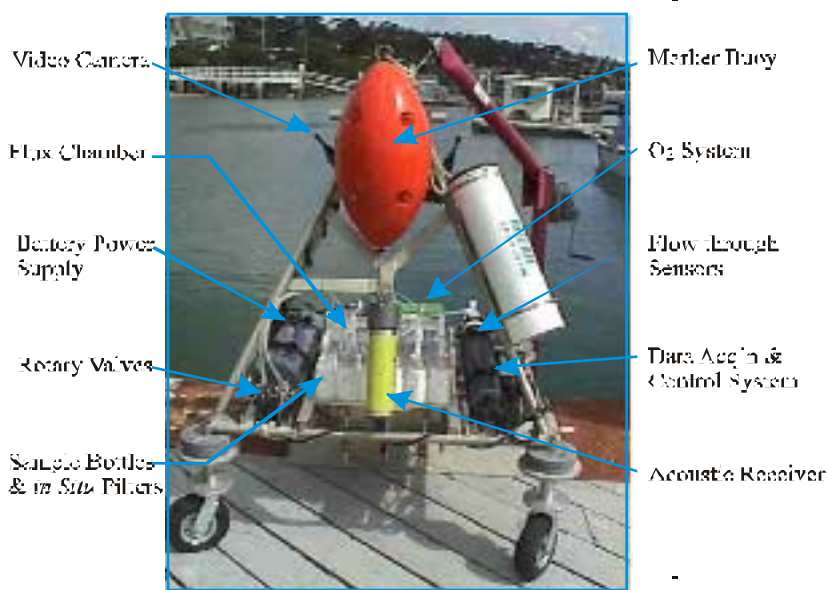


Figure 1. Benthic Flux Sampling Device 2

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 can be seen. 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. Further details and individual component discussion are provided in Section III.

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:

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;
11. Quantification of flux rates for selected trace metals based on a least-squares, linear regression of concentrations from 6 to 12 samples;
12. Identification of statistically significant flux rates based on comparison of rates measured in a "blank" BFSD chamber;
13. Verification of proper flux chamber seal and sample collection based on silica concentrations within the chamber during the measurement period;
14. 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.

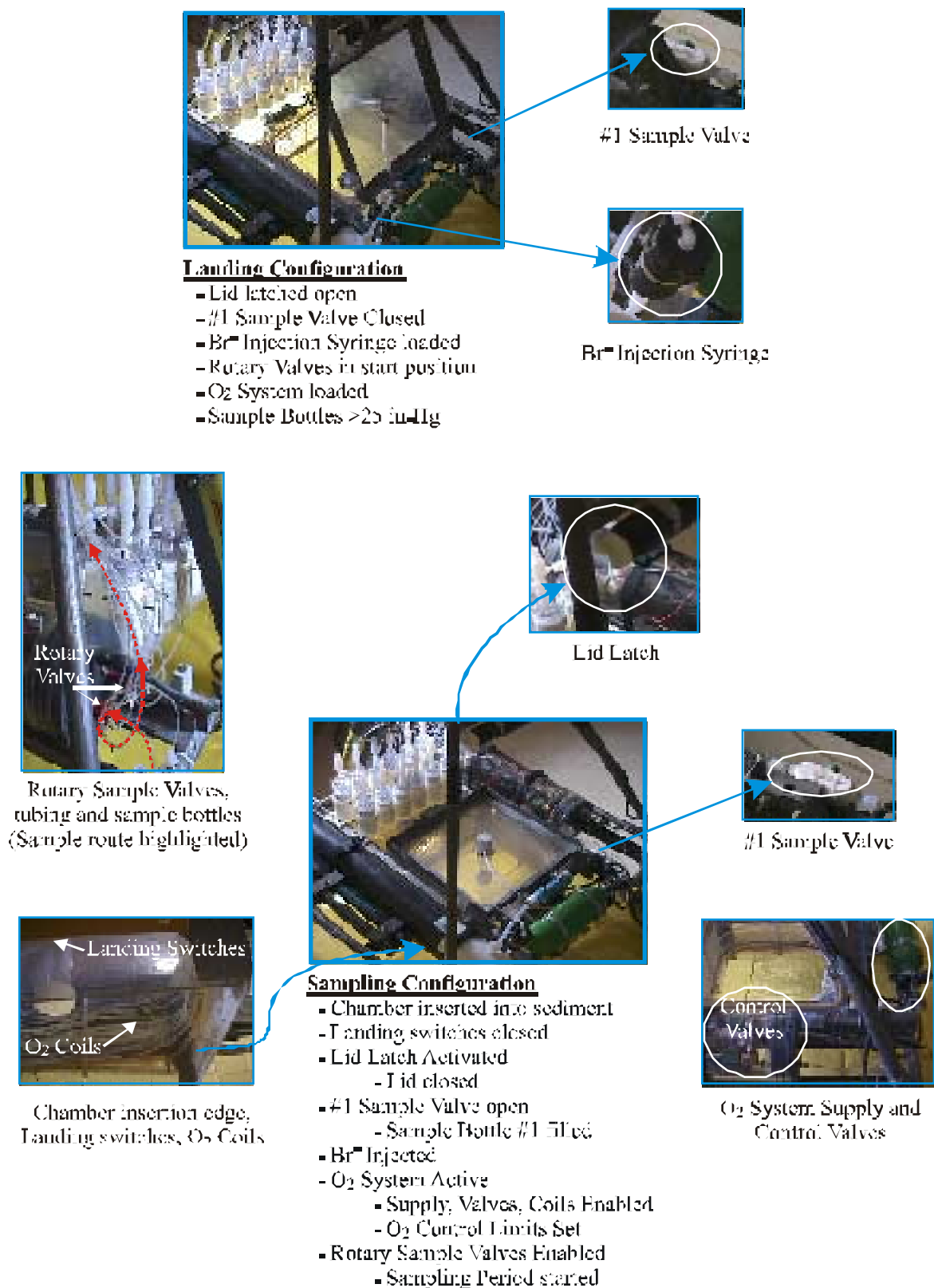


Figure 2. BFSD 2 Sampling Events

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-\$1000/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. The primary disadvantage of the BFSD2 is that it is currently limited to quantification of metal fluxes. Plans are in place to expand measurements to include organic contaminants. Other limitations include deployment time, depth and other physical conditions normally not factors for coastal measurements.

3.0 DEMONSTRATION DESIGN

3.1 OBJECTIVES OF THE DEMONSTRATIONS

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 California EPA certification evaluators and other observers, including local, state and federal regulators, Remediation Program Managers, academic, industry and other DoD. 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:

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.

3.2 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 3, 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.

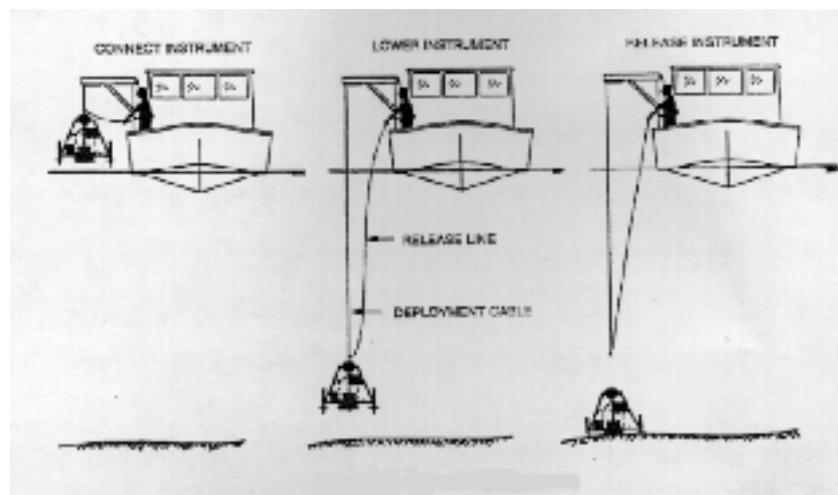


Figure 3. BFSD Deployment

As shown in Figure 4, 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.

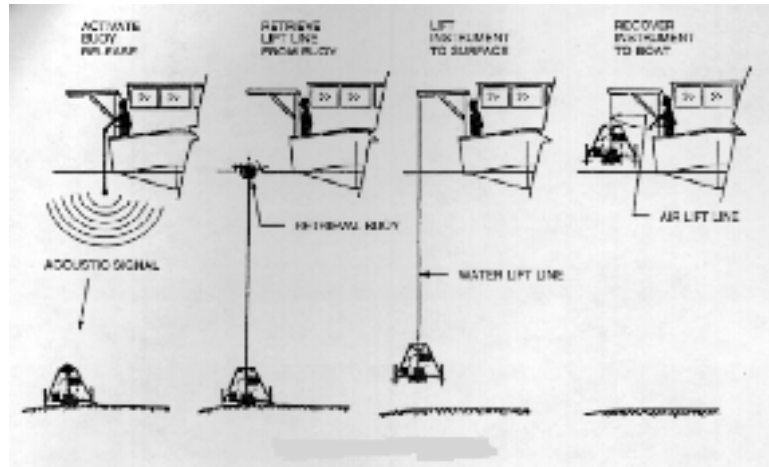


Figure 4. BFSD Retrieval

3.3 SAMPLING PROCEDURES

Discrete samples are drawn from the collection chamber, Figure 5, using a vacuum collection approach consisting of sample bottles, fill lines, in-line filters (with 0.45 micron membrane filters), check valves (Figure 6) 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. 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.

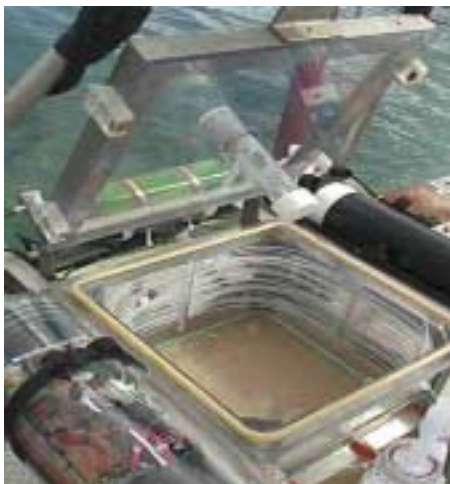


Figure 5. Collection Chamber



Figure 6. Sample Bottles

3.4 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 7 is 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 8 is a typical set of data obtained from a 72-hour deployment.

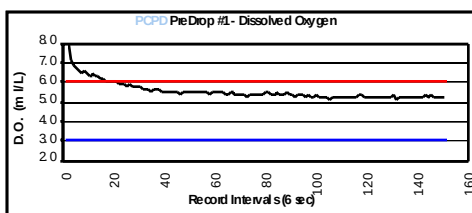


Figure 7. Ambient Oxygen Data

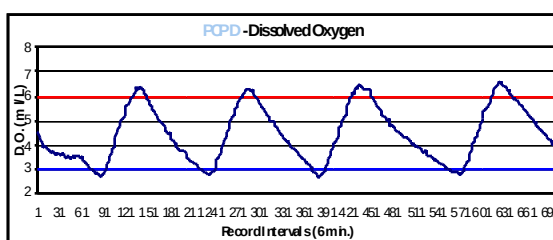


Figure 8. Operational Oxygen Control Data

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

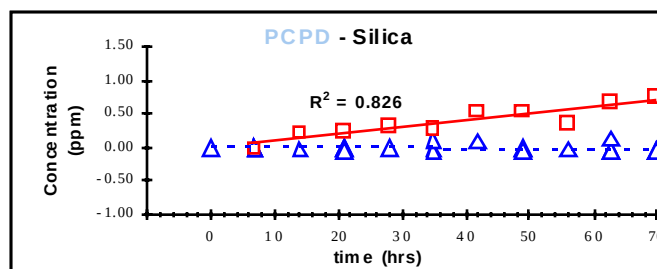


Figure 9. Silica Flux for Good Chamber Seal

Also, with a good chamber seal the ongoing bacterial degradation of organic material in the sediment consumes oxygen and generates carbon dioxide. This gradually lowers the chamber pH and Figure 10 is an example of this data for a good chamber seal with the sediment.

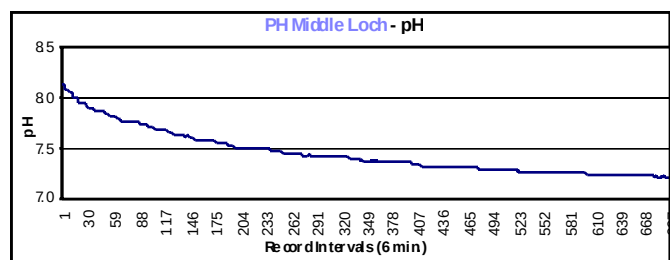


Figure 10. pH Data for Good Chamber Seal

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 also 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, 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 shown in Table 1 below.

Table 1. Blank Test Results Summary

Metal	Blank Flux ($\mu\text{g}/\text{m}^2/\text{day}$)			Repeatability ($\mu\text{g}/\text{m}^2/\text{day}$)		
	Test 1 (12)	Test 2 (6)	Test 3 (6)	Average Flux	+/- 95% C.I.	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/m ² /day)	-4	-3.3	1.4	-1.97	2.88	2.9

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 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. Appendix XX includes a set of spreadsheet products.

3.5 DEMONSTRATION SITE BACKGROUND

Two locations were selected for BFSD2 demonstrations. The first was San Diego Bay, California (Palma Creek area); and the second was Pearl Harbor, Hawaii (Middle Loch and Bishop Point). The locations and 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 to be 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. Demonstration logistical support requirements would be demonstrated by deployments in Pearl Harbor.
5. Data from prototype BFSF deployments conducted at the Paleta Creek site were available for use as reference data and for comparison with demonstration results.

3.5.1 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 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. Dissolved oxygen concentrations range from 4 to 8 milliliters per liter; 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 11, 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.



Figure 11. San Diego Bay, Paleta Creek Demonstration Site

Two demonstrations were conducted two weeks apart: June 6-8, 1998 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 BFSF deployments. The tests were conducted at about 18 +/- 3 feet depth, depending on tidal flow, and offshore about 30 feet from a quay wall. Deployment and retrieval was from the SSC SD research vessel R/V ECOS. Tables 2 and 3 below summarize the results of the two Paleta Creek demonstrations.

Table 2. BFSF 2 Results from the Paleta Creek Pre-Demonstration (PCPD)

Metal	Flux	+/- 95% C.L.	Flux rate Confidence (%)	Triplicate Blank Flux ($\mu\text{g}/\text{m}^2/\text{day}$)		Bulk Sediment ($\mu\text{g}/\text{g}$)	Overlying Water ($\mu\text{g}/\text{L}$)
	($\mu\text{g}/\text{m}^2/\text{day}$)	($\mu\text{g}/\text{m}^2/\text{day}$)		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	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) ^a (mm^2/day)	-1050.87	86.25	na	na	na	na	5.2
Silica (SiO ₂) ^a ($\text{mg}/\text{m}^2/\text{day}$)	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 3. BFS2 Results from the Paleta Creek Pre-Demonstration (PCP)

Metal	Flux	+/- 95% C.L.	Flux rate Confidence	Triplicate Blank Flux ($\mu\text{g}/\text{m}^2/\text{day}$)		Bulk Sediment	Overlying Water
	($\mu\text{g}/\text{m}^2/\text{day}$)	($\mu\text{g}/\text{m}^2/\text{day}$)	(%)	Average	+/- 95% C.L.	($\mu\text{g}/\text{g}$)	($\mu\text{g}/\text{L}$)
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) [*] (* $\text{mL}/\text{m}^2/\text{day}$)	-1341.12	160.18	na	na	na	na	4.7
Silica (SiO ₂) [*] (* $\text{mg}/\text{m}^2/\text{day}$)	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.

Figures 12 and 13 below illustrate graphical comparison of the results.

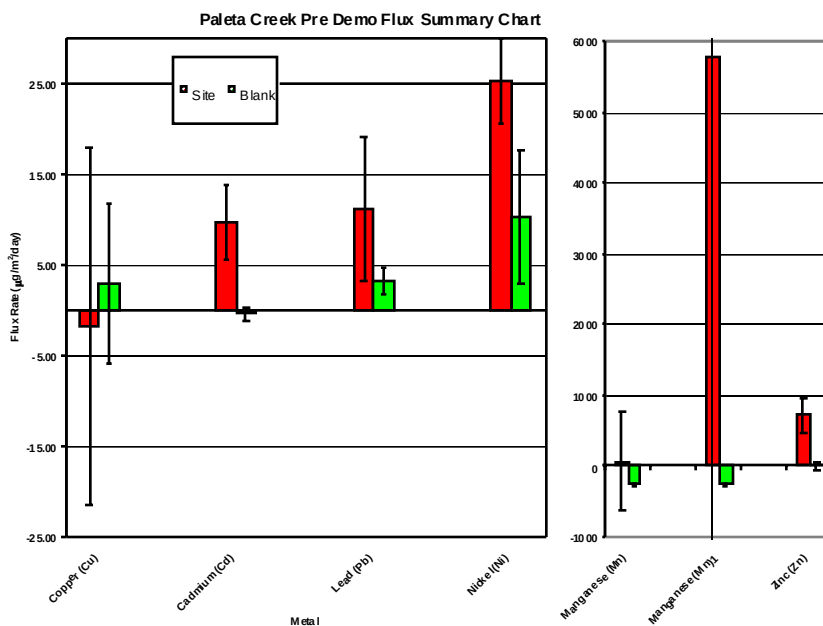


Figure 12. Paleta Creek Pre-Demonstration Results

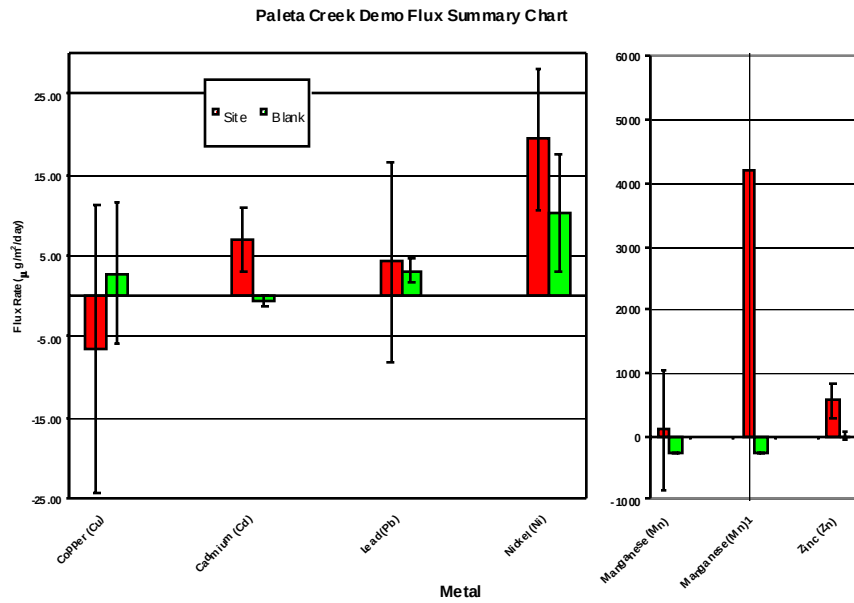


Figure 13. Paleta Creek Demonstration Results

Pearl Harbor, Hawaii: Pearl Harbor, Figure 14, 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 meters 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.



Figure 14. 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 more coarse than Middle Loch as a result of stronger tidal flows and contain calcium (coral) components. These differences affect the mobility and availability of metals to flux as well as the chamber seal integrity with the sediment.

The first demonstration was conducted Feb. 5-8, 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 second demonstration was conducted Feb. 11-14, 1999 within the area known as Alpha Docks, Marine Diving and Salvage Unit One (MDSU-1) located at Bishop Point. Tables 4 and 5 summarize the results of the Pearl Harbor Middle Loch and Bishop Point demonstrations.

Table 4. BFS2 Results from the Pearl Harbor Middle Loch (PHML) Demonstration

Metal	Flux ($\mu\text{g}/\text{m}^2/\text{day}$)	± 95% C.L. ($\mu\text{g}/\text{m}^2/\text{day}$)	Flux rate Confidence (%)	Triplicate Blank Flux ($\mu\text{g}/\text{m}^2/\text{day}$)		Bulk Sediment ($\mu\text{g}/\text{g}$)	Overlying Water ($\mu\text{g}/\text{L}$)
				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	1180	52.19
Manganese (Mn) ¹	213.159	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) ($\text{g}/\text{m}^2/\text{day}$)	-1085.52	64.84	na	na	na	na	4.17
Silica (SiO ₂) ($\text{mg}/\text{m}^2/\text{day}$)	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 5. BFS2 Results from the Pearl Harbor, Bishop Point (PHBP) Demonstration

Metal	Flux ($\mu\text{g}/\text{m}^2/\text{day}$)	± 95% C.L. ($\mu\text{g}/\text{m}^2/\text{day}$)	Flux rate Confidence (%)	Triplicate Blank Flux ($\mu\text{g}/\text{m}^2/\text{day}$)		Bulk Sediment ($\mu\text{g}/\text{g}$)	Overlying Water ($\mu\text{g}/\text{L}$)
				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	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) ($\text{g}/\text{m}^2/\text{day}$)	-567.12	54.96	na	na	na	na	65
Silica (SiO ₂) ($\text{mg}/\text{m}^2/\text{day}$)	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

The results for Bishop Point were significantly different than those of Middle Loch with the exception of Cadmium, which was nearly identical. Figures 15 and 16 below graphically illustrate results.

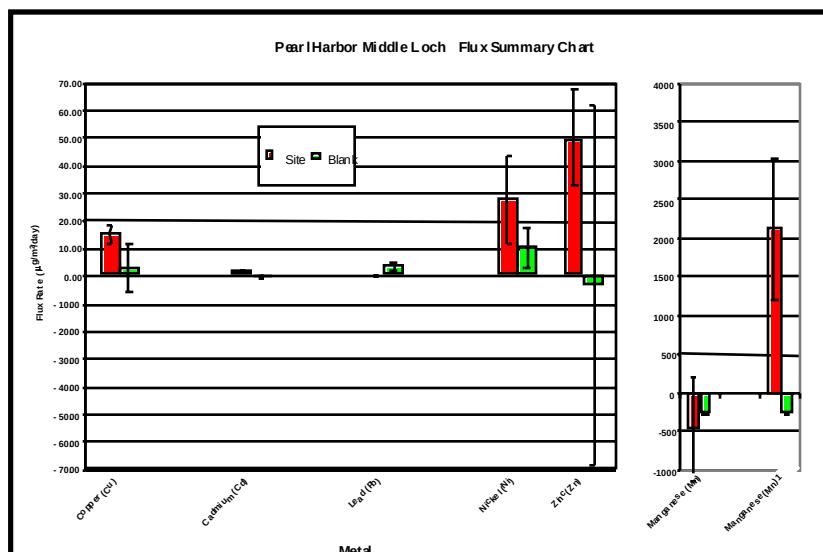


Figure 15. Pearl Harbor Middle Loch Demonstration Results

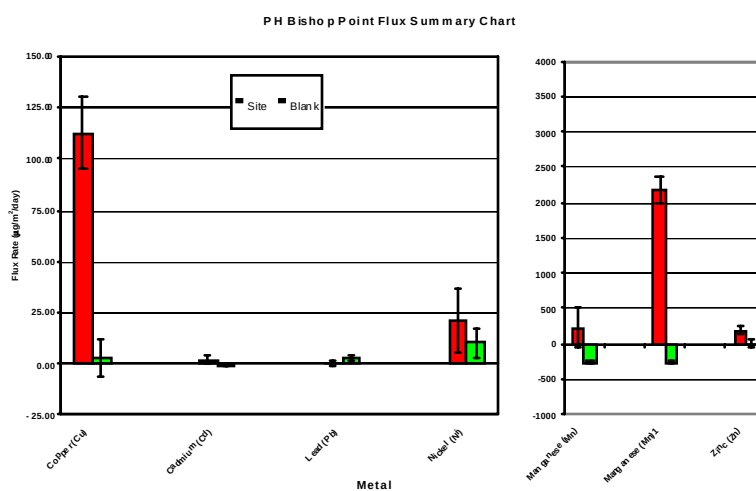


Figure 16. Pearl Harbor Bishop Point Demonstration Results

4.0 PERFORMANCE ASSESSMENT

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, 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 metal contamination mobility.

It was concluded that 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. The applicable performance capabilities and the demonstration objectives listed in Section II 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 trace metal 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 this study 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 Section III met the objectives listed in III.A. Both the technology demonstration team and the California EPA certification evaluators tasked with assessing the performance and results concluded that the applicable capabilities listed in Section II were met. Official State of California Performance Certification processes are underway and a 30-day Public Notice has been issued.

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5.0 COST ASSESSMENT

The expected operational costs for the Benthic Flux Sampling Device 2 (BFSD2) 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 17, 18 and 19 illustrate expected costs and schedules for the three phases of operations.

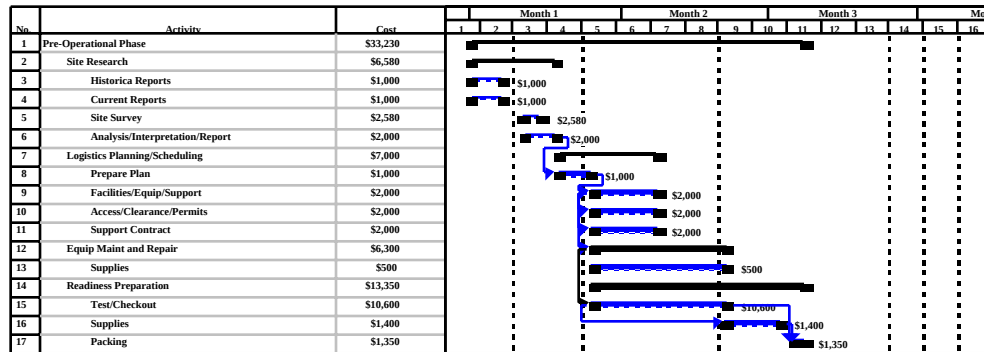


Figure 17. Pre-Operational Phase Schedule and Cost

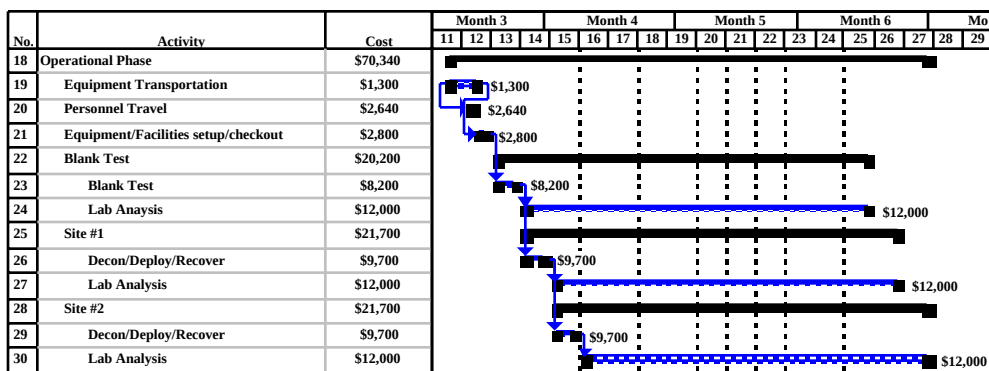


Figure 18. Operational Phase Schedule and Cost

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 workweek schedule. An accelerated schedule, which shortens turnaround time and includes weekend work periods, can achieve two deployments per week.

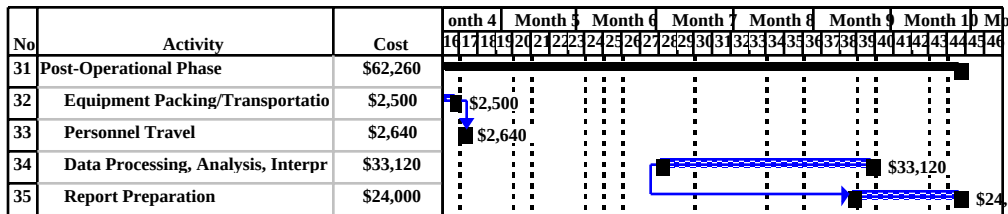


Figure 19. Post-Operational Phase Schedule and Cost

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 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 key reference 3, 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 introduce 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. 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, 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 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 additional issues.

6.0 IMPLEMENTATION ISSUES

6.1 COST OBSERVATIONS

The key factor affecting cost of BFSD2 deployment is analytical laboratory costs. 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.

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 California Environmental Protection Agency (CA EPA), Department of Toxic Substances Control (DTSC) Technology Evaluation and Certification Program known as "Cal Cert". 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 the BFSD2. Recognition and acceptance by the U.S. Environmental Protection Agency (US EPA), as well as private sector, Native American and foreign interests, is also promoted by their active participation in the ITRC. And, US EPA, state, local and private environmental professionals, as well as CA EPA evaluators were in attendance at field demonstrations, which included technology briefings and displays. Finally, certification by CA EPA includes public notifications and listings officially distributed to a wide range of recipients.

6.5 LESSONS LEARNED

Flexibility - As with any multi-faceted program which 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 work around efforts which ultimately recovered schedule losses. Technical approaches must flex to allow for changes. This project benefitted from a number of incremental and continuing product improvements which were accommodated within the technical approach without invalidating demonstration results.

Mother Nature - It again became clear from demonstration results that contaminated sediments are non-homogeneous 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 billion 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

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APPENDIX B

Data References

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 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:
 - S Draft and Final Demonstration Plans
 - S Draft and Final Reports
 - Individual Demonstration Test Reports
 - S Ex Situ, In Situ, Test and Checkout Reports
 - Protocols and Procedures
 - S Official Correspondence
 - S Narrative and Contract Data Requirements Reports
 - S CA EPA Certification Agreement
2. Microsoft Excel:
 - S Battelle Marine Sciences Analytical Data
 - S Computational Spreadsheet Workbooks
 - S Ex Situ, In Situ, Test and Checkout Data
 - S Financial Data
3. Microsoft Power Point:
 - S Proposal Viewgraph Presentation
 - S In Progress Review Viewgraph Presentations
 - S SERDP/ESTCP Viewgraph Presentation
4. Microsoft Project:
 - S Program Execution Schedule
 - S Individual Demonstration Schedules, Budgets, Tasking
 - S Ex Situ, In Situ, Test and Checkout Schedules
5. Qualcomm Eudora Pro:
 - S all e-mails (with attachments)
6. MicroGraphics Picture Publisher:
 - Photographic Images
 - S Composite Display Poster



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