CHEMICAL ANALYSIS, TOXICITY EVALUATION AND BIOACCUMULATION EXPOSURE OF SEDIMENTS FROM **HUMBOLDT BAY:**

BASELINE SURVEY III

Fiscal Year 1995

FINAL REPORT

Prepared for:

U.S. ARMY ENGINEERING DISTRICT
SAN FRANCISCO CORPS OF ENGINEERS
San Francisco, California

Prepared by:

TOXSCAN INC. and KINNETIC LABORATORIES, INC.
Watsonville, California

FEBRUARY 1996

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BASELINE SURVEY III

1.0 Introduction

Under Contract No. DACW07-92-D-002 from San Francisco District, Army Corps of Engineers (SFACOE), ToxScan, Inc. collected and analyzed sediment samples from **Humboldt Bay** for FY 1995, **Baseline Survey III** as per the project Scope of Services (**Appendix A**). Sediments were sampled by Kinnetic Laboratories, Inc., and returned to the ToxScan, Inc. laboratory at Watsonville, CA where they were assigned laboratory number **T-12046** for physical, chemical and bioassay analyses. Bioaccumulation exposures were performed on the sediment composites, but the exposed tissues were not analyzed. Samples collected, composites and analyses are summarized in **Table 1**.

2.0 Methods

2.1 Sediment Collection

Sediment samples from **Humboldt Harbor** were collected March 30, 1995 through April 4, 1995 from the F/V Sally Kay. Thirty five discrete samples from six areas in Humboldt Harbor were collected using Vibra-core and Smith-MacIntyre Grab sampling equipment. Materials from individual sites with fine grained material were composited for analysis, and discrete samples from each site were archived. A grab sample was obtained from the reference area with a Smith-MacIntyre grab. Samples were held at 4°C until delivery to the ToxScan laboratory in Watsonville on April 4, 1995.

Sample location target positions were taken from the project Scope of Services. Core and grab samples were taken as close to target locations as possible. Sample locations are plotted and labelled in **Figures 1** through **4**. The details of each sample (time collected, depth, and location) are summarized in **Table 2** and documented in the field log sheets presented in **Appendix B**.

Horizontal positioning was established with a Trimble series 4000 Differential GPS navigation system with base stations set on Army Corps of Engineers survey markers. Vertical measurements were provided by a JVC 90 series dual frequency fathometer calibrated by leadline to 0.1 foot at the expected depth range. Tidal stage was determined using "Tide.1" software (Micronautics Inc.) and verified daily with USGS benchmarks.

The vibra-core consists of a vibrating aluminum head and a ten foot long aluminum core tube. The core tube is capped with a stainless steel cutting tip and a stainless steel core catcher. The vibra-core is lowered slowly into the sediment; the vibration allows entry into the sediment from the mudline to the sample depth. If a sample was not obtained on the first attempt, core attempts were repeated until a sample was secured. The Smith-Macintyre grab consists of a set of spring-loaded galvanized steel jaws, triggered by impact with the sediment surface, which collects sediment to 6" below the mudline.

All sample contacting surfaces of the Vibra-Core and sample handling equipment were cleaned between each site using the following EPA approved method:

1. Wash with 2% Micro Laboratory Soap.
2. Rinse three times with reagent grade deionized water.
3. Rinse with 2N nitric acid.
4. Rinse three times with clean water.
5. Rinse with reagent grade acetone.
6. Rinse with reagent grade hexanes and allow to air dry.
5. Store in cleaned containers until use.

The Smith-MacIntyre Grab was cleaned using steps 1 and 2 above.

2.1.1 Sample Handling. Vibracore and Smith Macintyre grab samples were taken during this project. Handling procedures for each sample type are summarized below:

Vibracore Samples. Each core sample was measured for total core length. If the core achieved penetration to project dredge depth the desired sample (from dredge depth to sediment surface) was extruded into the compositing container.

Grab Samples. Each grab sample was evaluated for grain size, composition, and penetration. Grabs which had "washed out", or which were determined to have insufficient penetration, were rejected.

The individual samples and area composites were placed in appropriate containers in precleaned coolers, on ice, to reduce the temperature to the prescribed 4°C. All samples were transported to ToxScan's chemistry and bioassay facilities in Watsonville under chain of custody at the prescribed temperature. Subsamples of the four composites were subsequently shipped at temperature under chain of custody to Alta Analytical Laboratory Inc., El Dorado Hills, CA for tetra to octa chlorinated dioxins and furans analysis.

2.2 Water Collection

Reference water for bioassay tests was collected at mid depth at the reference site using an EPA protocol-cleaned peristaltic pump and cleaned silicon and teflon hoses. The hose was lowered into the water at one end of the reference site, and the vessel drifted with the current through the reference site while sampling. The water was pumped into 5-gallon cubitainers which were then stored at 4°C until delivery to the ToxScan laboratory in Watsonville.

2.3 Chemical and Physical Sediment Analysis

Sediment samples for chemical and physical analysis were collected in glass containers; samples for grain size analysis were collected in polyethylene containers. Prior to analysis, samples were stored in the laboratory at 4°C. Analyses were conducted according to the following methods:

Sediment Grain Size was determined using the methods described in Plumb (1981).

Interstitial Water Salinity and Total Ammonia values were determined for centrifuge-extracted sediment pore waters by salinometer-calibrated refractometer (YSI Model 33 Conductivity/Salinity Meter and Atago S-10 or S-28 Hand Held Refractometer), and by pH meter / ammonia probe (Fisher Accumet Model 925 with Orion Ammonia Electrode Model 95-12). One hundred to two hundred grams of sediment were centrifuged at 7,000 to 8,000 rpm until supernatant was clear (15 - 30 minutes).

Total and Water Soluble Sulfides. This method was adapted from EPA Method 376.1 (EPA 1983) and Standard Method 4500-S^{-2}-E (APHA 1992). Sediment samples were mixed with O_2-free DIW, and treated in a manner similar to aqueous samples. Hydrogen sulfide present in aqueous samples was purged into a zinc acetate trap using nitrogen gas. The sample pH was adjusted to about 4 if total sulfide was to be determined, or left unadjusted for free sulfide determinations. The zinc sulfide precipitate in the trap was oxidized with a known and excess amount of iodine, and the unreacted iodine was back-titrated with thiosulfate.

Oil and Grease, Total Petroleum Hydrocarbon. Samples were acidified to a low pH and extracted with fluorocarbon-113 in a separatory funnel. The fluorocarbon layer was separated from each sample, passed over sodium sulfate and collected for analysis of Oil and Grease using an Infrared spectrophotometer scanning the wavelengths from 3200 to 2700 cm^{-1}. To determine Total Petroleum Hydrocarbons, this above extract was passed through silica gel which extracted the vegetable oil fractions; the remaining petroleum fraction was then analyzed by Infrared spectrophotometric techniques as described below.

Total Organic Carbon (TOC). Analysis for total organic carbon followed the method of Gaudette, et al. (1974). One-to-two grams of sediment were placed in a 500 ml flask to which 10 ml of potassium dichromate ($K_2CR_2O_7$) had been added. Twenty ml of concentrated sulfuric acid (H_2SO_4) was then added while the flask was swirled. After 30 minutes, the sample was diluted to a volume of 200 ml with de-

ionized water (DIW), and 10 ml of phosphoric acid (H_3PO_4) and 0.2 g of sodium fluoride (NaF) were added. After more swirling, 15 drops of diphenylamine indicator was added and the sample was titrated with 0.5N ferrous ammonium sulfate.

Metals. Analyses for metals employed combinations of the following Varian spectrophotometers: SpectrAA 400P or 400Z with GTA 96 a Graphite Furnace and autosampler; or a SpectrAA 10 with VOA 76 hydride—cold vapor generator and flame autosamplers. Sample preparation prior to analysis by atomic absorption was accomplished by guidelines specified by Chapter 3, Sections 3.2 and 3.3, 7000 series (EPA 1986).

Organotins. Organotin species analysis was by the method of Uhler and Durrel (1989). Speciation was done by a n-pentyl derivatization using a Gas Chromatograph with a Flame Photometric Detector. A sediment sample was mixed with 5 ml of hydrobromic acid (HBr), converting cationic butyltins to the bromide complexes, which were then extracted with a toluene-tropolone mixture. Following this extraction a n-pentylmagnesium bromide was used to convert the butyltins to the n-pentyl derivatives. This extract was cleaned by passing it through a Florisil/Silica chromatograph column and then injected into the Gas Chromatograph with a FPD detector where butyltins were quantified.

Chlorinated Pesticides and PCB's. Analyses for these constituents were determined by Method 8080 (EPA 1986). A solid sample was mixed with anhydrous sodium sulfate, placed in an extraction thimble and extracted using acetone and hexane in a Soxhlet extractor. The extract was then dried, concentrated, and underwent a Florisil clean-up. The extract was analyzed by gas chromatograph with an electron capture detector.

Polynuclear Aromatic Hydrocarbons and Phthalates. Analyses for semivolatile compounds were by GC-MS techniques, following Method 8270 (EPA 1986). A solid sample was mixed with anhydrous sodium sulfate and sonicated in methylene chloride. The extract was concentrated and then cleaned up by gel permeation chromatography. The extracted sample was analyzed by gas chromatograph/ mass spectroscopy. The EPA 8270 method was modified slightly by the use of Varian Selective Ion Storage technique which eliminates interfering ions from the sample spectrum.

Dioxins and Furans. Sediment samples were analyzed for tetra to octa chlorinated dioxins and furans using EPA Method 8290. These analyses were performed by Alta Analytical Laboratory, Inc., El Dorado Hills, CA.

2.4 Bioassay and Bioaccumulation Test Procedures

Biological assessments of the Humboldt Bay sediments are summarized in **Table 3**.

2.4.1 Suspended Particulate Phase (SPP) Bioassays

Suspended particulate phase elutriates were prepared by procedures outlined in the "Green Book" (EPA/USACE 1991) using reference site water and test sediments. The test protocol for bivalves was as specified by ASTM (1989). Three concentrations (100%, 50%, 10%) of suspended particulate phase were tested. The lower concentrations were evaluated only if the 100% concentrations produced >50% inhibition of development. Three species were tested in suspended particulate phase bioassays: The larvae of a marine bivalve (the bay mussel, *Mytilus edulis*), a mysid (*Holmesimysis costata*), and a marine teleost fish (the speckled sanddab, *Citharichthys stigmaeous*).

Elutriate sanddab bioassays were performed at the Davenport laboratory, and elutriate bioassays with mysids and bivalve larvae were performed at the Watsonville laboratory. The positioning of test containers and other conditions in the laboratories were designed for uniform exposure to the controlled laboratory environment. Five replicates of test treatments were randomly assigned (complete random design) to the test containers by use of a random numbers generating program.

The sediment samples were placed in cleaned 5-gallon polyethylene buckets with laboratory seawater for elutriate preparation. The sediment to water ratio was 1:4 as specified in the Green Book. The mixtures were agitated by vigorous aeration for 30 minutes. After a one-hour settling period, the elutriates were siphoned off and used as suspended particulate phase media.

2.4.1.1 Bivalve Larvae (*Mytilus edulis*)

Mussels were induced to spawn by high-temperature stimulation. Eggs and sperm were collected in separate basins filled with aerated seawater at 20°C. Egg density was determined by microscopically counting several 1-ml aliquots taken from the well-mixed egg basin. Fertilization was accomplished by addition of an appropriate amount of sperm suspension, and confirmed by microscopic examination.

The control exposure, performed for quality assurance purposes, used seawater from our laboratory system. Five replicate dishes were used for each test exposure. Temperature, dissolved oxygen, pH and salinity were monitored in each test concentration and in controls at the beginning and end of the test.

Larvae were tested in 250 ml polyethylene beakers containing approximately 200 ml of test solution. After fertilization was confirmed an aliquot containing approximately 6000 fertilized eggs was pipetted into each test beaker. Gentle aeration was provided throughout the 48-hour duration of the test. Five extra beakers were prepared in addition to those required for test and control replicates. These

"extra" test containers were not incubated for 48 hours, but rather they were evaluated immediately after inoculation to provide the "initial recovery" data used to establish the mean number of embryos added to each experimental beaker.

At the end of the 48-hour exposure period the contents of each dish were poured through a 45μ nytex screen. Surviving larvae were retained on the screen. The test beaker was rinsed three times with seawater and each successive rinse was poured through the screen to ensure complete transfer of larvae. Larvae were quantitatively transferred from the screen into a graduated cylinder and the volume was adjusted with a seawater-formalin mixture. Contents of the cylinder were mixed by inversion to ensure uniform distribution of larvae, and a 1 ml aliquot was transferred to a Sedgwick-Rafter counting slide for microscopic evaluation. Larvae were scored for evidence of internal tissue inside a complete larval shell. Larvae which had a complete larval shell containing tissue were counted as normal, whereas empty shells and larvae with incomplete shells were scored as abnormal. Data were reported as percent of initial embryos which survived, and percent of survivors which showed normal development, as calculated below.

The raw data resulting from these bioassays included the following:

- Counts of embryos added to five replicate test containers which were <u>not</u> incubated for 48 hours (= initial recovery).
- Counts of normal and abnormal embryos from test containers (five replicates per sample, reference and control) which <u>were</u> incubated for 48 hours.

The results were calculated from these data as follows:

$$\%\ Survival = \frac{No.\ normal\ larvae\ recovered}{N} \times 100$$

$$\%\ Normal = \frac{No.\ normal\ larvae}{No.\ normal\ larvae + No.\ abnormal\ larvae} \times 100$$

where N = the mean initial number of embryos added (from initial recovery data).

For each test chamber other than controls, % survival data were adjusted to correct for mortality observed in the control exposures by use of **Abbott's correction**:

$$\textit{Corrected Sample \% Survival} = 100 - \left(\frac{\textit{mean \% control survival - \% sample survival}}{\textit{mean \% control survival}} \times 100\right)$$

Percent normal development data were similarly adjusted.

For the bioassay to be considered a valid test, an average of at least 70% of the exposed embryos must survive in the controls; abnormals were counted as mortalities as per the Testing Guidelines contained in SFACOE Public Notice No. 93-2: Response to Comments on Public Notice 92-5.

Following the Scope of Services, the 100% elutriate concentrations were evaluated initially. If Abbott's-corrected survival or normal development values were $\geq$50%, no further evaluations were performed. If these values were $\leq$50%, the 10% and 50% elutriate exposures were evaluated and EC_{50} and/or LC_{50} calculations were made using the Trimmed Spearman-Karber method. For LC_{50} calculations, abnormal larvae and calculated mortalities were added; whereas for EC_{50} calculations, separate abnormality counts were used, as per Public Notice 93-2 (see above).

A reference toxicant bioassay was also performed for quality assurance purposes, to verify the health and sensitivity of the test organism population. The reference toxicant used was cupric sulfate ($CuSO_4 \cdot 5H_2O$) dissolved in laboratory seawater. A second reference toxicant test was performed using ammonia as the toxicant.

2.4.1.2 Mysid (*Holmesimysis costata*)

Adult mysids (*Holmesimysis costata*) were collected from kelp beds near Monterey, California. The animals were gently aggregated with a dip net, corralled into a submerged bucket without removing them from the water and transported directly to the bioassay lab. In transit, holding tank temperatures were maintained within 2°C of the ambient temperature at sampling. Gentle aeration was supplied from a bottle of compressed oxygen. Throughout testing, the mysids were fed about 50 brine shrimp (*Artemia salina*) nauplii per mysid per day to prevent mortality from starvation and cannibalism.

Mysids were tested in one-liter polycarbonate tanks containing one liter of test solution. To initiate testing, mysids were sorted into groups of 10 in small containers with very small volumes of seawater. Mysids were transferred to the test containers by submerging the containers and slowly tipping the animals into the test medium. During the bioassays, the number of survivors of the original 10 animals per tank were recorded as experimental data at 4, 8, 24, 48, 72, and 96 hours after test initiation. At each of these checkpoints, dead animals (i.e., those nonresponsive to mechanical stimulus) were removed from the test containers.

A reference toxicant bioassay was also performed on the mysids for quality assurance purposes, to verify the health and sensitivity of the test organism population. The reference toxicant used was Sodium Dodecyl Sulfate (SDS) dissolved in laboratory seawater.

2.4.1.3 Teleost Fish (*Citharichthys stigmaeus*)

Speckled sanddabs were collected by otter trawl from Tomales Bay and kept in holding tanks until transported to the laboratory via overnight delivery. They were allowed to acclimate to laboratory conditions prior to testing. Fish were fed a high protein pellet food during the holding period until 48 hours before test initiation; they were not fed thereafter.

Sanddabs were tested in 10-liter aquaria and were individually transferred from holding tanks to aquaria to start the test. During the bioassays, the number of survivors of the original 10 animals per tank was recorded as experimental data at 4, 8, 24, 48, 72, and 96 hours after test initiation. At each of these checkpoints, dead animals (i.e., those nonresponsive to mechanical stimulus) were removed from the test containers.

A reference toxicant bioassay was also performed on the sanddabs for quality assurance purposes, to verify the health and sensitivity of the test organism population. The reference toxicant used was Sodium Dodecyl Sulfate (SDS) dissolved in laboratory seawater. A second reference toxicant test was performed using copper as the toxicant.

2.4.1.4 Initial Mixing Calculations

In cases where an EC_{50} or LC_{50} was obtained, calculations of initial mixing were made using standardized formulae developed by the USACOE and EPA (EPA/ACOE 1977).

2.4.2 Solid Phase (SP) Static Bioassay (Amphipod)

Solid phase static bioassays were conducted on the harbor sediments simultaneously with control and reference sediments. The amphipod *Rhepoxynius abronius* was tested following procedures outlined in ASTM (1990).

Salinity and total ammonia measurements were made on sediment interstitial water as received; in addition, a final pore-water ammonia measurement was taken from one replicate of each test sediment at test termination. Pore waters were extracted by centrifugation. Interstitial water salinity was measured using a salinometer-calibrated refractometer. Interstitial water ammonia concentrations were measured with an ammonia probe calibrated to three concentration standards (see Sediment Chemical and Physical Analysis- Section 2.3).

In each test, five replicates of each station and reference treatment were randomly assigned to test jars. A 2-cm deep layer of appropriate sediment was added to each jar on the day prior to test initiation, and each test jar was provided with aeration via pasteur pipet. Each test was started on the following day by randomly assigning 20 amphipods to each jar, and continued for 10 days under static conditions with constant illumination and aeration. Daily measurements of environmental test conditions (temperature, salinity, pH, dissolved oxygen) were made in each test container, and the number of animals which had appeared on the sediment surface was noted.

At the end of the ten day exposure period, the contents of each jar were poured through a 0.5 mm sieve and the number of surviving amphipods counted. Survivors from each replicate were transferred into bowls containing control sediment and monitored for their ability to rebury within one hour. Test data for each replicate therefore include number of survivors and number of survivors able to rebury.

Reference toxicant bioassays were performed with each batch of test animals to verify the health and sensitivity of the test organism population. The reference toxicant used was cadmium chloride ($CdCl_2$) dissolved in laboratory seawater.

2.4.3 Solid Phase (SP) Flow-through Bioassays (Mysid Shrimp and Polychaete Worm)

Solid phase flow-through bioassays with mysids and worms were conducted on the harbor sediments simultaneously with control and reference sediments. Control sediments were collected from Tomales Bay. Testing for both species was performed at the Davenport facility where continuously flowing seawater is available, using testing procedures in EPA/COE (1991).

Mysids (*Holmesimysis costata*) were collected from kelp beds near Monterey, California. The animals were gently aggregated with a dip net, corralled into a submerged bucket without removing them from the water and transported directly to the bioassay lab. In transit, holding tank temperatures were maintained within 2°C of the ambient temperature at sampling. Gentle aeration was supplied from a bottle of compressed oxygen. Throughout testing, the mysids were fed about 50 brine shrimp (*Artemia salina*) nauplii per mysid per day to prevent mortality from starvation and cannibalism.

Polychaete worms (*Nephtys caecoides*) were collected from Tomales Bay and shipped overnight to the bioassay laboratory. They were kept in holding tanks with home sediment and overlying seawater until test initiation.

All sediments were sieved through a 1.0 mm screen to remove indigenous fauna, and a 3.0 cm layer of appropriate sediment was added to each test container. Tanks were then filled with lab seawater, and either twenty polychaete worms (*Nephtys caecoides*) or twenty mysids (*Holmesimysis costata*) were added to each container. Worms were tested in 31 L glass aquaria; mysids were tested in 1.5 L polycarbonate tanks fitted with small, screened drain holes. The small mysid containers were suspended

above the larger worm containers such that when the flow-through seawater system was activated, seawater passed through the mysid tanks, overflowed through the screened drain holes into the worm tanks, then drained to sea.

Solid Phase flow-through bioassays continued for 10 days. At least twice each day, environmental systems were checked for proper functioning. Once each day, the salinity and temperature of the system were measured. Dissolved oxygen and pH values of each tank were measured twice daily.

After the 10-day bioassay period, the contents of each tank were gently washed with seawater through a 0.5-mm nylon screen. The animals were retrieved from the screen and counted. Test data were the number of survivors of each species.

A reference toxicant bioassay was also performed on the mysids for quality assurance purposes, to verify the health and sensitivity of the test organism population. The reference toxicant used was Sodium Dodecyl Sulfate (SDS) dissolved in laboratory seawater. A second reference toxicant test was performed using ammonia as the toxicant.

2.4.4 Bioaccumulation Exposure

Clams (*Macoma nasuta*) and polychaete worms (*Nephtys caecoides*) were exposed to test and control sediments in an array of 31-liter flow-through glass aquaria, as follows: Five replicates of each harbor composite, reference composite and control sediments were randomly assigned to the test tanks. The control sediment was collected from Tomales Bay, CA. Sediments were screened through a 1.0 mm screen to remove indigenous fauna, and a 3.0 cm layer was added to each tank. Tanks were filled with water and 30 clams and 40 worms were added to each. After a one-hour settling time, the flow-through seawater system was activated and adjusted to a flow rate equivalent to 5 tank/volume changes per 24 hours (6.5 liters/hour).

Bioaccumulation exposures continued for 28 days. At least twice each day, environmental systems were checked for proper function. Each tank was monitored daily for temperature and D.O., and the seawater system was monitored daily for salinity and pH.

3.0 Results

Sediment physical, chemical and bioassay analyses are summarized in **Table 1**. Twelve samples from North Bay, Entrance and Bar were screened and analyzed for particle size distribution (PSD) only. Thirty-one samples were analyzed for bulk sediment chemistry: 26 discrete samples plus five harbor composites (SAMTB, EKUP, EKEX, FLTB, REF). Bioassay testing and bioaccumulation exposures were performed on the five composites and on the control sediment; subsamples of these sediments were analyzed for tetra to octa chlorinated dioxins and furans.

3.1 Sediment Physical Analysis

The particle size distributions of the sediment samples and composites are summarized in **Table 4**; details of grain size analyses are presented in **Appendix C**. Except for station NB9, the North Bay, Entrance and Bar samples each contained at least 90% coarse sediments by weight ($\Phi \leq 4$); NB9 contained 11.7% fines. Coarse sediment composition of the three harbor composites were as follows: Samoa Turning Basin (SAMTB) = 79.3%; Eureka Upper Channel (EKUP) = 35.1%; Eureka Upper Channel Extension (EKEX) = 15.9; and Field's Landing Lower Channel and Turning Basin (FLTB) = 16.9%. The disposal site reference (REF) composite contained 4.3% coarse sediments.

3.2 Bulk Sediment Chemistry

Results of bulk sediment chemical analyses of the Humboldt Harbor sediment samples and composites are summarized in **Table 4**. The laboratory reports are presented in **Appendix C**, and the laboratory QA plan summary is presented in **Appendix D**. Chains of Custody are Presented in **Appendix F**. The discussion below is generally limited to analyses of the harbor and reference composites; please refer to **Appendix C** for results of analyses of the individual samples.

Metals. The Humboldt Harbor sediment composites were analyzed for ten metals. Metals concentrations in the Harbor composites were similar to those found in the Reference composite. Within the Harbor composites, composite SAMTB tended to have the lowest metals concentrations. Individual accounts of the ten metals analyzed in these sediments are as follows:

- Arsenic concentrations ranged from 3.7 ppm to 4.9 ppm in the harbor composites. None of the harbor composites exceeded the 5.2 ppm found in the reference composite.

- Cadmium concentrations ranged from 0.1 ppm to 0.2 ppm in the harbor composites. SAMTB, EKEX and FLTB exceeded (by 2.0x) the 0.1 ppm found in the reference composite. Cadmium concentrations found in these sediments were near the detection limit.

- Chromium concentrations ranged from 120 ppm to 130 ppm in the harbor composites. Harbor composites EKUP and EKEX exceeded (by 1.1x) the 120 ppm found in the reference composite.

- Copper concentrations ranged from 11 ppm to 30 ppm in the harbor composites. Only harbor composite EKEX exceeded (by 1.1x) the 28 ppm found in the reference composite.
- Lead concentrations ranged from 4.9 ppm to 15 ppm in the harbor composites. EKUP (1.5X) and EKEX (1.1X) exceeded the 10 ppm found in the reference composite.
- Mercury concentrations ranged from 0.096 ppm to 0.13 ppm in the harbor composites. Only EKEX exceeded (by 1.1x) the 0.12 ppm found in the reference composite.
- Nickel concentrations ranged from 86 ppm to 130 ppm in the harbor composites. None of the harbor composites exceeded the 130 ppm found in the reference composite.
- Selenium concentrations ranged from 0.1 ppm to 0.2 ppm in the harbor composites. None of the harbor composites exceeded the 0.2 ppm found in the reference composite.
- Silver concentrations ranged from 1.3 ppm to 1.6 ppm in the harbor composites. None of the harbor composites exceeded the 1.7 ppm found in the reference composite.
- Zinc concentrations ranged from 44 ppm to 94 ppm in the harbor composites. EKUP (1.2x) and EKEX (1.4x) exceeded the 69 ppm found in the reference composite.

Butyltins. Three organotins (tri-, di-, and mono-butyltin) were measured in the Humboldt Harbor sediment composites. Composite EKEX contained 10 ppb tributyltin; a small amount (2 ppb) of dibutyltin was detected in the EKUP and EKEX composites. The reference sediment contained no detectable butyltins.

Semivolatiles. Phthalate esters and seventeen polynuclear aromatic hydrocarbons (PAHs) were measured in the Humboldt Harbor sediment composites. Several samples in this set were overdried during extraction. As a consequence the surrogate recoveries for nitrobenzene-d5 were below QC limits. The affected samples were re-extracted and reanalyzed. However, the second extraction took place between 9 and 11 days beyond the 14 day holding time. Both sets of data are reported in **Table 4** and in **Appendix C**. The results for the other analytes were comparable in the two analyses, except for individual sample SAM 6-B which had a much higher PAH content in the second extract. This inconsistency may be attributed to a lack of homogeneity in the sample.

Among the harbor composites, SAMTB consistently contained the lowest concentrations of semivolatiles, and EKUP the highest. Phthalate concentrations ranged from 200 to 1700 ppb in the harbor composites; EKUP (4.6x) and FLTB (3.5x) exceeded the 370 ppb measured in the reference composite. Total PAH concentrations ranged from 96 ppb (SAMTB) to 890 ppb (EKUP) in the harbor composites compared to 390 ppb detected in the reference sediment. PAH detections were as follows:

LPAHs. Six low molecular weight PAHs were detected in the harbor or reference composites. Total LPAH concentrations in the harbor samples ranged from 51 ppb (SAMTB) to 240 ppb (FLTB); the reference sample contained 230 ppb total LPAH.

- 2-methylnaphthalene concentrations ranged from 14 ppb to 77 ppb in the harbor composites; FLTB (1.1x) exceeded the 71 ppb detected in the reference composite.

- Naphthalene concentrations ranged from 13 ppb to 44 ppb in the harbor composites; EKUP (1.6x), EKEX (1.4X) and FLTB (1.2x) exceeded the 27 ppb detected in the reference composite.

- Acenaphthene was detected only in composite EKUP (13 ppb); none was detected in the reference sample.

- Fluorene concentrations ranged from <13 ppb to 32 ppb in the harbor composites; the concentrations in EKUP, EKEX and FLTB exceeded by 1.2x to 1.3x the 24 ppb found in the reference sample. None was detected in composite SAMTB.

- Phenanthrene concentrations ranged from 31 ppb to 110 ppb in the harbor composites; none of the harbor composites exceeded the 110 ppb detected in the reference composite.

- Anthracene was found (17 ppb) only in composite EKUP; it was not detected in the reference sample.

HPAHs. Nine high molecular weight PAHs (HPAHs) were detected in the harbor or reference composites. Total HPAH concentrations ranged from 60 ppb (SAMTB) to 620 ppb (EKUP) in the harbor composites, compared to 160 ppb in the reference sediment.

- Fluoranthene concentrations ranged from 20 ppb to 160 ppb in the harbor composites; except for SAMTB, each of the harbor composites exceeded (by 1.3 to 4.6x) the 35 ppb detected in the reference composite.

- Pyrene concentrations ranged from 25 ppb to 150 ppb in the harbor composites; except for SAMTB, each of the harbor composites exceeded (by 1.3 to 4.3x) the 35 ppb detected in the reference composite.

- Chrysene concentrations ranged from <13 ppb to 59 ppb in the harbor composites; EKUP (1.7x) and EKEX (1.2x) exceeded the 35 ppb detected in the reference composite.

- Benzo(a)anthracene concentrations ranged from <13 ppb to 41 ppb in the harbor composites; EKUP (2.6x) and EKEX (1.4x) exceeded the 16 ppb detected in the reference composite.

- Benzo(b)fluoranthene concentrations ranged from <13 ppb to 51 ppb in the harbor composites; EKUP (2.2x), EKEX (1.6x) and FLTB (1.1x) exceeded the 23 ppb detected in the reference composite.

- Benzo(k)fluoranthene concentrations ranged from <13 ppb to 29 ppb in the harbor composites; EKUP and EKEX exceeded the <13 ppb detected in the reference composite.

- Benzo(a)pyrene concentrations ranged from <13 ppb to 51 ppb in the harbor composites; EKUP, EKEX and FLTB exceeded the <13 ppb detected in the reference composite.

- Indeno[1,2,3-CD]pyrene concentrations ranged from <13 ppb to 32 ppb in the harbor composites; EKUP and EKEX exceeded the <13 ppb detected in the reference composite.

- Benzo[ghi]perylene concentrations ranged from <13 ppb to 51 ppb in the harbor composites; EKUP (2.7x), EKEX (1.6x) and FLTB (1.2x) exceeded the 19 ppb detected in the reference composite.

Chlorinated Pesticides and PCBs. The Humboldt Harbor sediment composites were analyzed for the eighteen chlorinated pesticides and four polychlorinated biphenyls (PCBs as Aroclors). None of the harbor composites, reference or Tomales Bay control sediments contained detectable amounts of these substances.

Dioxins and Furans. The Humboldt Harbor composites were analyzed for tetra to octa chlorinated dioxins and furans by Alta Analytical Laboratories, (El Dorado Hills, CA). The harbor composites contained from 87.0 pg/g to 503 pg/g total dioxins and from 18.0 pg/g to 84.7 pg/g total furans; FLTB contained the lowest concentrations and EKEX the highest concentrations of each. The reference site sediment contained 621 pg/g total dioxins and 3.65 pg/g total furans. TEQ's ranged from 0.76 at the reference site to 3.5 at EKEX.

Sediment Conventionals. The sediments were tested for total and water soluble sulfides, oil and grease, petroleum hydrocarbons, total volatile solids, percent solids, and total organic carbon. Composite EKEX generally contained the highest concentrations and SAMTB the lowest.

Total sulfides ranged from 79 ppm to 300 ppm in the harbor sediment composites. The reference composite contained 1.3 ppm total sulfides. Except for a trace amount (0.3 ppm) in the EKUP composite, no water soluble sulfides were found in the harbor composites, nor in the reference composite.

Oil and Grease concentrations ranged from <20 ppm to 80 ppm in the harbor sediments; EKUP, EKEX and FLTB each contained higher concentrations than the <20 ppm in the reference composite. Petroleum hydrocarbons were detected only in FLTB (46 ppm). Volatile solids ranged from 2.0% to 4.3% in the harbor composites, and was 3.9% in the reference sediment.