SAN FRANCISCO BAY PILOT REGIONAL MONITORING PROGRAM 1991-1992 SUMMARY PROGRESS REPORT

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PROGRESS REPORT

This report summarizes the data collected in the San Francisco Bay 1991-1992 Regional Monitoring Program. This is a progress report describing the work that has been completed to date. There were five different contracts written for the San Francisco Bay Regional Monitoring Program that were funded by the Bay Protection and Toxic Cleanup Program. Each deal with different components of the monitoring program or wasteload allocation studies: 1) sediment analysis, 2) bioaccumulation, 3) water column toxicity, 4) water column chemistry (organics) and 5) wasteload allocation. The Sediment Report and Water Column Toxicity Report are submitted with this summary as draft finals. All of the chemical analysis for the sediment study is not yet completed. The Bioaccumulation Report is submitted in final form. Analysis of the water column samples for organic chemistry is not yet complete. The wasteload allocation studies are on a four year time schedule. Progress on these studies is included in this report.

In addition, since the Regional Monitoring Program had many contracts and many subcontractors in each contract (the sediment contract had six contractors) the final reports do not analyze the data in a fully integrated fashion. We are currently trying to hire statisticians to thoroughly analyze all of the data collected in the program so that we can extract the most information from the enormous amount of data we have. An integrated approach to data analysis is necessary in order to use this information to guide our decisions in the future. Once all of the monitoring reports are final and an integrated statistical analysis of the data is completed, a final version of this summary report will be issued.

EXECUTIVE SUMMARY

This report is a summary of the progress to date on the San Francisco Bay Regional Water Quality Control Board's Pilot Regional Monitoring Program (RMP). The RMP was funded by the Bay Protection and Toxic Cleanup Program. The main goal of this program was to develop a regional monitoring and surveillance program that could be used as a prototype in other bays and estuaries in the state. This was accomplished by setting up monitoring programs and special studies to evaluate various techniques and protocols used to sample water, sediment and tissue and to measure chemical contamination and toxicity. A second purpose of the program was to identify toxic hot spots in the Bay and in critical habitats (marshes, creeks and mudflats) around the Bay.

This was a multi-media program in which chemical contamination and toxicity was measured in water and sediments and bioaccumulation of contaminants was measured in tissues. The program was divided into two major monitoring programs two special study programs and a data management component. The two monitoring components were the Bay Monitoring Surveys and the Critical Habitat Investigations.

In the Bay Monitoring Surveys, chemistry and toxicity was measured in the water and sediments at stations ranging from the South Bay to the Sacramento and San Joaquin Rivers. The purposes of the Bay Monitoring Surveys were to: 1) monitor stations that in a longterm monitoring program would indicate spatial and temporal trends in toxicity and chemistry throughout the Estuary, 2) determine background for different basins in the Estuary and 3) determine if there was toxicity or high levels of contaminants at Bay stations.

Critical Habitat Investigations were conducted primarily to determine if there were high levels of contaminants or toxicity " hot spots" in the marshes, mudflats or creeks surrounding the Estuary. Toxicity was measured in the sediments. Chemical analyses was performed on sediment samples for a suite of metals and organics. Investigations of toxicity in the water column of critical habitats focused on stormwater runoff in two systems: 1) The Crandall Creek and Demonstration Urban Stormwater Treatment (DUST) marsh (DUST system) which retains stormwater in a freshwater marsh and 2) Arrowhead Marsh where stormwater is discharged into San Leandro Bay.

A special study was performed on a sediment gradient to: 1) determine which toxicity tests or type of toxicity tests (solid phase, elutriate, or pore water) could best distinguish between highly contaminated, moderately contaminated, and relatively uncontaminated sites, 2) evaluate the degree to which field replication increases the ability to distinguish between sites, 3) determine the effect of sample depth, 4) determine the relationship between toxicity and factors that may effect toxicity including the levels of chemical contaminants, total organic carbon, grain size, ammonia and sulfides and 5) determine the relationship between toxicity test results and benthic community analysis. Shallow and deep samples were collected at stations in Castro Cove, which has been historically

contaminated with effluent from an oil refinery. Five field replicates were collected at each station. Toxicity tests were performed on whole sediment, elutriates and porewater. Chemical analyses were performed on whole sediment and porewater. Samples for benthic community analysis were collected from these stations. In addition, for another program, biomarkers were measured in fish exposed to the sediment in the laboratory.

A bioaccumulation study was performed in order to: 1) describe the distribution of trace metals and organics in organisms in the San Francisco Estuary, 2) determine the differences in contaminants in organisms collected in wet and dry seasons, 3) determine the differences between mussels transplanted to shallow and deep water column depths at the same station, 4) determine the effect of depurating sediment from the guts of organisms on the contaminant levels in the whole bodies, 5) determine the optimum length of exposure for transplant organisms and 6) determine the differences in uptake in three species, each with their own salinity tolerances.

To manage the data for the entire RMP a common format was developed for all laboratories participating in the program. This allowed data to be more easily interpreted, analyzed and thoroughly checked for quality assurance. All laboratories in the program were provided with consistent formats with QA programs integrated into the data input system to insure accurate data entry. Data were generated at each of the laboratories and sent to EcoAnalysis for review.

For the sediment portion of the Bay Monitoring Surveys and Critical Habitat Investigations, stations were identified where sediment was toxic or showed elevated levels of metals or organics (see results). Sediment was monitored at 15 stations baywide during wet and dry seasons. For the Critical Habitat Investigations 32 sediment stations were monitored. Preliminary studies and data from the monitoring programs indicated that: 1) for the amphipod test <u>Eohaustaurius estuarius</u> seemed more sensitive than <u>Hyalella azteca</u> and <u>Rhepoxinius abronius</u>, even when a 28 day growth test was conducted with <u>Hyalella</u>, 2) the <u>Menidia</u> growth and survival test, using an elutriate, is not sensitive and should not be used in a monitoring program, 3) diver cores seemed to be the best way to collect undisturbed sediment samples, next best was the box core and 4) chemical analysis indicated that the technique used for homogenizing samples was adequate. Eohaustaurius seems to be an excellent organism for estuarine monitoring because it is tested in solid phase, is sensitive and can be tested at ambient salinity.

Only preliminary analyses have been completed on data from the gradient study but these analyses seem to indicate that: 1) toxicity was greater in deep samples, 2) this toxicity was not caused by high levels of ammonia or hydrogen sulfide, 3) toxicity tests were able to distinguish between stations, 4) field replicates were more variable than laboratory replicates, 5) three laboratory replicates may be sufficient to distinguish between stations, 6) in the bivalve larvae test, porewater samples were much more toxic than elutriate samples from the same sediment, 7) abnormality in the bivalve larvae test was highly correlated with abnormality in the sea urchin test, 8) abnormality in neither

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the urchin or bivalve test were correlated with the sea urchin fertilization test, and 9) sampling cores may be suitable containers for conducting amphipod tests.

For the water column portion of the Bay Monitoring surveys, monitoring of organic contaminants and toxicity was conducted at 15 and 12 stations, respectively, within the Estuary in June 1991 and April 1992. The results of the organic contaminant monitoring will be available in January 1993. Toxicity testing indicated statistically significant toxicity during the first sampling event at two stations. Each station had significant toxicity in one toxicity test. There was no significant toxicity in the second sampling event.

Investigations of toxicity in the water column of critical habitats detected toxicity in both the DUST system and Arrowhead Marsh following storm events. The DUST system was further investigated to study the fate of toxicity in the receiving waters following storm events of different intensity.

Bioaccumulation results indicated that: 1) bivalves at most of the stations within San Francisco Bay accumulated contaminant levels that were significantly higher than the controls collected at sites in more pristine locations outside of the Bay, 2) stations in the South Bay, especially Coyote Creek, were significantly higher than the Central or Northern Bay stations for DDT, PCBs, chlordane and PAHs, 3) Stations in the South and Central Bays were significantly higher than the North Bay for silver, 4) there were no significant differences in contaminant levels between wet and dry seasons, 5) there were no significant differences between mussels deployed near the surface and those deployed near the bottom, 6) a small number of metals at each station were significantly different between depurated and undepurated mussels, 7) an equilibrium appeared to be reached in mussels during the three and four month transplants for copper, mercury, lead, selenium, and chlordane, but no equilibrium was reached for silver, PCBs and possibly DDT after 120 days, 8) the patterns exhibited for DDTs, PCBs, and chlordanes for deploment time experiments were similar indicating a similar source of these compounds and 9) ovsters and mussels exhibited similar concentrations of chlordane, DDT and PCBs but PAHs differed and all metals differed greatly between the two species.

Although all of the data from the program has not been thoroughly analyzed, there are already several major accomplishments of the RMP: 1) a Baseline Monitoring Program has been established which will start in 1993, using the techniques and protocols evaluated during the RMP, to measure temporal and spatial trends in chemistry, toxicity and bioaccumulation throughout the San Francisco Estuary on an ongoing basis, 2) toxic hot spots were identified throughout the Bay and in critical habitat areas, 3) most of the marshes and mudflats in the Estuary were surveyed for chemical contamination and toxicity, 4) as the first step in setting up a statewide database, a format was generated for data and laboratories in the Bay Protection Program were trained to use these formats so that data could be easily checked for quality assurance, and integrated for statistical analysis, 5) data generated in this program can be combined with other data to generate Apparent Effects Threshold (AET) values for San Francisco Bay and 6) problems in identifying toxic hot spots and generating sediment quality criteria were identified and future studies were recommended to make the program more scientifically rigorous and provide more certainty in the final results (see Recommendations for Future Studies).

Besides the Regional Monitoring Program, studies are also underway supporting the development of a wasteload allocation for South San Francisco Bay. In the first phase, a predictive water quality model was developed based on available water quality and hydrodynamic data, using the EPA model WASP4. The second phase includes collection of time series of suspended sediment data to improve the ability to model transport of pollutants associated with sediments.

INTRODUCTION

The State Water Resources Control Board established the Bay Protection and Toxic Cleanup Program in April 1990 in order to implement Sections 13390-13396 of the California Water Code (Chapter 5, Division 7). One of the requirements under the Water Code is to develop an ongoing monitoring and surveillance program in bays and estuaries of the state. The primary goal of the Pilot Regional Monitoring Program (RMP) was to develop a monitoring and surveillance program for the San Francisco Estuary that could be used as a prototype for the rest of the state. In addition, this program was designed to identify toxic hot spots in the Bay and in marshes surrounding the Bay and to collect data that can be used to develop sediment quality objectives. In a second part of this report, the progress of wasteload allocation studies is described.

The RMP was primarily a monitoring program but special studies were also undertaken to determine the best methods and stations to use to monitor the Estuary. A multi-media approach was used in order to evaluate the ultimate fate and effects of contaminants in this complex estuarine system. Measurements of chemical contaminants, exposure of organisms to these contaminants and toxic effects of contaminants on organisms were all measured. In the water column, chemistry, toxicity and bioaccumulation were measured. In the sediments, chemistry, and toxicity in both whole sediment and in pore water were measured. In addition, biomarkers were measured in fish exposed in the laboratory to sediment samples synoptically collected for chemistry and toxicity.

Chemical measurements included a suite of metals and organics. At least three different toxicity tests were used to evaluate the effects of contaminants in both water and sediment. Bioaccumulation was measured in three different species of shellfish deployed in the water column. These data will not only be used for the immediate needs of the Bay Protection and Toxic Cleanup Program but also to determine background concentrations in the Estuary and to evaluate spatial and temporal trends in chemistry, bioaccumulation and toxicity.

Included in the program was a data management component. Under this part of the program, a common format was developed so that data could be more easily interpreted, analyzed and thoroughly checked for quality assurance. Although analysis is included in this report for each component of the program, a thorough statistical analysis integrating all portions of the program is currently being planned. All of the data previously mentioned are included in this report except for water column metals analysis and biomarker measurements, which were funded under another program and are on a different time schedule. For a more thorough description of methods and results consult the original reports.

PART I. REGIONAL MONITORING PROGRAM

The RMP included two major monitoring components: Bay Monitoring Surveys and Critical Habitat Investigations. The purposes of the Bay Monitoring Surveys were to: 1) monitor stations that in a longterm monitoring program would indicate spatial and temporal trends in toxicity and chemistry throughout the Estuary, 2) determine background for different basins in the Estuary and 3) determine if there was toxicity or high levels of contaminants at Bay stations. The Bay Monitoring Surveys included chemical and toxicity measurements in the water column and in the sediment. In the water column, metals were analyzed at 27 stations, organics at 14 stations and toxicity at 12 stations. Sediment chemistry and toxicity were measured at 15 stations. Bioaccumulation in shellfish was measured at 8 stations. Each group of stations was a subset of the 27 water column stations. However some sediment stations, although located in the same general vicinity as the water column stations, were changed due to the composition of the sediment. The stations ranged geographically from the South Bay to the Sacramento and San Joaquin Rivers.

Critical Habitat Investigations were conducted primarily to determine if there were high levels of contaminants or toxicity " hot spots" in the marshes and mudflats surrounding the Estuary. Sediment chemistry and toxicity were measured in most critical habitats around the Estuary, except for the South Bay which has been extensively monitored in the recent past. Water column toxicity was measured in several of these marshes, although most of the work relating to water column toxicity concentrated on the effect of runoff on the Demonstration Urban Stormwater Treatment (DUST) marsh in the South Bay and Arrowhead Marsh in San Leandro Bay.

Special studies on sediment toxicity and bioaccumulation were also conducted and are described in those sections below. In addition, a data management component was included so that all of the data would be consistent and could be integrated for quality assurance and statistical analysis.

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SEDIMENT

Study Design

Several preliminary studies were conducted for the sediment monitoring programs to determine: 1) the most appropriate amphipod species and endpoints to use in an estuary with a wide range of salinities and 2) a fine grain reference site. These studies are discussed in more detail in the Sediment Report. Tests exposed the amphipod Hyalella azteca to two freshwater reference sediments (Del Valle Reservoir and Lake Mendocino) and two contaminated sediments (Coyote Creek and Mayfield Slough). The duration of the tests were 14 and 28 days. Endpoints were 14 day survival and for the 28 day test three growth measurements. Echaustaurius estuarius was exposed to two estuarine reference (Brazil Beach in Tomales Bay, and Drakes Estero) and two estuarine contaminated sediments (Oakland Inner Harbor and Castro Cove). The duration of the test was 10 days and the endpoint was survival. In addition, both Hvalella and Echaustaurius were exposed to low salinity sediments (3-4 ppt) from Lake Mendocino, Blanco Drain, Mayfield Slough and Stockton Harbor to determine if <u>Eohaustaurius</u> could be used at low salinities. The results of these studies indicated that 1) the most appropriate amphipod test to use for the sediment monitoring programs was the 10 day amphipod test, using Eohaustaurius and measuring survival, 2) Eohaustaurius could be run in estuarine sediment down to 4 ppt but it had low survival in freshwater sediment that was salted up and 3) the best fine grain reference site out of those tested was Brazil Beach in Tomales Bay. However, after testing with Brazil Beach sediment showed toxicity in consecutive studies, including the first Critical Habitat survey, the site was changed to Marconi Cove in Tomales Bay. Still, throughout the study Marconi Cove sediments exhibited sporadic toxicity.

Additional samples were collected at Drakes Estero, Tomales Bay, Oakland Inner Harbor, Del Valle Reservoir, Mayfield Slough, Lake Mendocino and Coyote Creek for pore water analysis. Samples were taken with a sampling core. Pore water was extracted with syringes inserted at different depths. Pore water was analyzed for ammonia, nitrite plus nitrate, phosphate, dissolved oxygen, silicate, manganese, silver, iron and lead.

Bay Monitoring Surveys

Composite samples of the depositional layer were collected at 15 stations during the dry season (August 1991) and 14 during the wet season (April 1992) (Figure 1 and 2; Table 1 and 2). A fine grain sample could not be collected at Davis Point during the wet season. The depositional layer was defined by being brown in color, loosely compacted and lacking the smell of hydrogen sulfide. Because of the highly dynamic nature of the San Francisco Estuary, due to wind, tides and currents, sediment is constantly resuspended and redeposited. In this program we decided not to sample the top 2 cm, as is done in most sediment surveys, because we felt that in most areas that depth was constantly in a state of flux. To truly characterize a site we decided to sample a deeper layer. We sampled down to the interface where the existence of hydrogen sulfide was evident. The sulfide layer was not sampled because of possible confounding effects in toxicity test results.

Sediment was homogenized and analyzed for concentrations of metals and organics and for toxicity. Three toxicity tests were used in the dry weather run. These were the solid phase 10 day amphipod test using <u>Eohaustaurius</u> and two elutriate tests, the bivalve larvae test measuring development, and the <u>Menidia</u> beryllina test measuring growth and survival. The <u>Menidia</u> test was deleted from the wet weather run because after much testing it proved to be less sensitive than the other tests.

Critical Habitat Investigations

Composite samples of the depositional layer were collected at 32 stations located in marshes or mudflats around the Estuary (Figure 3; Table 3). Four separate surveys were conducted, each in a separate part of the Estuary. The sediment was analyzed for metals and organics and tested for toxicity using the same three toxicity tests used for the Bay Monitoring samples. However, several tests from freshwater stations were conducted using the 7 day test for <u>Daphnia magna</u>, which measures reproduction.

Gradient Study

The main purposes of the gradient study were to: 1) determine which toxicity tests or type of toxicity tests (solid phase, elutriate, or pore water) could best distinguish between highly contaminated, moderately contaminated, and relatively uncontaminated sites, 2) evaluate the degree to which field replication increases the ability to distinguish between sites, 3) determine the effect of sample depth, 4) determine the relationship between toxicity and factors that may effect toxicity including the levels of chemical contaminants, total organic carbon, grain size, ammonia and sulfides and 5) determine the relationship between toxicity test results and benthic community analysis.

Castro Cove was chosen as the study site. There were four station locations on a distance gradient away from an historic outfall from a petroleum refinery (Figure 4). Station locations were chosen based on historic data and a reconnaissance survey. At three of the four stations, including the most contaminated and the least contaminated, samples were taken at two depths (the depositional layer, referred to as shallow, and one foot, referred to as deep). The depositional layer at station GD23, the third station from the source, could not be sampled because of an intense infestation of tube worms at the station that was not there during the reconnaissance survey five weeks before. In addition, sediment from Carr Inlet in Puget Sound, Washington was also sampled at two depths and used as an

additional clean control for all of the toxicity tests, including pore water tests, in the study. A full chemical analysis was conducted on the sediment and pore water from Carr Inlet. At all seven stations (each depth was considered a separate station) five field replicates were collected. Each field replicate was a composite made up of at least five cores.

Twelve liters of sediment were collected for each field replicate and homogenized. Sediment was then separated for pore water or whole sediment/elutriate analysis. Whole sediment was analyzed for metals, organics, grain size and total organic carbon. The 10 day amphipod test, using <u>Eohaustaurius</u> was conducted with whole sediment. In addition, speckled sanddabs, <u>Citharichthys stigmaeus</u>, were exposed to this sediment for 60 days in the laboratory, after which a series of biomarkers were measured (these results will be reported in a separate report). The bivalve larvae development test was also conducted on an elutriate of the sediment using the same techniques that were used in the monitoring portion of the program.

Pore water was squeezed from the sediment and used for chemical analysis and toxicity tests. Pore water was analyzed for organics, metals, ammonia, sulfides, pH and dissolved oxygen. Pore water toxicity tests measured: 1) bivalve larval development, 2) sea urchin fertilization, development, cytologic and cytogenic effects, 3) nematode broodsize and mutagenic effect and 4) bacterial mutagenicity. In addition, a different pore water sampler was used to extract pore water at different depths. Concentrations of ammonia, hydrogen sulfide, dissolved oxygen, nitrite plus nitrate, silicate and manganese were measured in each sample.

In addition to chemical measurements, toxicity tests and biomarker measurements, samples were collected at each of the four station locations (GD10/20, GD11/12, GD23 and GD12/22) for benthic community analysis. Five field replicates were collected at each location.

A dilution experiment was also conducted on sediment from the gradient study to determine: 1) whether <u>Eohaustaurius</u> or <u>Rhepoxinius</u> was more sensitive to Castro Cove sediments and 2) if salinity effected toxicity to <u>Eohaustaurius</u>. The 10 day amphipod test was performed for both species on dilutions of Carr Inlet and a mix of GD10 and GD20 sediments (sediments from the most toxic site). Sediment was mixed to achieve six concentrations: 100, 80, 60, 40, 20, and 0 % . <u>Eohaustuarius</u> was tested at 10 and 25 ppt. <u>Rhepoxinius</u> was tested at 28 ppt.

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Methods

Sampling

Sediment was sampled by four different methods: 1) a modified Gray-Ohara box core, 2) diver operated cores, 3) diver operated scoops, and 4) hand held scoops. The method used depended on the environment being sampled. For the Bay Monitoring Surveys the box core was always used. For the Critical Habitat Investigations one of the other three methods was used depending on whether the sediment was exposed or underwater. Diver operated cores or scoops were used if the sediment was underwater. Hand held scoops were used if the tide was out and the sediment was not underwater. Diver operated scoops were considered the least effective in maintaining the integrity of the top layer of sediment. These were used for the first of four Critical Habitat Investigations but after this were only used for collecting reference sediment. For the Gradient Study, except for Carr Inlet sediment, only diver cores were used. Diver cores were the best method for maintaining the integrity of the top layer of sediment.

All sampling equipment was made of Teflon, polyethylene, or polycarbonate and was pre-cleaned and protectively packaged prior to entering the field. New sampling equipment, except for the sampler, was used at each station. All sampling equipment (excluding the sediment sampler) was cleaned by: a 2-day soak and wash in Micro brand detergent, 3 Milli-Q water rinses, 3 deionized water rinses, a 3-day soak in 10% HCL or HNO3, 3 Milli-Q water rinses, air dry, 3 petroleum ether rinses, and air dry. The sediment sampler was cleaned prior to entering the field by: a vigorous Micro brand detergent wash and scrub, a tapwater rinse, a 10% HCL rinse, and a petroleum ether rinse. To avoid crosscontamination, the sediment sampler was thoroughly cleaned between sampling at each station with a seawater rinse, scrubbing with Micro brand detergent, a seawater rinse, 1% HCl rinse and a methanol rinse.

The San Francisco Estuary is a highly dynamic system. Wind, currents and tides constantly resuspend and redeposit sediment. Organisms reburrow and are exposed to deeper sediment when it is resuspended. In most sediment studies, the top 2 cm of sediment is sampled. A decision was made in this study that the top 2 cm was not deep enough to characterize a site in this Estuary. Yet, at that time it was unclear how much effect ammonia and hydrogen sulfide would have on toxicity tests if we sampled the sulfide layer. Also, it was felt that the mobilization of sulfides could create artificial conditions by either extracting metals from the pore water during homogenization or releasing metals during bioassay exposure. For these reasons the decision was made to measure as deep as possible without sampling the sulfide layer. For all studies, except the deep samples in the Gradient Study, the depositional layer was sampled. This layer was characterized by being brown in color, relatively noncompacted and lacking the smell of hydrogen sulfide.

This layer ranged, depending on the site from 1 cm to 20 cm. The average depth for the Bay Monitoring Surveys was 10 cm.

Most samples were a composite of grabs. The amount of grabs varied from 1 to 20 depending on the depth of the depositional layer at that site, the greater the depth the fewer the grabs. The Bay Monitoring Surveys averaged 6 grabs. Sediment was placed in a tub and homogenized. It was then divided up for the various types of analyses conducted in the study.

For the Gradient Study whole sediment was sampled from the depositional layer and to a depth of one foot using a diver core. Pore water was collected from each sample. For every field replicate homogenized sediment was divided into sediment that would be used for whole sediment analysis and sediment that would be used for pore water analyses. The sediment to be used for pore water analyses was squeezed by a whole core squeezing method developed by Bender et al. (1987). This method utilizes mechanical force to squeeze pore water from interstitial spaces. The pore water was then divided for the various types of chemical analyses and toxicity tests.

A second method was used for sampling pore water at various depths. This method used a pore water squeezer to collect dissolved (<0.45um) pore water samples, in replicate, from depths of 0, 1, 2, 4, 6, 8, 10, 14, 18, 22 and 26 cm. Filtered water samples were drawn directly into acid-cleaned polyethylene (LDPE) syringes; the syringe contents were filtered through a 0.45um teflon syringe filter into an acid-cleaned LDPE bottle. The samples were then acidified with subboiling quartz distilled (2x) acids in a trace element clean laboratory. Samples collected by this technique at Drakes Estero, Tomales Bay, Oakland Inner Harbor, Del Valle Reservoir, Mayfield Slough, Lake Mendocino and Coyote Creek were analyzed for ammonia, nitrite plus nitrate, phosphate, dissolved oxygen, silicate, manganese, silver, iron and lead. Castro Cove samples were also collected by this method. These samples were analyzed for ammonia, hydrogen sulfide, dissolved oxygen, nitrite plus nitrate, silicate and manganese.

Organic Chemistry

Organic contaminants were measured in sediments and pore waters. Concentrations of PAHs, PCBs, and chlorinated pesticides in sediments were measured with established techniques. All sediment values are reported in dry weight. Concentrations of the same compounds in pore waters were measured with experimental techniques, due to the sensitivity limitations of the small volumes available.

Sediments were freeze-dried, mixed with kiln-fired sodium sulfate, and soxhletextracted with methylene chloride. The methylene chloride was then replaced by hexane. Lipids were removed by florisil-column chromatography. Sediment extract volumes were concentrated to approximately 1-4 ml and analyzed by both electron-capture gas chromatography (Varian 3400 GC with 8100 autosampler) and by GC/MS (Saturn II, also with 8100 autosampler).

Pore water samples in the gradient study, about 50 ml, were extracted three times with methylene chloride in a separatory funnel. The methylene chloride was reduced and replaced by hexane. Pore water extract volumes were reduced to 5-10 microliters before analysis by GC/ECD and GC/MS to achieve the necessary sensitivity.

For total organic carbon analysis, aliquots of freeze-dried or oven-dried sediments were prepared by agitation in 1N HCl, repeating the process until there was no further evolution of carbon dioxide. After centrifugation and decanting, sediments were rinsed with Milli-Q treated water, centrifuged again, and dried at 60 degrees. Subsequent steps in the analysis were undertaken by using established methods (Froelich, 1980; Hedges and Stern, 1983; and suggested procedures of the manufacturer). The methods are comparable to those of the recent validation study of the EPA method MARPCPN conducted by the Chesapeake Biological Laboratory of the University of Maryland.

Metals Chemistry

Two different methods were used to prepare whole sediment samples for chemical analysis. The first involved a near total (aqua regia) digestion consistent with the recommended procedures of the United States Environmental Protection Agency for sediment analyses (EPA, 1974). This procedure provides a conservative measure of trace element concentrations in sediment and can be used to compare concentrations with historical measurements and numerical sediment guidelines and standards. The second procedure extracted "biologically available" trace elements by using a dilute acid (0.5 N HCl) extraction procedure (Flegal et al., 1981). This procedure was developed for the State Water Resources Control Board to monitor trace element concentrations in marine sediments and wastewater sludge. Research has indicated that this extraction method is consistent with the extraction for acid volatile sulfides (Ditoro, 1990).

The first method of digestion was used to prepare samples that were analyzed for aluminum, chromium, cobalt, copper, iron, lead, magnesium, manganese, nickel, phosphorus, silver, vanadium and zinc. The second method was used to prepare samples that were analyzed for aluminum, cadmium, iron, magnesium, manganese, phosphorous and vanadium. Elemental concentrations were measured by Graphite furnace atomic absorption spectrometry (GFAAS), flame atomic absorption spectrometry (AAS), and/or inductively coupled plasma atomic emission spectrometry (ICP-AES). All samples were measured in duplicate.

Total arsenic, mercury, and selenium were analyzed by American Environmental Corporation. Methods used for these metals were: arsenic (EPA Method 7061), mercury (EPA Method 7471) and selenium (EPA Method 7741). The instrument used for detection was in all cases a GFAAS. Tributyltin was analyzed by Toxscan, Incorporated using a gas chromatograph with a flame photometric detector. All metals values for the project are reported in dry weight.

Pore water samples were concentrated with an APDC/DDC organic extraction, which was based on the procedures described by Bruland et al. (1985). This method was necessary because of the small volumes of pore water that could be extracted. The total dissolved (< 0.45um) concentrations of pore water samples were measured with microtechniques based on procedures used to measure total dissolved trace element concentrations in surface waters in the San Francisco estuary (Flegal et al., 1991). Therefore, this set of data may be compared to other measurements of trace element concentrations in surface waters. Pore water samples were analyzed for cadmium, cobalt, copper, iron, lead, manganese, silver and zinc. Concentrations were measured by GFAAS and by ICP-AES.

Additional pore water measurements collected at various depths and analyzed for dissolved ammonia, phosphate, silicate, and nitrate plus nitrite used the procedures described by Gieskes and Peretsman (1986).

Toxicity Tests

For the first Bay Monitoring Survey and the Critical Habitat Investigations three sediment toxicity tests were performed: the amphipod, bivalve larvae and Menidia test. The 10 day amphipod test measuring survival was performed on whole sediment (ASTM, 1992). The amphipod <u>Eohaustaurius estuarius</u> was used so that all tests could be conducted at ambient salinity. <u>Rhepoxinius abronius</u> was tested at a subset of stations to compare the sensitivity of the two species. Control (home) sediment was used in all tests. In addition, fine grain sediment from Tomales Bay was run as a reference sediment.

Elutriate tests were performed with bivalve larvae measuring development and with the inland silverside, <u>Menidia beryllina</u>, measuring growth and survival. The <u>Menidia</u> test was used because 1) it has been shown to be sensitive in water column tests, 2) we wanted to determine possible toxic effects on fish and 3) <u>Menidia</u> has a broad salinity tolerance. Elutriates were prepared by mixing sediment with dilution water in a sediment-to-water ratio of 1:4 by volume (EPA/ACOE, 1991) and shaken vigorously for 10 seconds (Tetra Tech, 1986). The one liter mixture was allowed to settle for 24 hours and then carefully decanted

into a one liter Erlenmeyer flask.

Toxicity tests with bivalve larvae were conducted following ASTM guidelines (ASTM, 1991) with adaptations for elutriate testing given in the Puget Sound Protocols (Tetra Tech, 1986). Pacific oysters, <u>Crasssostrea gigas</u>, were used in all tests except the third marsh run, which was run in December when spawnable oysters were unavailable. At that time, oysters were replaced by bay mussels, <u>Mytilus edulis</u>. Toxicity tests measuring growth and survival in <u>Menidia beryllina</u> followed the EPA protocol (Weber et al., 1988). A subset of stations were also tested measuring growth and survival in the topsmelt <u>Atherinops affinis</u> (Anderson et al., 1990). Both tests are growth and survival tests in which young larvae are exposed to test solution for 7 days. However, <u>Atherinops</u> is a local species and <u>Menidia</u> is imported. For the second Bay Monitoring Run, which was the last monitoring run to be conducted, larval fish tests were dropped from the tests because they were insensitive in the previous tests. Several tests from freshwater stations were conducted using the 7 day test for <u>Daphnia magna</u> measuring reproduction described by Nebeker et al. (1988).

In the gradient study both the amphipod test using <u>Eohaustaurius</u> and the elutriate bivalve larvae test were performed on test sediment. Protocols were the same as described above. In addition, other toxicity tests were performed on whole sediment and on pore water. The amphipod test using <u>Eohaustaurius</u> was performed within cores used to collect sediment in the field. At three stations in the gradient study, five separate core tubes (10 cm diameter) were taken in to the field and used to sample sediment at each field replicate (5 per station) to a depth of 10 cm. These cores were capped, top and bottom, in the field with 10 cm of overlying water which was retained throughout transport. The actual collection cores were then used as the test containers.

Several toxicity tests were performed in pore water extracted from the sediment. The bivalve larvae test was performed using the same methods as in the elutriate tests (ASTM, 1991). The echinoderm fertilization test was conducted according to methods described by Anderson et al. (1990). Development scoring, cytogenic analysis and cytologic analysis were all conducted on the same samples. Cytogenic and cytologic evaluations were conducted according to the methods of Hose and Puffer (1983). The echinoderm, <u>Strongylocentrotus purpuratus</u> was used for all echinoderm tests. A bacterial mutagenicity test was conducted on <u>Salmonella</u> according to the methods of Kado et al., (1983, 1986). This assay is a simple modification of the <u>Salmonella</u>/microsome test of Ames et al. (1975). The nematode (<u>C. elegans</u>) broodsize and mutagenicity assay was performed using methods of Rosenbluth et al. (1983) and Anderson et al. (submitted MS). This test assesses alterations in broodsize in the F1 and F2 generations as well as mutations in a specific target region of the genome.

All toxicity tests had five laboratory replicates except in the gradient study. After statistically analyzing data from the previous studies, we determined that laboratory variability was so low that using three laboratory replicates instead of five did not effect the ability to distinguish between stations. Field variability was expected to be much greater than laboratory variability, therefore, five field replicates were collected at each station. Positive reference toxicants were used for all tests. Dissolved oxygen, pH, temperature and ammonia were monitored in the tests. Grain size was also measured to evaluate the amphipod tests. In the gradient study sulfides were also measured.

Benthic Analysis

For the gradient study five replicate cores (.018m2/core) were collected from each of the four main gradient stations (GD10/20, GD11/21, GD23 and GD12/22). Cores were immediately screened through .5mm mesh, and fixed in 10% formalin. Samples were transferred four days later into 70% isopropyl alcohol, sorted, identified to the lowest possible taxon, and counted under a dissecting microscope.

Results/Discussion

A thorough, integrated, statistical analysis of the sediment results has not been completed. Although toxicity test results are complete, all of the chemical analyses are not. Therefore, toxicity test results are described, but the results for chemical analysis and the integration of chemical analysis with toxicity test results is considered preliminary. The results for each study and each type of analysis are discussed in that section.

Bay Monitoring

Organic Chemistry

For sediment samples from the Bay Monitoring surveys, PAH concentrations ranged from 81 to 6300 ng/g with a median value of 810 ng/g. A review of PAH residue data previously obtained from San Francisco Bay by the Status and Trends program of NOAA (NOAA, 1988) provided a mean (arithmetic) of about 2.5 ppm dry weight.

In almost all samples, the combustion profile dominated the petroleum profile. In only one of the Dumbarton Bridge samples and one of the Redwood creek samples did most of the PAHs derive from petroleum rather than combustion sources. Combustion residues derive primarily from the atmosphere (the principal local source is probably automobile exhaust) and surface runoff during rainstorms. PAH residues that derive from petroleum and petroleum products are generally from spills, those released into disposal systems and as components of surface runoff.

Metals Chemistry

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In general, distributions of the chemicals measured could be classified into two principal groups. These were 1) the elements which show some anthropogenic enrichment in some locations (Ag, Cd, Cu, Pb, and Zn) and 2) those with less pronounced perturbations (Co, Cr, Ni, and V). This was true for both Bay and Critical Habitat surveys.

All trace elements, except V, showed a significant difference with season at several stations. However, when stations were pooled there was no significant difference between seasons.

In order to evaluate the potential for toxicity based on sediment chemistry, trace element concentrations were compared to concentrations which caused toxic effects in previous studies and the enrichment of the element relative to its natural abundance. The Effects Range-Low (ER-L) and Effects Range-Median (ER-M) values of Long and Morgan (1990) are presented to provide a basis for evaluating the potential adverse effects of contamination. The average continental crustal abundance (CA) of each element (Lof, 1987) has been included to provide a measure of the enrichment or depletion of each element relative to its average natural concentration. Figures 5-12 show concentrations of trace elements (Ag, Cd, Cr, Cu, Ni, Pb, and Zn) measured in the Bay Monitoring runs along with ER-L, ER-M and CA values. Table 4 illustrates the mean, standard deviation, median, maximum and minimum concentrations for trace elements in the Bay Monitoring surveys.

The ER-L value of 35 ppm lead was exceeded by stations BB31 (Oyster Point), BD20 (Petaluma River), and BD51 and BD52 (Napa River) during both wet and dry monitoring runs. Lead concentrations in sediments at BC50 (Stauffer) exceeded the ER-L during the wet weather run. BC10 (Yerba Buena Island), BC30 (Richardson Bay), BD40 (Davis Point), BD30 (Point Pinole), BF10 (Pacheco Creek) and BF20 (Grizzly Bay) exceeded the ER-L during the dry weather sampling. The highest concentration of lead in the bay sediments was at Davis Point (BD40), where the lead concentration was equal to the ER-M of 110 ppm.

Most stations which exceeded the ER-L values for lead also exceeded the ER-L values for zinc. This is reflected by the highly significant correlation between lead and zinc concentrations. Sediment concentrations of zinc and

lead in San Francisco Bay are greater than their average crustal abundances.

Only Davis Point had silver concentrations which exceeded its ER-L value of 1 ppm. But, all stations sampled were enriched with respect to the average crustal abundance of silver, some as much as ten-fold.

The only station that exceeded the ER-L value for copper was a boat yard in Richardson Bay (BC30). Copper concentrations were four times higher than samples collected outside of the boat yard (BC31) during wet weather. These concentrations appear to be due to contamination of sediments due to boat yard activities.

None of the Bay sediments exceeded the ERL for cadmium (5 ppm). That value is 50 times greater than the average crustal abundance of cadmium. The ERL for chromium was exceeded at many stations and the ER-M for nickel was exceeded in sediments at every station. The ER-M for nickel is much higher than its average crustal abundance.

The chemical concentrations of replicate samples collected from each homogenate were highly precise. This indicates that the homogenization of composite samples at each station was successful.

Toxicity Tests

<u>Amphipod tests</u> - Due to sporadic toxicity in the fine grain reference sediment, it was difficult to determine what actually constituted a toxic response. In the dry weather Bay Monitoring survey the reference site was not significantly different than the controls but in the wet weather survey it was. Contractors statistically compared test sediment to both home and reference sediment (Table 5). This approach makes sense except that some of the response of the organisms in test sediment, when statistically compared to home sediment due to the lack of an adequate reference sediment, may be due to fine grain size rather than toxicity. In this summary, since these data are being used to identify toxic hot spots, a consistent 25% effect level compared to home sediment will be used to identify stations that were toxic. This issue is more thoroughly discussed in the Recommendations for Future Studies section.

In the August 1991 dry weather Bay Monitoring survey, stations that showed a 25% reduction in survival compared to home sediment included:

BA20 - Extreme South Bay

BA30 - Dumbarton Bridge

BA40 - Redwood Creek

BB31 - Oyster Point Marina

BC30 - Richardson Bay, Anderson's Boat Yard

BD20 - Petaluma River, Lt. 18

BD51 - Napa River, West Bank, Mare Island

BF10 - Pacheco Creek

BF20 - Grizzly Bay

These stations were the same stations that had significantly less survival than both the home and reference sediment in statistical tests.

In the April wet weather Bay Monitoring survey stations showing a 25% reduction compared to home sediment included:

BA20 - Extreme South Bay

BA30 - Dumbarton Bridge

BA40 - Redwood Creek

BB31 - Oyster Point Marina

BC31 - Richardson Bay, outside channel

BC50 - Staufer

BD20 - Petaluma River, Lt. 18

BD52 - Napa River, East Bank, Vallejo

BF20 - Grizzly Bay

BG21 - Sacramento River in Sherman Lake

These stations and BF10 (Pacheco Creek) and BC10 (Yerba Buena Island) had significantly less survival than home sediment in statistical tests.

In addition, <u>Rhepoxinius</u> was exposed to sediment from BA20, BA40, BB30, BC30, BC50 and BD40 for the dry weather run. Using the same method that was used for <u>Eohaustaurius</u> to determine toxicity, only BA20, Extreme South Bay, was toxic. This was also the only station with significantly reduced survival compared with both the reference site and controls (Table 6).

Grain size was significantly correlated to survival for <u>Eohaustaurius</u> but not for <u>Rhepoxinius</u>. However, grain size may not be all that is directly effecting the amphipods. Sediment with larger grain size probably also has a lower concentration of contaminants. Ammonia did not exceed 6 ppm in any test, therefore, it is not expected that ammonia contributed to toxicity.

Differences in survival were not significant for tests run with sediments collected in the wet weather versus those collected in the dry weather run. This is consistent with the results of chemical analysis, which showed no significant differences in trace metal concentrations between pooled wet and dry weather samples.

<u>Daphnia Test</u> - The <u>Daphnia</u> test was run on samples from stations BG21 and BG31. There was no significant difference in reproduction when compared to sediment from Lake Mendocino, the freshwater reference site (Table 7).

<u>Bivalve Larvae Tests</u> - For the August 1991 dry weather run, BA40 (Redwood Creek) and BF 10 (Pacheco Creek) were significantly different than seawater controls. Reference sediments were not tested at the same time as test sediments for this run. For the April 1992 wet weather run BD20 (Petaluma River,Lt. 18), BG21 (Sacramento river at Sherman Lake) and BG32 (San Joaquin River at Kimball Island) were significantly different than both the seawater control and the reference sediment. See Table 8 for the means and standard deviations at each station.

<u>Menidia Tests</u> - The <u>Menidia</u> test was only performed on sediments collected in the August 1991 monitoring run. There were no samples that were significantly different than either the seawater controls or the reference sediment (Table 8b). This test was dropped from the April 1992 monitoring run because of its lack of sensitivity.

Critical Habitat Investigations

Organic Chemistry

In the sediment samples from this part of the study PAH concentrations ranged from 35 to 9,100 ng/g, with a median of 1,200. Higher concentrations in these areas may reflect both proximity to runoff input sources and higher organic carbon/silt levels.

Metals Chemistry

Figures 13-21 show concentrations of trace elements (Ag, Cd, Cr, Cu, Ni, Pb, and Zn) measured in the Critical Habitat surveys along with ER-L, ER-M and CA values. By far the highest metals concentrations were found at Peyton Slough (MF22). The concentration of copper in this sample exceeded the TTLC (2.5 g/kg). The concentration of zinc (4.39 g/kg) approached the TTLC (5.0 g/kg). The concentration of cadmium was the highest found in the entire study (19.51 mg/kg). All of these concentrations far exceed the ER-M for these metals. Yet, there were no toxic effects in the bivalve larvae test, a test that is particularly sensitive to metals. In the amphipod test, although there was significant toxicity, survival was 60%. This illustrates the importance of being able to estimate the bioavailable fraction of metals. Additional analysis is being conducted on this sample. Historically the site was used for copper slag. See the Recommendations section for a further discussion of this issue.

Sediments from San Leandro Bay (MB11) and Cordinices Creek were above the ER-M levels for lead (110 ppm) and zinc (260 ppm), as well as the ER-L for copper (70 ppm). Sediments from Cordinices Creek also exceeded the ER-L value for silver (1 ppm). Silva Island Marsh (MC61) exceeded the ER-M value for lead and the ER-L value for zinc. Emeryville Marsh exceeded the ER-M value for zinc and the ER-L value for lead. All of these samples were collected near urban storm drains.

In Tomales Bay, sediment concentrations exceeded the ER-M value for chromium (80ppm) and the ER-L value for nickel (50 ppm). In fact, the chromium and nickel concentrations of sediments in Tomales Bay were the highest in the entire data set. Yet, chromium concentrations were below the average crustal abundance. Serpentine deposits in the area may account for elevated levels of chromium and nickel, although almost all sediments sampled in the RMP exceeded the ER-M for nickel (Fig.3-A-4 and Fig.3-B-4). The ER-M for nickel is well below its average crustal abundance.

Toxicity Tests

<u>Amphipod Tests</u> - In two out of the four marsh surveys, survival in the reference sediment was poor. Therefore, the same method for reporting toxicity as was used in the Bay Monitoring runs will be used for the Critical Habitat Surveys. Table 9 shows mean survival and statistical analysis for each station, comparing results from each station to both the home and reference sediment.

Stations showing a 25% reduction in survival compared to home sediment included:

MF10 - Boynton Slough C1

MF11 - Boynton Slough C3

MF12 - Boynton Slough C4

MF20 - Hill Slough, below bridge

MF21 - Hill Slough, above bridge

MF22 - Peyton Slough, back end of slough

MD31 - Tolay Creek mouth

MD32 - Napa Slough at bridge

MD33 - Sonoma Creek at Tubbs

MD34 - Sonoma Creek at bridge

MC30 - Emeryville Marsh at EBMUD storm drain

MC50 - Corte Madera Marsh S of Industrial Rd.

MD20 - Gallinas Cr. at John F. McInnis County Park

MD21 - Novato Creek at Lock

Regression analysis indicated that the percent sand of samples from critical habitat sediments accounted for little of the variability in survival for the <u>Eohaustaurius</u> tests.

<u>Daphnia Test</u> - The <u>Daphnia</u> test was run on stations MF10 (Boynton Slough C1), MF11 (Boynton Slough C3), MF20 (Hill Slough, below bridge) and MF21 (Hill Slough, above bridge). The only station that showed a significant decrease compared to reference sediment, which had high reproduction, was MF20. The <u>Daphnia</u> test was less sensitive than the amphipod test in detecting toxicity.

<u>Bivalve Larvae. Menidia and Atherinops Tests</u> - Results for these three tests are summarized in Table 10a and 10b. The reference sediment was toxic in two out of the four marsh runs for the bivalve larvae test. These were the same samples that were toxic in the amphipod test. Since the runs where the reference site was toxic were the only runs where test sample toxicity was observed, only samples that were significantly more toxic than seawater controls will be listed. These stations for the bivalve test are:

MF10 - Boynton Slough, C1 MF11 - Boynton Slough, C3 MF12 - Boynton Slough, C4 MF13 - Chadbourne Slough, CR2 MF23 - Peyton Slough, mouth of slough MD10 - Miller Creek at Las Gallinas discharge MD11 - Miller Creek upstream from discharge at fence MC61 - Silva Island Marsh at Seminary Dr. storm drain

MF20 and MF21 were not tested.

The only sample that was toxic to <u>Menidia</u>, besides the Lake Mendocino reference sediment, was MC61 (Silva Island Marsh at Seminary Dr. storm drain). <u>Atherinops</u> was used to test for toxicity on the 8 Suisun Marsh stations. Only MF21 (Hill Slough, above bridge) was toxic to this species. Due to the general insensitivity of the elutriate fish tests they were dropped from the final Bay Monitoring survey.

Gradient Study

Organic Chemistry

The highest concentrations of PAHs in the entire Regional Monitoring Program were measured in Castro Cove. At the station closest to the source, PAH concentrations were 21 and 8.4 ppm, geometric means, in deep and shallow sediments, respectively. At the intermediate stations the geometric mean total PAHs in deeper sediments were 1.1 and 0.9 ppm, and at the Point Pinole Pilings (PPP) station, the station farthest from the source, concentrations were 0.6 and 0.9 in deep and shallow sediments respectively. With the exception of PPP, the PAHs in the Castro Cove stations derived principally from petroleum, and were associated with complex mixtures of other petroleum hydrocarbons. The "fingerprint" of PAH compounds in the surface sediments at PPP was the typical combustion profile characteristic of most areas of San Francisco Bay.

In the gradient study, contaminant variables were highly and significantly correlated with each other, and with related variables such as the organic carbon and nitrogen content. Thus mortality in the amphipod test was significantly correlated with all of the contaminant variables measured. Development of oyster larvae in the elutriates, however, was most significantly associated with the organic carbon and nitrogen content of the sediments, rather than with the contaminants, suggesting that variables such as small particulate material in the elutriate might be contributing to the measured effects.

Metals Chemistry

Concentrations of trace metals in pore waters collected for the gradient are displayed in Table 11. Concentrations of trace metals in sediments are displayed in Table 12. Comparisons of bulk aqua regia extractable concentrations of trace metals in sediments were poor predictors of pore water concentrations. Dilute acid leach extractions, which are not yet completed, may provide a better measurement of the "labile" concentration of particulate metals.

Toxicity Tests

<u>Amphipod Tests</u> - Three types of amphipod tests were conducted in the gradient study that were described in the Study Design. They were: 1) the standard amphipod test using <u>Eohaustaurius</u>, 2) a test exposing <u>Eohaustaurius</u> to sediment in cores that were used for sediment collection and 3) an experiment with dilutions of Castro Cove and Carr Inlet sediment using <u>Rhepoxinius</u> and <u>Eohaustaurius</u> at two different salinities.

For the standard amphipod toxicity test, results yield evidence of a toxicity gradient related to chemical concentrations. Toxicity and chemistry did not show a distance gradient except that the least toxicity was observed at the station farthest from the source and the greatest toxicity was observed closest to the source. In the middle stations hydrodynamics and possibly dredging may have mixed sediments in a way that the toxicity and chemistry of the two middle stations were reversed. Trace metal assays for chromium, zinc, copper, nickel, lead, cadmium, and silver were highest in the station closest to the source. Conversely, the lowest trace metal concentrations were in the deep core farthest from the source, the only station to not differ significantly from the controls. In general, the ranking of toxicity from most toxic to least toxic for this test was: GD10 deep, GD20 shallow (both of these station were closet to the outfall), GD23, GD12 (PPP shallow), GD11 and GD21 (which showed no difference between the shallow and deep at the same station), and GD22 (PPP deep). Statistical tests have not yet been done to determine if stations differed significantly from each other.

All stations except PPP (deep) differed significantly from the control. Variance among field replicates was low. Regression analysis indicated that toxicity was significantly correlated with (most metals), PAHs, total organic carbon (TOC) and grain size. Particle size of the sediments is critical in determining toxicity not only because of its mechanical effect on burrowing ability but also effects on contaminant and TOC concentration and bioavailability.

The amphipod tests using sampling cores showed the same trend although they seemed to show less sensitivity. Amphipod mortality was 5% in samples of home sediment tested in core tubes. These results from negative controls indicate the suitability of the core tubes as test containers. Intact cores from PPPP, the gradient reference site, showed 29% mortality, while the two Castro Cove stations tested (GD10/20 and GD11/21), with this method, had 50% and 54% mortality respectively.

The range of concentrations tested for Castro Cove sediment (100%, 80%, 60%, 40%, 20% and 0%) was too broad to establish a strong dose response. Over 80% mortality occurred in the first dilution (20% Castro Cove). However, salinity did not have an impact on the survival of <u>Eohaustaurius</u>. Survival was almost identical at salinities of 10 and 25 ppt. <u>Rhepoxinius</u> did not test well and exhibited unsatisfactory survival (56%) in the Carr Inlet control.

<u>Bivalve Larvae Test (elutriate and pore water)</u> - There was a significant difference in toxicity between the pore water and elutriate samples in the deep cores (P=0.0001) and a notable difference in toxicity between the pore water and elutriate samples in the shallow layer samples (Table 13). Pore water samples detected significant toxicity at 4 of the 5 Castro Cove stations.

By comparison, elutriate samples found only one station (GD20) to be significantly more toxic than the reference station (PPP), and this was only in the deep station. These results suggest that pore water tests were more sensitive than elutriates in detecting sediment toxicity, consistent with the fact that elutriates are more dilute fractions of the sediment than pore waters.

Deep cores were more toxic than shallow cores, perhaps indicating that recent deposits are less contaminated with substances toxic to the test organisms. Using the results from deep cores, both elutriate and pore water tests were able to distinguish a statistical difference between stations.

For these tests, variability among field replicates was greater than variability among laboratory replicates. Perhaps more effort should go in to field replication than laboratory replication. For these tests only three laboratory replicates were used.

Oyster pore water toxicity test results were not correlated with pore water ammonia concentrations. In the beginning of the study there was concern about the possible effects of ammonia on pore water toxicity test results, especially in the deep cores. Neither ammonia or hydrogen sulfide seemed to be a problem in the pore water tests.

Oyster pore water toxicity test results were significantly correlated with the results of amphipod solid phase tests, and very significantly correlated with results of sea urchin embryo development in pore waters. They were not correlated with sea urchin fertilization test results.

Toxicity results from elutriate samples, but not pore water samples, were significantly correlated with grain size. There may be a physical effect of fine grain particles in the elutriate.

<u>Sea urchin tests (pore water)</u> - No differences in fertilization success were observed when comparing deep core samples, however, the two shallow layer samples tested (GD10 and GD12-PPP) were both significantly more toxic than the deep samples taken at the same station. The Carr Inlet control was not used in any of the statistical tests because high toxicity was observed in the full core sample. This was also observed in the bivalve larvae test.

The responses observed with the sea urchin development assay contrast with those observed using the fertilization assay. For the development assay, highly significant differences in toxicity of full core samples were observed among stations. When the means of the field replicates for GD20, GD21 and GD23 were compared to the mean of the field replicates for PPP all stations were significantly more toxic than PPP. For this test the shallow layer samples were not significantly more toxic than the deep samples, in fact, one deep sample was more toxic than the shallow.

Additional data were obtained by scoring 25% and 50% dilutions of one laboratory replicate for each field replicate for the deep core samples. Results showed that their order of toxicity from most toxic to least, based on EC50 values and 95% confidence intervals was: 1) GD23, 2) GD20 and GD21 and 3) GD22 - PPP the least toxic. Field variability was also characterized using this method. For the deep core samples, coefficients of variation ranged from 15% for GD20 to 50% for GD22 - PPP. However, the PPP value is especially high because of one anomalous field replicate.

It should be noted that an unusual response was observed in all of the samples in which development was scored: the hatching of gastrula had not occurred normally. For the purposes of this study only, they were considered normal embryos. Still, the sea urchin development data demonstrated excellent concordance with the oyster development data. For both tests, GD20, GD21 and GD23 samples elicited almost 100% abnormal embryos: whereas PPP only elicited moderate toxicity. For all echinoderm studies, as with other pore water studies, water quality parameters were in acceptable ranges, including measurements of ammonia.

Sea urchin cytology and cytogenetic data are still preliminary. However, they indicate that the Castro Cove gradient stations did not exhibit high genotoxic potential but that cytologic aberrations may reflect the potential for cytotoxic effects at the site.

<u>Bacterial Mutagenesis (pore water)</u> - Of the samples tested there were two that elicited mutagenic activity. Both of the samples that tested positive were from the GD23 deep core group of extracts.

<u>Nematode Broodsize and Mutagenesis (pore water)</u> - Results of this test indicate that some pore water samples may be slightly toxic to the nematode but that the substances causing toxicity were not highly mutagenic.

Benthic Community Analysis

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All stations were moderately similar in species richness (number of taxa), with the highest diversity at station GD23 (29 taxa) and the lowest at the station closest to the source (16 taxa). Faunal assemblages were similar for

all stations, with one or two species dominant in each of the three major taxonomic groups; crustaceans, polycheates, and bivalves. Crustaceans were by far the numerically most important group for all stations. These samples were not collected synoptically with the other samples but were collected two weeks later.

Recommendations For Future Studies

During the performance of the sediment studies and the analysis of data it became apparent that there were several areas that needed further study in order truly identify a toxic hot spot and to develop meaningful sediment quality criteria:

1. In this study and in others conducted by the Regional Board several sites with no or few sources of contamination and low chemical concentrations exhibited high levels of effects in toxicity tests. This occurred in both the amphipod and the bivalve larvae tests. Sites where this occurred were Tomales Bay, Drakes Estero and Bolinas Lagoon. In order to truly identify a toxic hot spot the cause of the effects (mortality or abnormality) in these areas should be ascertained. This could be done with sediment Toxicity Identification Evaluations and positive interference studies.

2. A fine grain reference site needs to be identified in order to have a "clean" sample with the same characteristics (grain size, TOC) as the test sediments for statistical comparison. Investigators in other areas of the country are also finding significant effects at "clean" reference sites. Although finding a reference site that does not produce significant effects is the preferable approach, if this is not possible, a different approach needs to be considered by the Bay Protection Program in defining what actually constitutes a significant effect. This is particularly important for the amphipod test.

Another approach may be to use the reference sediment for comparison, when there is no significant difference between home sediment and reference sediment. When there is a difference, a 25% decrease in survival between home sediment and test sediment could be used. Fine grain sediment usually does not account for more than 10-15% mortality (personal communication with Ted DeWitt). Unfortunately, this provides an inconsistent evaluation of what constitutes "toxicity". Other possible options may be to use an alternative methods based on quantitatively determining the effect of fine grain sediment on the species of amphipods being used in tests, pooling reference site data or making a decision considering the impact of fine grain sediment and potential environmental impact. 3. Methods for determining the bioavailable fraction of metals in a sample should be evaluated. This issue became particularly apparent in the Peyton Slough sediment sample. In this sample copper exceeded hazardous waste levels and zinc approached those levels and yet there was no toxicity in the bivalve larvae test and 60% survival in the amphipod test. Digestion for total metals was used for these measurements. Since acid volatile sulfides have only been found to be useful for cadmium, other methods such as a weak acid leach or just measuring the fine grain portion of the sediment should be tested. Toxicity tests should be conducted and metal concentrations should be measured by these three methods plus total metals concentrations.

4. Several areas dealing with sampling need to be better addressed. Depth of sample should be better evaluated. The sample depth may be station or area specific. It should be based on the depth that contaminants in sediment may be bioavailable. The artifacts of homogenizing sediment that contain a high sulfide layer should also be considered. Power analyses should also be conducted to determine the optimal amount of grabs in a composite sample. In addition, statistical analyses should be performed to determine if more effort should be going in to field replication and less in to laboratory replication.

BIOACCUMULATION

Study Design

The purposes of the bioaccumulation study were to 1) describe the distribution of trace metals and organics in organisms in the San Francisco Estuary, 2) determine the differences in contaminants in organisms collected in wet and dry seasons, 3) determine the differences between mussels transplanted to shallow and deep water column depths at the same station, 4) determine the effect of depurating sediment from the guts of organisms on the contaminant levels in the whole bodies, 5) determine the optimum length of exposure for transplant organisms and 6) determine the differences in uptake in three species, each with their own salinity tolerances.

Shellfish were deployed at eight stations, two in the Sacramento - San Joaquin River Delta, two in San Pablo Bay, one in Central San Francisco Bay and three in the South Bay (Figure 22). The project was conducted in two phases; once during the dry season (initiated on 4/1/91) and once during the wet season (initiated on 12/16/91). The species tested was mostly <u>Mytilus californianus</u>. Freshwater clams (<u>Corbicula sp.</u>) and oysters (<u>Crassostrea gigas</u>) were also deployed at more freshwater stations because of their tolerance to low salinity waters. However, during one season clams deployed in the Sacramento River were lost and during the other season clams deployed in the San Joaquin River were lost. This limited the amount of data for <u>Corbicula</u>.

At several stations uptake rates were compared between oysters and mussels. <u>Mytilus</u> was transplanted for 30, 60, 90 and 120 days. All other shellfish were transplanted for 90 days. At two sites during the dry season and three sites during the wet season the effect of depuration on mussels was tested by depurating half the organisms. The effect of depth of deployment was tested by deploying mussels at two depths, surface and one meter off the bottom, at three stations. Chemical analysis of tissue samples included analysis for metals, PCBs, DDTs and PAHs.

Methods

Experimental mussels were collected with stainless steel knives at Bodega Head, California, and were handled with polyethylene gloved hands. Phase I (wet weather) oysters were collected at Drakes Bay, California by Johnsons Oyster Company. Phase II (dry weather) oysters were collected by Ted Keiper of the Mad River Oyster Company in Humboldt Bay, California. Control samples were taken at the time of collection to serve as baseline indicators. Control samples were frozen within 12 hours of collection and stored for later analysis. In addition, field blanks were also collected and handled in an identical manner to transplanted specimens but were not deployed. Transplanted bivalves were placed in mesh bags and transported in coolers to transplant sites. After exposures of 30, 60, 90 or 120 days, the samples were collected and frozen at -10 C until

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dissection. Samples were thawed and dissected in a filtered air positive-pressure room with stainless steel scalpels that had been tested for contamination (Stephenson et al. 1979). Detailed methodologies are found in Phillips (1988). All samples were homogenized with a Brinkman Tissue Homogenizer equipped with a titanium shaft that was cleaned with detergent, methanol and petroleum ether before each homogenization.

Levels of selenium, arsenic, silver, chromium, and lead were determined by GFAAS. Copper, manganese, cadmium, and zinc were determined by FAAS. Dry weights were used in the plots and statistics. Although lipid concentration was measured, data were not normalized to lipid weight since this is usually not done for bivalve bioaccumulation studies (Phillips, 1980). Detection limits are given in the California State Mussel Watch reports (e.g. Phillips, 1988).

The analytical procedure for organics followed that described by MacLeod et al. (1985). The extraction method involved a cleanup step with high pressure liquid chromatography with analysis on Hewlett Packard HP 5890 for pesticides and PCBs and a Finigan Ion Trap #ITD 800 for the PAHs. Detection limits for organics are also provided in Phillips (1988).

Results/Discussion

Since field blanks did not differ significantly from controls, field blank values were used in all statistical comparisons. The results of statistical tests between field blanks and bivalves transplanted in San Francisco Bay are given in Table 14. They indicate that a fairly high percentage of stations were significantly higher in metals than field blanks (35 to 78% in Phase I- dry season and 71-86% in Phase II- wet season). The range is given since tests were performed on 30, 60 90, and 120 day transplants. The percentage of tests that were significantly different increased directly with duration of exposure in Phase I, but no trend was apparent in Phase II (most metals were elevated after 30 days and remained high). Since no field replicate analysis was conducted for organics, no statistical analyses were performed.

Stations within San Francisco Bay were tested for geographic trends. Stations were near channels in different basins of the Estuary. Therefore, trends were for general areas of the Estuary and not for localized areas of contamination. The results of the statistical tests between stations indicate that, in general, stations in the southern end of the Bay (Coyote Cr., Dumbarton Br., Redwood Cr.) were significantly different than the stations in the northern end (Pt. Pinole, Davis Pt.) or central part of the Bay (Treasure Island). In Phase I the longer the transplant duration the greater the number of statistical tests that were significant between stations. In Phase II no such trend existed. Further resolution of differences was not increased by using different species, depurated mussels, or mussels that were deployed near the bottom. An interesting exception was that oysters were better than mussels in resolving differences between stations for zinc. Table 15 reports the mean values for Phase I and Phase II for the stations furthest south (Coyote Cr. or Dumbarton), Treasure Island which is centrally located and receives the most flushing, and the stations furthest away from the mouth of the Bay in the north (Davis Point or Point Pinole), which should be reflective of contaminants from the Sacramento-San Joaquin River Delta. Silver was much higher in the South and Central Bays than in the North. There were no apparent trends for mercury, lead, cadmium or zinc that could be statistically verified. There was some evidence of a trend of slightly higher levels of selenium, and copper in North and/or Central Bay.

No replicate analyses were done on the organic levels in bivalves, so statistical tests could not be performed. However, levels of most of the organics (PCBs, DDTs and chlordanes) were generally higher in the South Bay. The station at Coyote Creek was exceptionally high in comparison to the control site or the other stations in the Bay. PAHs were highest in the Central Bay but were also fairly high in the South Bay.

In comparing wet and dry seasons, there was no difference between Phase I and Phase II mussels for any metals. In oysters, there were significant differences only in cadmium, mercury and zinc levels at Coyote Creek. Since there was a drought during both transplant periods there was not much difference in runoff between Phase I and Phase II. A more interesting comparison would be between seasons when there is average or above average rainfall.

In comparing samples deployed at different depths, there were no differences between mussels deployed at shallow depths or 1 m off the bottom in either Phase I or Phase II for any metals.

A low percentage of metals were significantly different between depurated and undepurated mussels. Most of the metals tested were not significantly different or were only significantly different in one of the five stations on which this test was performed. The exceptions were lead and selenium which differed in two to three tests of the five performed. Selenium is particularly interesting since it differed significantly between depurated and undepurated only during Phase I, indicating a possible flux of selenium laden sediment during that period.

The ratios of concentrations of metals and organics for mussels and oysters is illustrated in Table 16. The results indicate that there was a near one to one correspondence between the species for chlordane, DDT and PCBs, but not for PAHs. The metals differed greatly between species. Mussels accumulated more of some metals and oysters more of others. This suggests that the two species cannot be used interchangeably for metals and PAHs.

The duration of exposure was studied at 30, 60, 90 and 120 days and indicates that in most cases mussels accumulate more contaminants with longer deployments (Table 17, Figures 23-26). Cadmium is the exception in that the levels in mussel controls and field

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blanks from Bodega Head were higher than in any of the mussels after transplantation to the Bay. In this study, an equilibrium appeared to be attained during the three and four month transplants for copper, mercury, lead, selenium and possibly DDT. No equilibrium was obtained in mussels for silver and PCBs after 120 days. The sum of the PAHs showed a rapid increase the first month and a decrease or leveling off after 2 months. The patterns exhibited for DDTs, PCBs, and chlordanes were similar indicating a similar source of these compounds. The transplant duration in future studies should be as long as possible since silver, PCBs and possibly DDT did not approach equilibrium over the 4 month interval of this experiment. If these contaminants are excluded then a transplant interval of 3 to 4 months would be adequate. In the Mussel Watch program mussels are deployed from 4 to 5 months. In order to compare stations a consistent time period should be used.

In this study an unsuccessful attempt was made to deploy caged <u>Macoma</u> to measure sediment uptake. An attempt was also made to collect <u>Potamocorbula</u>. Further studies should be made with <u>Potamocorbula</u> to evaluate its utility as a biomonitoring tool since it has a wide salinity tolerance.
WATER COLUMN

Study Design

Bay Monitoring Surveys

The primary objective of the water column portion of the Bay Monitoring Surveys was to assess the current water quality of the San Francisco Bay-Delta and the Sacramento and San Joaquin Rivers in comparison to the chemical specific and toxicity water quality objectives established in the Bays and Estuaries Plan and Inland Surface Water Plan (SWRCB 1991 a,b). Organic chemical analysis and chronic toxicity tests were performed on water samples collected throughout the Estuary to determine if objectives were being met.

Organic contaminants were measured in the water column in order to 1) evaluate concentrations of specific constituents for compliance with the Statewide Plan's water quality objectives, 2) start generating data so that long-term trends can be determined, 3) identify areas of high organic contaminant concentrations or hotspots, 4) accumulate data for application in bay wide pollutant fate and transport models, and 5) provide information for the interpretation of chronic toxicity testing of ambient waters. Water samples were collected using an onboard pumping system separating the particulate and dissolved fractions. Samples were collected at 15 stations goegraphically distributed throughout the Estuary on two separate occasions (June 1991 and April 1992).

The objectives for chronic toxicity testing were similar to those for organic contaminants. Samples were collected from 12 of the 15 stations for toxicity testing. Two different species were used for toxicity testing: <u>Strongylcentrotus sp.</u> (sea urchin) and <u>Menidia beryllina</u> (silverside fish).

Critical Habitat Investigations

Toxicity tests were performed on samples collected from critical habitats (i.e. wetlands) that received the discharge of treated wastewater or stormwater runoff. Stormwater investigations related toxicity in wetlands to storm intensity.

Methods

Organic Chemistry

Organic contaminant sampling was accomplished using an onboard pumping system. Water was pumped by a Teflon impeller pump through a 3/4 inch Teflon tubing to a filter holder with a glass fiber filter with a rated pore size of 0.3 um. Filters were changed whenever the flow rate began to fall off, typically every 20 liters in San Francisco Bay. Water was then passed through four polyurethane plugs mounted in series. Approximately 100 liters were passed through the sampling system at each station. The polyurethane plugs were exhaustively cleaned in the laboratory prior to field sampling by soxhlet-extraction, a minimum of three days with 2:1 hexane:acetone and a minimum of three days with methanol. The plugs were then sealed in teflon bags for transport to the field. The remaining sampling equipment was rinsed with methanol prior to use in the field. The system was transported to the field in a closed state to prevent contamination.

Custom-built soxhlet extraction units were used to extract the organics from both plugs and filters; an acetone extraction is followed by hexane. Water was removed by partitioning into hexane in a separatory funnel; extracts were reduced to 1-2 ml for cleanup with florisil-column chromatography. Florisil was activated at 650 degrees centigrade for 4 hours and deactivated with 0.5% water. The column (18 grams florisil) was eluted with hexane (volume sufficient to elute p,p' - DDT), 30% methylene chloride in hexane (volume sufficient to elute p,p' - DDT but not dieldrin, and 50% methylene chloride in hexane (volume sufficient to elute dieldrin).

Extract volumes were concentrated to approximately 0.1 - 1.0 ml and analyzed by both electron capture gas chromatography and mass spectroscopy (Varian 3400 autosampler). The STAR data system of the GC converts the analogue signals to integrated areas, which are compared with those of authentic standards eluting at the same retention time, and . produces a report with compound names and amounts in picograms. The data system of the GC/MS identifies compounds based on a combination of retention times and spectral characteristics and also reports compounds identified, and the amounts in nanogram or picograms of each. Both report files are converted to an ASCII format, in which they can be read into the data management system.

Toxicity Tests

Toxicity tests were generally conducted according to EPA and ASTM protocols. Modification or deviation from protocols are documented in the Quality Assurance Project Plan developed by the contractor and approved by the Regional Board's Quality Assurance Officer.

Different test organisms were used in each survey depending on seasonal availability and salinity of the ambient waters. Each toxicity test had varying endpoints ranging from mortality to inhibition in growth or reproduction. A summary of each survey and test organism is presented below.

Toxicity tests used in the Bay Monitoring Surveys were the larval fish growth and survival test using <u>Menidia beryllina</u> (silverside minnow) and the sea urchin fertilization assay using <u>Strongylocentrotus purpuratus</u>. The silverside minnow test involved exposing 7-9 day old fish to test solutions. Seawater collected from the Bodega Marine Laboratory was used as a seawater control and Arrowhead Spring water with artifical salts was used as a salinity-adjustment control. The test duration for the silverside minnow was 7 days. Statistical comparison are made between the control survival and growth and the test solutions. The sea urchin test involves exposing sperm to the test solution and then adding eggs to examine fertilization success. The test duration was approximately 40 minutes. The same control waters were used in the sea urchin test.

The Critical Habitat Investigations employed a number of different toxicity tests depending on the salinity of the water being tested. In water samples with higher salinities, marine tests using the silverside minnow, sea urchin, mussel development assay (Mytlius sp.), and mysid survival assay (Mysidopsis bahia) were performed. Freshwater tests included the water flea survival and reproduction assay (Ceriodaphnia dubia), the fathead minnow larval growth assay (Pimephales promelas), and algal growth assay (Selenastrum).

Results/Discussion

Bay Monitoring Surveys

The organic chemistry results from the bay surveys are not currently available. It is anticipated that the results will be available in January 1993. Toxicity testing indicated statistically significant toxicity during the June 1991 survey. <u>Menidia</u> survival was statistically different than controls at station BF30 (Port Chicago). Sea urchin fertilization was inhibited at BA40 (Redwood Creek). On other assay or station exhibited significant toxicity. No significant toxicity, using the same tests, was observed in the April 1992 survey.

Critical Habitat Investigations

The results of toxicity screening in the two critical habitat systems indicated that <u>Ceriodaphnia dubia</u> is the preferable test organism for evaluating effects of stormwater discharges. This conclusion is supported by the monitoring results generated by the Santa Clara and Alameda Counties stormwater monitoring programs, in which the incidence of response of <u>Ceriodaphnia</u> was much higher than that of <u>Pinephales promelas</u> or <u>Selenastrum</u>. The most useful measure in the <u>Ceriodaphnia</u> test was mortality as expressed by the median time to lethality (LT₅₀).

The first storm occurring in October 1991 produced nearly 2 inches of rain, effectively flushing the DUST system. Samples collected following the storm event exhibited toxicity to <u>Ceriodaphnia</u> with generally low conductivity values. A second storm in November 1991 produced a horizontal conductivity gradient in the DUST system. Toxicity and conductivity data from these two events is depicted in Figure 27. Toxicity is expressed in time units indicating the duration of exposure which caused mortality in 50% of the test animals (median time to a LT_{50}). Linear regression of the LT50 versus sampling site (dotted line) yielded a slope which was not significantly different from zero (p=0.778) for the October storm and a slope difference from zero (p=0.026) for the November storm. Toxicity and conductivity correlations were r=0.75 and r=0.97 for the October and November storms, respectively. The conductivity reflects the degree of dilution and thus provides an indicator of the potential toxicity from stormwater.

Another storm event in March 1992 demonstrated cessation of toxicity (Figure 28). Flow through the DUST system ceased three days after the storm. At this time the water was still toxic and was retained in the creek , and the debris basin. Four days later, no toxicity was detected in the debris basin (Station 5) nor was there any detected in the creek (Station 3). This indicates that dissipation of toxicity could be related to toxicity-removal processes which may take place due to retention time.

DATA MANAGEMENT

To manage the data for the entire RMP, EcoAnalysis Inc. developed a common format for all laboratories participating in the program. This allowed data to be more easily interpreted, analyzed and thoroughly checked for quality assurance. All laboratories in the program were provided with consistent formats with QA programs integrated into the data input system to insure accurate data entry. Data were generated at each of the laboratories and sent to EcoAnalysis for review.

EcoAnalysis performed the following operations to combine and review the various datasets: 1) data were extracted from the form received and read to SAS datasets for quality assurance review, 2) data received were compared to master list of data collected, 3) data were reviewed for consistency in station designations (codes), station descriptions, sampling dates, replicate designations and measurement units, 4) ranges of data values were reviewed, 5) apparent outliers and missing data were checked with the respective Principal Investigator and 6) when necessary, laboratory replicates were averaged.

MAJOR ACCOMPLISHMENTS OF PROGRAM

- 1. The Pilot Regional Monitoring Program evaluated techniques and protocols used to measure chemical contamination, toxicity and bioaccumulation in the Estuary. As a result of this program, a \$1.15 million Baseline Monitoring Program will be started in the Estuary this year. Chemical contamination and toxicity in the water column and sediment, and bioaccumulation in the water column will be monitored. This will be a program that will measure longterm temporal and spatial trends and act as the backbone and point of comparison for our Local Effects Monitoring Programs.
- 2. In the pilot RMP most of the marshes and mudflats in the Estuary were surveyed for chemical contamination and toxicity. Information was generated for vast areas of critical habitats.
- 3. Toxic hot spots were identified throughout the Bay and also in critical habitat areas.
- 4. A format was generated for data, and laboratories were trained to use these formats, so that data could be easily checked for quality assurance, and integrated for statistical analysis. Laboratories trained to use this system are those being used for the statewide Bay Protection Program. This provides the first step in setting up the statewide database.
- 5. Data generated in this program can be combined with other data to generate Apparent Effects Threshold (AET) values for San Francisco Bay. These values will be used to guide in the evaluation of sediment chemistry, for sediment cleanup and for marsh restoration.
- 6. Techniques were developed and protocols were evaluated that will be used in the statewide Bay Protection Program. Problems that arose are currently being addressed by designing studies to identify fine grain reference sites, determining the cause of toxicity in areas with no sources of contamination, refining toxicity test protocols and determining the best technique to measure the bioavailability of metals. In the long run this will make the program more scientifically rigorous and provide more certainty in the final results of the program.

PART II. WASTELOAD ALLOCATION STUDIES

Introduction

One of the tasks identified in the Bay Protection and Toxic Cleanup Program workplan was the development of a wasteload allocation for South San Francisco Bay based on a predictive water quality model. EPA requires wasteload allocations for water bodies where water quality objectives are exceeded. The goal of a wasteload allocation is first, to determine the maximum loading of pollutants to the water body which will result in attainment of water quality objectives, and second, to allocate the total allowable load among the existing sources, including point sources, nonpoint source, and background.

An important tool in developing wasteload allocations is a predictive water quality model, which is a model of the fate and transport of pollutants. Many processes may affect the fate or transport of pollutants including hydrodynamics, sediment dynamics, chemical speciation, biological uptake, degradation and volatilization. In most aquatic systems these processes are far too complex to simply measure. Predictive water quality models attempt to integrate available data describing the system and use simplifying assumptions where necessary to estimate resulting water quality conditions from different pollutant loading scenarios. Model results can be used to identify possible wasteload allocations and select the most reasonable alternative.

South San Francisco Bay

South San Francisco Bay has long been identified as an area of concern due to the combination of the large volume of wastewater discharged by the cities of San Jose, Sunnyvale and Palo Alto, and the limited amount of flushing flows due to low fresh water inflows. Improved treatment over the past two decades has resolved some of the problems associated with waste discharge such as low oxygen levels and eutrophication. Current concerns are focused on the impacts of toxic pollutants. South San Francisco Bay south of Dumbarton Bridge was listed by both the State of California and the US EPA on the Clean Water Act Section 304(l) list of water bodies impacted by toxic pollutants from point source discharges. The toxic pollutants that were identified were cadmium, copper, lead, mercury, nickel, selenium and silver.

Due to the history of concern, South Bay has been extensively studied and water quality data for this area are more complete than for most other parts of the Bay. However, there are still significant limitations to much of the data including lack of adequate detection limits and low precision. In addition a high percentage of South Bay is shallow or intertidal, so that measurement of basic hydrodynamic variables such as currents or depth is difficult or impossible.

Approach

Model development has two distinct components: modelling of available data and collection of additional data to improve the model. These components are two parts of an iterative process; data collection supports initial modelling efforts which in turn serve to define the most important data gaps. Once those gaps are filled, a more sophisticated model can be developed. Therefore, a phased approach to the wasteload allocation has been undertaken. The first phase was data compilation and model development based on existing data. Although the uncertainty of the initial model results was expected to be great, it was hoped that the results would be useful in supporting Regional Board regulatory actions limiting the discharge of pollutants to South Bay. Generalized models can be useful in making such decisions, as long as the uncertainty associated with their predictions is taken into account.

The second phase includes data collection to address questions related to sediment transport. The lack of understanding of the fate and transport of pollutants associated with sediments has been identified as one of the greatest limitations in developing a predictive water quality model. This phase also includes some hydrodynamic modelling to improve the estimate of residence time for conservative substances in South Bay, and to estimate the residence time of sediment particles.

Phase 1

Scope

The first phase was to perform initial modelling based on available data. The work in this phase was performed by EPA's Center for Exposure and Assessment Modelling. This phase was funded by a grant from the San Francisco Estuary Project and State funds previously earmarked for the wasteload allocation in addition to Bay Protection funds. The purpose of the study was to develop a water quality model to examine the fate and transport of metals in the South Bay, and to recommend possible wasteload allocations based on the model. A secondary goal was to identify the highest priority data needs to improve the ability to model the system.

The study included five major tasks:

- 1. Review of available data
- 2. Nontidal (tidally averaged) water quality simulation
- 3. Tidal water quality simulation
- 4. Modelling of the partitioning of metals between the dissolved and total phases.
- 5. Prediction of the results of reducing loading of metals to South Bay.

The water quality model was initially intended to evaluate copper, lead and nickel. Modelling of selenium and mercury is not feasible at this time because concentrations in water that can cause problems are lower than commonly used detection limits. Copper, lead, and nickel were identified as higher priority than cadmium, chromium, or silver based on frequency of exceedance of water quality objectives or effluent limitations. Initial model runs were better able to predict existing concentrations of copper than nickel or lead. In addition, the water quality objective for copper is the most frequently exceeded. For these reasons, most of the study focused on copper.

Methods

Water quality modelling was performed using the US EPA water quality model Water Quality Analysis Program or WASP4. WASP4 is essentially the coding of a series of equations based on the principle of conservation of mass. The water body is divided into a series of segments, and a mass balance of the pollutant in each segment is calculated based on physical transport into and out of the segment, and chemical or biological transformation or accumulation within the segment. WASP4 has the ability to account for sediments as a source or sink of pollutants.

Physical transport of pollutants is driven by hydrodynamics. The nontidal model takes into account advective transport produced by the inflows from the three treatment plans and from local runoff. All other circulation including wind and tidally driven currents is accounted for in a dispersion factor. The purpose of the nontidal analysis is to describe the large scale and long term behavior of the system.

The steps in the modelling process were as follows:

- 1. Generate a computerized grid system describing South Bay as far north as the Oakland Bay Bridge.
- 2. Estimate the dispersion coefficient for each segment based on a previous study of South Bay.
- Input loadings from point sources and stormwater. Parameters included flow, metals concentrations and suspended solids.
- 4. Simulate suspended solids concentrations and calibrate with historical data.
- 5. Simulate metals concentrations, and calibrate with recent water quality data.

For the tidal analysis, the two dimensional vertically averaged hydrodynamic and sediment transport model SED2D was used to describe the variation in currents over the tidal cycle. This model was linked to WASP4 to examine variation in water quality over the tidal cycle.

Partitioning of copper was modeled using the geochemical speciation model MINTEQA2. MINTEQA2 was used to predict partitioning of copper between the dissolved and total phase for a variety of conditions. Typical partition coefficients were estimated for each segment of the model. These partition coefficients were used as input parameters to the WASP4 model.

Results

The final report from CEAM is due in December, 1992. This summary of results is based on the draft report.

One of the greatest limitations in modelling the transport of metals was the lack of knowledge concerning sediment transport. For this study, the assumption was made that, on an annual basis, South Bay south of Dumbarton is neither net depositional or net erosional. Under this assumption, sediment resuspension may affect water column concentrations of pollutants, but sediment movement does not serve as a net transport mechanism into or out of the South Bay. Because this assumption only seemed reasonable as an average annual condition, the model predictions were limited to annual average conditions. While ultimately the differences between wet weather and dry weather conditions will be very important to understand, annual average conditions allow us to address some important long term questions.

The model was able to predict existing concentrations of total copper and nickel fairly well. Predictions of lead concentrations were consistently too high and further assessment of lead was not pursued. Comparison of two storm water loading conditions; median of 1977 to 1989, and average of 1988-1990 (drought conditions) showed that reduced stormwater loadings could decrease ambient concentrations by 1 ug/L or more in South Bay.

An assessment of the response time showed that if all loads were removed, the time for copper concentrations to be reduced by 50% ranges from 5 to 16 years depending on the segment.

The contribution from point and non point sources both north and south of Dumbarton . to total copper concentrations south of Dumbarton was estimated. Nonpoint sources south of Dumbarton were identified as accounting for the greatest fraction.

Copper concentrations resulting from reducing pollutant loadings from the treatment plants and from storm water were predicted. Results showed that, even in the scenario with greatest reductions, (treatment plants discharging at 2.9 ug/L and storm water loading reduced by 50%) copper concentrations in the furthest south segment would be greater than the water quality objective of 4.9 ug/L. However, this scenario did show significant reductions in copper concentrations, and since the model over-estimates current concentrations in the southernmost part of the Bay, predicted concentrations may

be too great as well.

In summary, the quantitative model results have such a high degree of uncertainty that they cannot be used in regulatory decisions. However, the qualitative results are very useful in elucidating the relative importance of various sources of pollutants and the response of the system. This information is currently being incorporated into a Regional Board staff report supporting proposed mass loading reductions of copper to the Lower and South Bay. In addition the model results provide a good overview of our current understanding of pollutant transport in the South Bay and of topics where information is lacking.

Phase 2

Scope

Phase 2 has two components, a data collection element and a hydrodynamic modelling element. The purpose of the data collection is to characterize sediment resuspension by collecting time series of suspended sediment concentrations at various locations in Lower and South Bay. The suspended sediment data will be compared to wind, tide and delta outflow data to identify the major factors influencing sediment movement. This task will add to our understanding of sediment dynamics in South Bay to improve the basis of future water quality modeling efforts.

The purpose of the hydrodynamic modeling is to estimate residence times for dissolved substances under dry weather conditions, and to estimate how sediment residence times are likely to differ from those of dissolved substances. These two estimates should represent maximum and minimum residence times for pollutants. This information will be useful in improving estimates of allowable loading levels of pollutants to South Bay.

The Phase 2 work is being conducted by the US Geological Survey in Sacramento. The work is currently underway and will not be complete until June, 1994.

Methods

1. Data Collection and Analysis

Time series of suspended sediment concentrations are being collected at three deep water sites: San Mateo Bridge, Dumbarton Bridge, and Channel marker 17, south of Dumbarton. Suspended sediment measurements are collected at 15 minute intervals by in situ optical backscatter sensors (OBS) connected to data loggers. OBSs were deployed at two depths, mid-water and near-bottom. In addition, OBS sensors will be deployed for shorter time period (about two weeks) in shallow water areas.

Every two weeks, data is collected, the OBS sensors are cleaned and calibration samples

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are collected at the location and depths of the OBSs. Calibration samples are analyzed for total suspended sediment concentration and particle size distribution.

Suspended sediment data will be correlated with tide, wind, and fresh water inflow data, to assess the relative importance of these factors in causing resuspension.

2. Hydrodynamic modelling

Hydrodynamic modelling will be conducted using a two dimensional model currently under development by USGS. Estimates of residence times for dissolved substances will include the effects of tidal mixing. The model has the ability to estimate residence times for dissolved particles by tracking the path of a neutrally buoyant particle. To estimate residence time of sediment particles, the computer code will be modified so that the particle becomes stationary below a certain threshold velocity, when particles would be expected to settle out.

Progress to Date

OBSs were deployed at San Mateo Bridge in December 1991 and at Channel Marker 17 in February 1992. Due to difficulties in obtaining permits from CalTrans, the OBSs at Dumbarton Bridge were not deployed until September 1992. All sites have been serviced at two week intervals since their deployment. Calibration curves are being developed.

Initial data evaluation suggests that, during calm wind conditions and energetic tides, sediment concentrations fluctuate with tides, with peaks occurring at low slack water. This result is consistent with the hypothesis that sediment is resuspended in the shallows by tidal currents and advected northward with the ebb tide.

The hydrodynamic modeling has not been completed.

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FIGURES AND TABLES



Figure 1. Bay Run #1 station locations collected on August 26-28, 1991 with a modified Gray-Ohare grab.



Figure 2. Bay Run #2 station locations collected on March 30-April 1, 1992 with a modified Gray-Ohare grab.



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Figure 3. San Francisco Bay areas of marsh sampling.

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GD10 AND GD20

Figure 4 Gradient stations locations collected on May 25-27, 1991 with diver cores.

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Figure 5 : Ag Concentrations in SF Bay Sediments

Concentrations given in ppm dry weight. ER-L & ER-M values from Long and Morgan (1990). Crustal abundance from Lof (1987).

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Figure 6 : Cd Concentrations in SF Bay Sediments

Concentrations given in ppm dry weight. ER-L & ER-M values from Long and Morgan (1990). Crustal abundance from Lof (1987).

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Figure 7: Cd Concentrations in SF Bay Sediments

Concentrations given in ppm dry weight. Crustal abundance from Lof (1987).

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Figure 8 : Cr Concentrations in SF Bay Sediments



Figure 9 : Cu Concentrations in SF Bay Sediments



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Figure 10: Ni Concentrations in SF Bay Sediments



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Figure 11: Pb Concentrations in SF Bay Sediments

Concentrations given in ppm dry weight. ER-L & ER-M values from Long and Morgan (1990). Crustal abundance from Lof (1987).



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Figure 12: Zn Concentrations in SF Bay Sediments

Concentrations given in ppm dry weight. ER-L & ER-M values from Long and Morgan (1990). Crustal abundance from Lof (1987).

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Figure 13: Ag Concentrations in Bay Area Creeks and Marshes

Concentrations given in ppm dry weight. ER-L & ER-M values from Long and Morgan (1990). Crustal abundance from Lof (1987).

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Figure 14: Cd Concentrations in Bay Area Creeks and Marshes



Figure 15: Cd Concentrations in Bay Area Creeks and Marshes

Concentrations given in ppm dry weight. Crustal abundance from Lof (1987).



Figure 16: Cr Concentrations in Bay Area Creeks and Marshes

Concentrations given in ppm dry weight, ER-L & ER-M values from Long and Morgan (1990). Crustal abundance from Lof (1987).

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Figure 17: Cu Concentrations in Bay Area Creeks and Marshes



Figure 18: Cu Concentrations in Bay Area Creeks and Marshes

Concentrations given in ppm dry weight. ER-L & ER-M values from Long and Morgan (1990). Crustal abundance from Lof (1987).

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Figure 19: Ni Concentrations in Bay Area Creeks and Marshes



Figure 20: Pb Concentrations in Bay Area Creeks and Marshes

Concentrations given in ppm dry weight. ER-L & ER-M values from Long and Morgan (1990). Crustal abundance from Lof (1987).

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Figure 21: Zn Concentrations in Bay Area Creeks and Marshes

Concentrations given in ppm dry weight. ER-L & ER-M values from Long and Morgan (1990). Crustal abundance from Lof (1987).





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TREASURE I-PAHa-PHASE 1

REDWOOD CR .-- PAHa-- PHASE 1





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Figure 24

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TREASURE I-DDT -- PHASE 1

REDWOOD CR--DDT--PHASE 2

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Figure 25



Figure 26

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Figure 27: Spatial Distribution of toxicity and conductivity in the DUST System after a big and a small storm.

Hollow circle, conductivity; full inverted triangle, LT_{50} as calculated by the graphical method; dotted line, linear regression of LT_{50} vs sampling site. Resulting slopes of -1.4 with std. err. of 4.54 for the October 1991 (2") storm, and a slope of 31.7 with std. err. of 9.2 for the November 1991 (0.2") storm.



Figure 28: Survival of Ceriodaphnia in DUST System samples taken after the storm of March 14, 1992.

Five field-replicates in each station had 5 test animals each, with daily renewal and feeding. Survival in all control chambers was 100% at test termination, which was after 7 days except for the test with March 15 samples. Mean survival after 5-day exposure (Station 5, full diamonds) or 7-day exposure (Station 3, full circles) is presented.

STATION CODE	STATIONS*	DATE	LAT	LONG	# GRABS	DEPTH	SAL(ppt)	TEMP
BA20	EXTREME SOUTH BAY	8/29/91	37 28 59	122 05 28	3	9	28	23
BA30	DUMBARTON BRIDGE	8/29/91	37 30 44	122 08 07	2	10	32	22
BA40	REDWOOD CREEK	8/2 9 /91	37 31 42	122 11 51	6	14	28	21
BB31	OYSTER POINT MARINA	8/29/91	37 39 50	122 22 34	20	7	35	21
BC10	YERBA BUENA ISLAND	8/28/91	37 48 46	122 21 31	4	17	35	18
BC30	RICHARDSON BAY	8/28/91	37 52 16	122 29 50	2	10	38	18
BC50	STAUFFER	8/28/91	37 54 10	122 19 59	4	7	35	18
BD20	PETALUMA RIVER	8/28/91	38 06 42	122 29 00	3	7	30	20
BD30	PINOLE POINT	8/27/91	38 00 56	122 21 47	8	9	25	18
BD40	DAVIS POINT	8/27/91	38 03 20	122 15 10	4	12	25	19
BD51	NAPA RIVER (West bank Mare Island)	8/27/91	38 05 17	122 15 15	2	21	21	20
BF10	PACHECO CREEK	8/27/91	38 02 49	122 05 37	1.0	5	17	19
BF20	GRIZZLY BAY	8/26/91	38 05 42	122 01 54	1	12	12	19
BG21	SACRAMENTO RIVER (at Sherman Lake)	8/26/91	38 03 06	121 47 42	8	9	4	20
BG31	SAN JOAQUIN RIVER (south Kimball is.)	8/26/91	38 02 01	121 49 42	11	10	4	19

Table 1. Bay Run #1 stations and corresponding data.

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Table 2. Bay Run #2 stations and corresponding data.

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STATION CODE	STATIONS*	DATES	LAT	LONG	# GRABS	DEPTH	SAL(ppt)	TEMP
BA20	EXTREME SOUTH BAY	3/30/92	37 29 02	122 05 16	1	16	20	16
8A30	DUMBARTON BRIDGE	3/30/92	37 30 43	122 08 11	1	8	22	16
BA40	REDWOOD CREEK	3/30/92	37 31 41	122 11 50	2	10	24	16
BB31	OYSTER POINT MARINA	3/30/92	37 40 19	122 22 45	2	13	26	16
BC10	YERBA BUENA ISLAND	3/30/92	37 48 46	122 21 30	2	13	27	15.5
8C31	RICHARDSON BAY	3/31/92	37 52 22	122 29 38	7	10	28	16
BC50	STAUFFER	3/31/92	37 54 10	122 19 58	2	8	25	15
BD20	PETALUMA RIVER	3/31/92	38 06 42	122 29 00	5	6	15	17
BD30	PINOLE POINT	3/31/92	38 00 56	122 21 47	8	8	22	16.5
BD52	NAPA RIVER (East bank Vallejo)	4/1/92	38 05 22	122 15 08	5	15	11	17
BF10	PACHECO CREEK	4/1/92	38 02 44	122 05 44	11	10	5	16
BF20	GRIZZLY BAY	4/1/92	38 05 39	122 01 54	7	6	5	17.5
BG21	SACRAMENTO RIVER (at Sherman Lake)	4/1/92	38 03 10	121 47 38	6	9	2	17.5
BG32	SAN JOAQUIN RIVER (southwest Kimball Is.)	4/1/92	38 02 01	121 49 43	13	7	1	17

STATION CODE	STATIONS	DATE	SALINITY (ppt)	TYPE OF COLLECTION
MA10	COYOTE HILLS SLOUGH	11/25/91	19	TUBES
MB10	SAN LEANDRO BAY/ARROWHEAD MARSH	11/25/91	30	TUBES
MB11	SAN LEANDRO BAY/GARRETSON POINT	11/25/91	30	TUBES
MB20	SAN LORENZO CREEK	11/25/91	34	TUBES
MC10	RICHMOND INNER HARBORHOFFMAN MARSH	11/26/91	30	TUBES
MC20	CERRITO CREEK MOUTH	11/26/91	32	TUBES
MC21	CORDORNICES CREEK MOUTH	11/26/91	30	TUBES
MC30	EMERYVILLE MARSH/EBMUD STORMDRAIN	2/21/92	28	NON-DIVER SCRAPE
MC50	CORTE MADERA MARSH S. OF INDUSTRIAL ROAD	2/17/92	28	NON-DIVER SCRAPE
MC51	CORTE MADERA CREEK/LARKSPUR FERRY MARSH	2/17/92	27	NON-DIVER SCRAPE
MC60	SILVA ISLAND MARSH/BEHIND CHEVRON	2/18/92	27	NON-DIVER SCRAPE
MC61	SILVA ISLAND MARSH/SEMINAR DR. STORMDRAIN	2/18/92	28	NON-DIVER SCRAPE
MD10	MILLER CREEK/LAS GALLINAS DISCHARGE	2/19/92	27	NON-DIVER SCRAPE
MD11	MILLER CREEK/UPSTREAM FROM DISCHARGE	2/19/92	28	NON-DIVER SCRAPE
MD20	GALLINAS CREEKJOHN F. MONNIS COUNTY PARK	2/19/92	28	NON-DIVER SCRAPE
MD21	NOVATO CREEK/AT LOCK	2/19/92	28	NON-DIVER SCRAPE
MD30	PETALUMA RIVER MOUTH/E, BANK MARSH	11/1/91	27	TUBES
MD31	TOLAY CREEK MOUTH	11/1/91	26	TUBES
MD32	NAPA SLOUGH/BRIDGE	11/1/91	26	TUBES
MD33	SONOMA CREEK/TUBBS	11/1/91	26	TUBES
MD34	SONOMA CREEKBRIDGE	11/1/91	26	TUBES
MD35	INLET EAST OF NAPA SLOUGH	10/31/91	25	TUBES
MD36	MARE ISLAND NORTHERN TIP	10/31/91	23	TUBES
MD37	MARE ISLAND CENTRAL/AT PILES	10/31/91	25	TUBES
MF10	BOYNTON SLOUGH C:	7/23/91	20	DIVER SCRAPE
MF11	BOYNTON SLOUGH C3	7/23/91	20	DIVER SCRAPE
MF12	BOYNTON SLOUGH C4	7/23/91	20	DIVER SCRAPE
MF13	BOYNTON SLOUGH CR2	7/23/91	20	DIVER SCRAPE
MF20	HILL SLOUGH/BELOW BRIDGE	7/24/91	20	DIVER SCRAPE
MF21	HILL SLOUGH/ABOVE BRIDGE	7/24/91	21	DIVER SCRAPE
MF22	PEYTON SLOUGH/BACK END OF SLOUGH	7/24/91	20	DIVER SCRAPE
MF23	PEYTON SLOUGHMOUTH OF SLOUGH	7/24/91	21	DIVER SCRAPE
RS10	TOMALES BAY/ BRAZIL BEACH	•	29	DIVER SCRAPE
RS11	TOMALES BAY/ MARCONI COVE		22	DIVER SCRAPE
RS20	LAKE MENDOCINO	•••	20	DIVER SCRAPE

Table 3. Marsh stations and corresponding data.

4/8/91,7/16/91

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9/3/91,10/31/91,11/26/91,2/21/92,4/2/92 4/24/91,6/10/91,7/16/91,9/16/91

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Fall, 1991 (Dry Weather); n=15

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Spring, 1992 (Wet Weather) n = 14

	Mean	SD	Median	Max	Min
Cr	76	8	78	87	61
Zn	112	16	111	137	77
Со	16	2	16	19	14
Ni	76	8	76	90	62
V	61	6	63	73	50
Cu	45	24	39	124	22
Cd	0.25	0.14	0.23	0.74	0.12
Pb	39	24	36	110	8
Ag	0.60	0.27	0.63	1.16	0.10

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	Mean	SD	Median	Max	Min
Cr	79	12	83	92	47
Zn	109	17	115	127	73
Co	16	2	16	20	11
Ni	74	11	- 77	92	51
V	61	9	62	81	41
Cu	41	8	40	54	24
Cd	0.24	0.10	0.21	0.49	0.12
Pb	29	11	29	56	9
Ag	0.42	0.14	0.43	0.63	0.13

Values Reported in mg analyte per kg dry sediment (ppm)

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Table 5 Bay Sediment Toxicity Tests - Eohaustorius Mean survival \pm SD of Eohaustorius estuarius in bay test sediments, "Home" (H) treatments, and reference sediments (RS11). Significant differences between survival in test sediments and "home" and reference tretments is indicated (ANOVA Fisher multiple range test of arcsin(x) transformed % survival values, p,0.01). n= 5 replicates, with 20 or 16 individuals/replicate.

				Significant	Difference
Test Date	Station	Mean	±SD	RS	H
9/20/91	RS 11	17	2		
n=20	н	19	1		
	BA 20	9	2	X	x
	BA 30	10	3	X	X
	BA 40	10	2	Х	X
	BB 31	14	2	Х	X
	BC 10	19	1		
	BC 30	10	4	х	х
	BC 50	17	1		х
	BD 20	12	3	Х	X
	BD 30	15	4		х
	BD 40	18	1		
	BD 51	11	2	Х	х
	BF 10	14	2	Х	х
	BF 20	13	2	x	x
	BG 21	17	2		
	BG 31	19	0		
4/15/92	RS 11	10	2		
n=16	н	· 14	1		
ĺ	BA 20	7	2		Х
	BA 30	8	3		х
	BA 40	10	0		Х
	BB 31	10	2		Х
	BC 10	11	1		X
	BC 31	9	5		Х
	BC 50	8	1		X
	BD 20	9	2		X
	BD 30	14	2	Х	
	BD 52	9	3		X
	BF 10	11	1		x
	BF 20	8	3		x
	BG 21	9	3		X
	BG 32	14	2	х	

Table 6 Bay Sediment Toxicity Tests - Rhepoxinius

Mean survival \pm SD of *Rhepoxinius abronius* in bay test sediments, "Home " (H) treatment, and reference sediment (RS 11). Significant differences between survival in test sediments and "Home" and reference treatments are indicated (ANOVA Fisher multiple range test of arcsin(x) transformed % survival values, p<0.01). n= 5 replicates, with 20 individuals/replicate.

Test Date	Station	Mean	±SD	RS 11	Difference H
9/18/91	RS 11	19	1		
	н	20	1		
	BA 20	13	• 5	Х	x
1	BA 40	17	2		
	BB 3	17	2		
	BC 30	14	2		х
	BC 50	· 17	2		
	BD 40	16	-4		

Table 7 Bay Sediment Toxicity Tests - Daphnia

Mean survival \pm SD and mean number of babies \pm SD of *Daphnia magna* in bay test sediments and reference sediment (RS 20). No significant difference between treatments was found (ANOVA Fisher multiple range test of arcsin(x) transformed % survival values and number of babies, p<0.05). n= 5replicates, with 10 individuals/replicate.

		Mean±SD					
Test Date	Station	Survival	# of B	abies			
9/19/91	RS 20	9 1	56	37			
	BG 21	9 1	70	37			
	BG 31	9 1	55	41			

Table 8 Bay Survey Results.

8a Summary results from larval bivalve and larval fish elutriate toxicity tests from the bay surveys. All data are means ± standard deviations of five laboratory replicates. Date indicates the month samples were collected. "Not tested" indicates samples determined before testing to be outside the salinity range of the test species. "Control" indicates organisms incubated in Granite Canyon seawater adjusted with distilled water to the test salinity.

	Oyster Larvae	% Abnormal	Menidia Larvae	(August 1991)
Station	August 1991	April 1992	% Mortality	Weight (mg)
Control	23.0 ± 6.9	15.5 ± 8.0	15.0 ± 10.0	
Control*	3.3 ± 0.6*			
RS11	11.6 ± 5.9*	16.5 ± 15.2	15.0 ± 19.1	0.78 ± 0.51
BA20	17.4 ± 7.2	22.1 ± 11.8	15.0 ± 19.1	0.90 ± 0.24
BA30	24.4 ± 7.5	16.3 ± 9.6	20.0 ± 28.3	0.78 ± 0.10
BA40	72.0 ± 11.1	14.1 ± 3.6	30.0 ± 11.5	0.70 ± 17.3
BB31	25.6 ± 7.6	8.8 ± 5.0	30.0 ± 20.0	0.62 ± 0.17
BC10	15.9 ± 6.5	13.2 ± 5.9	0.0 ± 0.0	1.05 ± .079
BC30	31.9 ± 9.9	14.2 ± 5.7	15.0 ± 30.0	0.97 ± 0.21
BC50	18.9 ± 5.6	8.3 ± 2.3	5.0 ± 30.0	0.61 ± 0.23
BD20	28.3 ± 10.8	47.9 ± 18.5	27.5 ± 22.2	0.74 ± 0.25
BD30	29.7 ± 7.5	16.0 ± 5.4	15.0 ± 19.1	0.83 ± 0.15
BD40	17.9 ± 3.5		25.0 ± 30.0	0.91 ± 0.10
BD51	29.6 ± 8.6		15.0 ± 10.0	0.65 ± 0.26
BD52		12.7 ± 6.5		
BF10	45.3 ± 3.7	11.1 ± 7.7	40.0 ± 28.3	0.92 ± 0.22
BF20	3.6 ± 7.3*	6.4 ± 3.9	47.5 ± 25.0	1.08 ± 0.48
BG21	Not Tested	97.5 ± 2.9	45.0 ± 41.2	0.90 ± 0.27
BG31	Not Tested		5.0 ± 10.0	0.77 ± 0.08
BG32		95.4 ± 2.6		

* Samples from these two stations were tested separately at a later date. See text and Table 4.

Table 8bBay sites exhibiting significant toxicity to test organisms in sediment elutriate tests. Data were analyzed by ANOVA using laboratory replicates to define the error term.

Test Series Species & Date		Sites Significantly More Toxic Than Seawater Controls	Sites Significantly More Toxic Than Reference Sites		
Bay #1	Bivalve	BA40, BF10	NA		
August 91	Menidia	None Significantly Different	None Significantly Different		
Bay #2	Bivalve	BD20, BG21, BG32	BD20, BG21, BG32		

Table 9 Marsh Toxicity Tests - Echaustorius

Mean survival \pm SD of *Eohaustorius estuarius* in marsh test sediments, "Home" (H) treatments, and reference sediment (RS 10 or RS 11). Significant differences between survival in test sediments and "Home" and reference treatments are indicated for significance levels listed (ANOVA Fisher multiple range test of $\arcsin(x)$ transformed % survival values). n=5 replicates, with 20 individuals/replicate in all tests except 7/26/91, in which there were 12 individuals/replicate.

Test Date	Station	Mean	450	RS	H
7/16/01	RS 10	2	2	10	11
n=0.01	H	10	1		
F-0.01	ME 10	4	i		x
	ME 11	5	2.		x
	ME 12	5	2		x
	ME 13	8	3	x	~
	ME 20	- 6	2	А	x
	ME 21	5	3		x
	MF 22	6	ž		x
	ME 23	8	1	x	
11/9/91	RS 11	17	2		
p=0.05	Н	19	1		
F 0.00	MD 30	16	3		x
	MD 31	13	3	X	x
	MD 32	12	2	x	x
	MD 33	10	2	x	x
	MD 34	10	2	x	x
	MD 35	15	2		х
	MD 36	18	3		
	MD 37	19	1	X	
12/19/91	RS 11	18	0		
p=0.01	Н	19	2		
-	MA 10	17	3		
	MB 10	15	2		X
	MB 11	17	2		
	MB 20	17	2		
	MC 10	18	2		
	MC 20	19	2		
	MC 21	16	1		
2/26/92	RS 11	10	2		
p=0.05	Н	18	1		
	MC 30	11	5		X
	MC 50	. 12	3		X
	MC 51	14	3	X	x
	MC 60	17	2	X	
	MC 61	16	2	X	X
	MD 10	15	4	Х	x
1	MD 11	15	3	Х	X
	MD 20	. 8	3		х
	MD 21	10	2		Х

Table 10 Marsh Survey Results. 10aSummary results from larval bivalve and larval fish elutriate toxicity tests from the marsh surveys. All data are means ± standard deviations of five laboratory replicates. Date indicates the month samples were collected. "No: tested" indicates samples determined before testing to be outside the salinity range of the test species. "Control" indicates organisms incubated in Granite Canyon seawater adjusted with distilled water to the test salinity.

		Oyster Larvae	Menidia	Menidia Larvae		ps Larvae
Date	Station	% Abnormal	% Mortality	Weight (mg)	% Mortality	Weight (mg)
July 91	Control	15.7 ± 10.0	7.5 ± 6.8	0.70 ± 0.08	0.0 ± 0.0	0.98 ± 0.12
	RS10	74.8 ± 6.9	7.5 ± 11.2	0.75 ± 0.10	4.0 ± 8.9	1.15 ± 0.15
	LM	100.0 ± 0.0	24.7 ± 12.9	0.72 ± 0.13	28.0 ± 30.3	0.98 ± 0.31
	MF10	94.6 ± 2.6	10.0 ± 10.5	0.80 ± 0.09	0.0 ± 0.0	1.16 ± 0.12
	MF11	61.0 ± 6.9	5.0 ± 6.8	0.73 ± 0.08	0.0 ± 0.0	1.11 ± 0.08
	MF12	63.3 ± 13.9	10.4 ± 10.6	0.72 ± 0.07	4.0 ± 8.9	1.11 ± 0.10
	MF13	73.4 ± 7.3	12.5 ± 12.5	0.82 ± 0.08	8.0 ± 17.9	1.09 ± 0.02
	MF20	Not Tested	5.0 ± 6.8	0.76 ± 0.08	4.0 ± 8.9	0.97 ± 0.16
	MF2 1	Not Tested	10.4 ± 10.6	0.68 ± 0.06	48.0 ± 26.8	1.14 ± 0.21
	MF22	12.3 ± 6.6	5.0 ± 6.8	0.79 ± 0.07	0.0 ± 0.0	1.21 ± 0.12
	MF23	39.9 ± 10.1	2.5 ± 5.6	0.69 ± 0.05	0.0 ± 0.0	1.14 ± 0.10
Oct. 91	Control	1.9 ± 1.7	8.0 ± 11.0	1.03 ± 0.19		
	RE11	1.2 ± 1.1	4.0 ± 8.9	1.11 ± 1.24		
	MD30	2.6 ± 2.0	0.0 ± 0.0	1.25 ± 0.17		
	MD31	1.4 ± 0.6	0.0 ± 0.0	1.28 ± 0.24		
	MD32	1.8 ± 1.2	4.0 ± 8.9	1.15 ± .26		
	MD33	1.5 ± 1.4	8.0 ± 11.0	1.18 ± .28		
	MD34	0.4 ± 0.6	4.0 ± 8.9	1.69 ± .741		
	MD35	0.7 ± 0.6	0.0 ± 0.0	1.46 ± 0.13		
	MD36	1.1 ± 0.7	0.0 ± 0.0	1.16 ± 0.29		
	MD37	1.2 ± 1.1	0.0 ± 0.0	1.15 ± 0.23		

Oct. 91 Oyster Larvae in Pore Water[‡]

Control	4.7 ± 1.3
RE 11	$10.7 \pm 5.9 \ (n = 2)$
MD36	6.5 ± 4.2
MD37	4.5 ± 2.1

[†] Pore water = supernatant water remaining above settled sediment in original sample jars.

		Mussel Larvae	Menidia	Larvae
Date	Station	% Abnormal	% Mortality	Weight (mg)
Nov. 91	Control	0.8 ± 0.4	4.0 ± 8.9	0.76 ± 0.15
	RS11	2.4 ± 2.5	8.0 ± 17.9	0.60 ± 0.17
	MA10	1.7 ± 1.1	17.0 ± 9.7	0.87 ± 0.07
	MB10	1.2 ± 1.9	0.0 ± 0.0	0.70 ± 0.10
	MB11	1.0 ± 0.7	20.0 ± 20.0	0.94 ± 0.16
	MB20	0.8 ± 0.5	16.0 ± 16.7	0.79 ± 0.13
	MC10	1.5 ± 0.8	8.0 ± 11.0	0.75 ± 0.09
	MC20	2.1 ± 1.9	12.0 ± 11.0	0.86 ± 0.07
	MC21	1.4 ± 0.8	8.0 ± 11.0	0.88 ± 0.05

Table 10 (Continued).

		Oyster Larvae	Menidia	a Larvae	
Date	Station	% Abnormal	% Mortality	Weight (mg)	
Feb. 92	Control	14.9 ± 4.6	8.0 ± 11	0.74 ± 0.09	
	RS11	51.1 ± 7.0	0.0 ± 0.0	0.84 ± 0.15	
	MC30	19.5 ± 7.5	8.0 ± 11.0	0.89 ± 0.14	
	MC50	27.1 ± 8.0	0.0 ± 0.0	0.76 ± 0.15	
	MC51	20.2 ± 8.6	12.0 ± 11.0	0.77 ± 0.15	
	MC60	26.4 ± 15.9	0.0 ± 0.0	0.94 ± 0.12	
	MC61	99.1 ± 1.6	24.0 ± 26.1	0.89 ± 0.48	
	MD10	29.2 ± 14.0	4.0 ± 8.9	0.80 ± 0.14	
	MD11	98.6 ± 1.4	4.0 ± 8.9	0.84 ± 0.09	
	MD20	25.7 ± 10.3	8.0 ± 11	0.87 ± 0.08	
	MD21	26.0 ± 5.6	4.0 ± 8.9	0.84 ± 0.09	

Table 10b Sites exhibiting significant toxicity to test organisms in sediment elutriate tests from the marsh survey. Data were analyzed by ANOVA.

Test Series & Date	Species	Sites Significantly More Toxic Than Seawater Controls	Sites Significantly More Toxic Than Reference Sites
Marsh #1	Bivalve	All except MF22 (incl. Ref Sites)	LM, MF10
July 91	Menidia	LM	LM
	Atherinops	LM, MF21	LM, MF21
Marsh #2	All Tests	None Significantly Different	None Significantly Different
October 91			
Marsh #3	All Tests	None Significantly Different	None Significantly Different
November 91			
Marsh #4	Bivalve	RS11, MD10, MD11, MC61	MD11, MC61
February 92	Menidia	MC61	MC61

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Table 11 : Porewater concentrations of trace elements for gradient study

		РЪ	Pb	Ag	Ag	Zn	Zn	Cu	Cu	Cd	Cd	Ni	Ni	Mn	Mn
CODE	Station	avg ppb	SD	avg ppb	SD	avg ppm	SD	avg ppb	SD	avg ppb	SD	avg ppb	SD	avg ppm	SD
GD10	EVSO4 shallow	142	108	6.7	7.9	31	13	509	200	85	30	6377	773	1940	616
GD20	EVSO4 deep	77	22	6.3	4.6	10	3	379	187	20	17	2948	1037	467	46
GD1	Pt. Pinole piling shallo	148	70	12.9	13.0	242	414	3034	3131	329	162	6377	1736	4646	1163
GD22	Pt.Pinole piling deep	80	83	27.2	44.4	34	9	284	122	182	185	3324	766	2137	81
GD21	CC2 deep	16	9	24.6	20.2	17	8	396	137	10	7	2364	477	969	146
GD23	CC4 deep	2	5	5.4	10.8	10	3	242	46	13	19	2474	315	1463	222
C110	Carr Inlet shallow	340	n = 1	39.9	n == 1	13	n = 1	1651	n=1	139	n=1	2101	n = 1	81	n = 1
C120	Carr Inlet deep	79	n = 1	0.0	n = 1	13	n = 1	248	n = 1	8	n = 1	1174	n = 1	494	n = 1

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Table 12 : Sediment concentrations of trace elements for gradient study

Code	Location	Cr	Cr	Zn	Zn	Cu	Cu	Ni	Ni	Pb	Pb	Cd	Cd	Ag	Ag
		avg ppm	SD												
GD10	EVSO4 shallow	86	6	135	6	74	18	86	4	33	2	0.37	0.06	0.30	0.03
GD20	EVSO4 deep	100	4	191	15	154	48	100	2	-58	5	1.05	0.14	0.42	0.02
GDN	Pt.Pinole piling shallow	91	8	130	4	47	2	82	2	30	2	0.20	0.00	0.28	0.02
GD22	Pt.Pinole piling deep	63	3	84	4	25	1	48	1	21	3	0.30	0.03	0.17	0.02
GD21	CC2 deep	61	9	90	12	37	7	49	7	25	4	0.41	0.06	0.16	0.02
GD23	CC4 deep	86	11	148	22	53	10	82	11	49	17	0.70	0.27	0.32	0.08
C110	Carr Inlet shallow	41	n = 1	55	n = 1	25	n = 1	30	n = 1	13	n = 1	0.59	n = 1	0.17	n = 1
CI20	Carr Inlet deep	27	n=1	57	n = 1	40	n = 1	31	n = 1	12	n = 1	0.57	n=1	0.16	n=1

Five field replicates for each station, except for Carr Inlet

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Table 13a Comparisons of various factors affecting larval oyster toxicity test results from the Castro Cove gradient study. ANOVA tests were conducted using means for each field replicate (n=5). Comparisons between field replicates were made using laboratory replicates to define the ANOVA error term.

* Indicates significant differences.

^b Individual comparisons among sites are given below in Table 3c.

Comparison	Samples Used in Comparison	<u>Probability</u>
Between Sites	shallow layer, pore water	0.58
Between Sites	deep core, pore water	0.0001*b
Between Sites	shallow layer, elutriates	0.24
Between Sites	deep core, elutriates	0.03*b
Shallow layer (.38) vs Deep Core (.58)	pore water, PP and EVS 04	0.35
Shallow layer (.10) vs Deep Core (.15)	elutriate, PP, EVS 04, and CC2	0.44
Pore water (.38) vs Elutriate (.11)	shallow layer, PP and EVS 04	0.06
Pore water (.79) vs Elutriate (.13)	deep core, PP, EVS 04, CC2 & CC4	0.0001*
Between Field Reps	shallow layer, pore water, PP	0.0001*
Between Field Reps	shallow layer, pore water, EVS 04	0.0001*
Between Field Reps	deep core, elutriate, CC2	0.03*
Between Field Reps	all others	> 0.05

Table 13b Individual comparisons of sites within the gradient study indicate the following sites had significantly greater toxicity than reference sites at p < 0.05 using Dunnett's multiple comparison test. The proportion abnormal for each site is given in parentheses.

Type of Sample	Reference Site	Sites with Significant Toxicity
Deep Core, Pore Water	GD22 (0.17)	GD20 (0.99)
		GD23 (1.00)
		GD21 (0.98)
		(CI20 (1.00))
Deep Core, Elutriate	GD22 (0.09)	GD20 (0.29)

Table 14

at 30, 60, 90, and 120 days during Phase 1 and II. *-significant difference for metal in at 30, 60, 90, and 120 days during Phase 1 and II. *-significant difference for metal in Phase 1 Duration Site Names Sign. Diff. Ag Cd Cu Hg Pb S Mussels		led
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Image: second systemImage: second systemNo. of metalsImage: second systemImage:		
No. of metalsNo. of		
Phase 1DurationSite NamesSign. Diff.AgCdCuHgPb9Mussels30 daysRedwood Creek230 daysTreasure Island3		
MusselsImage: Sector of the secto	1 4	Zn
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Oysters 90 days Redwood Creek 5 • • • 90 days Treasure Island 4 • • • • • 90 days Dumbarton Bridge 4 • • • • • 90 days Dumbarton Bridge 4 • • • • • 90 days Pt Pinole 4 • • • • • Phase II • • • • • • •		
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90 days Treasure Island 6 + + + +	•	•
90 days Dumbarton Bridge 6 * * * *	*	*
90 days Davis Point 4 + +	+	
90 days Coyote Creek 5 • •	•	•
90 days Pt Pinole 5 * * *	4	•
120 days Redwood Creek 6 • • •		*
120 days Treasure Island 6 • • • •	•	
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90 days Treasure I-depurated 6 • • • •	•	•
90 days Dumbarton-depurated 6 • • • •		
90 days Redwood-deep 6 • • • •		
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		+
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90 days Dayis Point 5 • • •	•	

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		Table 15		
CONTAMINA	NTS IN SOUTH, CENTRAL AN	ID NORTH BAY	MUSSELS	
	MEAN	MEAN	MEAN	PREDOMINANT
CONTAMINANT	SOUTH	TREASUREI	NORTH	TREND
SLVER	0.305	0.345	0.15	NORTHLOW
CADMIUM	7.25	8.3	9.5	NORTH SLIGHTLY HIGH
COPPER	10	12.5	12.1	CENTRAL NORTH SLIGHTLY HIGH
MERCURY	0.25	0.295	0.235	NONE
LEAD	2.355	2.5	3.05	NORTH SLIGHTLY HIGH
SELENIUM	1.75	3.1	2.55	NORTH, CENTRAL SLIGHTLY HIGH
ZINC	230	230	230	NONE
SUM DOT	226.5	68	92	SOUTHHIGH
SUM CHLORDANE	60.05	20.35	17	SOUTHHIGH
SUM PAH	429.5	936	246.5	CENTRAL AND SOUTH HIGH
SUMPCB	391.5	213	86.5	SOUTH AND CENTRAL HIGH
ME	ANS ARE FROM TWO VALU	ES (PHASE 1 A	ND PHASE II)	

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R	ATIOS BETWE	EN MUSSELS AN	DOYSTERS		MEAN					MEAN
		MUSSELS	OVSTERS	RATIO	RATIO		MUSSELS	OVSTEPS	RATIO	RATIO
D	DT	117	132	0.89		COPPER	13	240	0.05	
		72	110	0.65			13	200	0.07	
		58	97	0.60			7.5	253	0.03	
[]		73	124	0.59			9	180	0.05	
		267	228	1.17	0.78		10	417	0.02	0.04
a a	LORDANE	18	18	1.00		MERCURY	0.27	0.12	2.25	
		17	31	0.55			0.3	0.13	2.31	
		19	20	0.95			0.2	0.13	1.54	
		25	25	1.00			0.22	0.12	1.83	
		92	70	1.31	0.96		0.2	0.2	1.00	1.79
SU	MPAHS	104	807	0.13		MANGANESE	26	49	0.53	
		621	1905	0.33			26	76	0.34	
		99	773	0.13			23.6	95	0.25	
-		116	978	0.12			32	88	0.36	
		659	1423	0.60	0.26		22.9	56	0.41	0.38
50	MPCBS	129	169	0.76		LEAD	2.2	0,52	4,23	
, 1		300	318	0.94			2.5	0.51	4,90	
·	· · · · · · · · · · · ·	187	263	0.71			1.8	0.59	3.05	
		252	299	0.84			1.9	0.54	3.52	
		647	368	1.76	1.00		3.9	1.6	2.44	3.63
SL	VER	0.2	5.9	0.03		SELENIUM	2.6	2.7	0.96	
1		0.92	6.1	0.15			3	3.5	0,86	
		0.3	8.3	0.04			2.3	3.5	0.66	
		0.41	5.9	0.07			1.2	3.3	0.36	
		0.1	8	0.01	0,06		2.5	4.3	0.58	0.68
CA	DMIUM	8.9	6.1	1.46		ZNC	260	1100	0.24	
		7.6	6.6	1.15			260	1100	0.24	
		9.8	8	1.23			240	1400	0.17	
		7	7.8	0.90			250	900	0.28	
		10.1	8.1	1.25	1.20		200	1133	0.18	0.22
OH OH	POMUM	15	6	2.50		ALUMINUM	1433	410	3.50	
		8	2.8	2.86			1233	770	1.60	
		6.1	5	1.22			1400	640	2.19	
		9.7	1,8	5.39			1633	953	1.71	
		4.8	4.1	1,17	2.63		1800	750	2.40	2.28

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Table 17

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Relative rankings of heavy metal concentrations at times of 0, 1, 2, 3, and 4 months in musses in Phase I and It

bevic Blavram	d by Knes are not eignifican	Hy different.					
1376	W	8	8	9	E	æ	
Redwood Creek	4 6 2 1 0 4	2 7 0 7 6	0 3 4 2 1	2 3 4		2 6 1 7 0	0
Treesure Island	0 I 2 3 4		0 2 4 3	E	0 1 2 4 3	7 6 1 2 0	-
1 194					•••		
Redended Creek	0 3 1 2 4	2 0 5	2 7 6 1 0		2 7 6 6 0	0 1 3 2 4	• I
Traeure Island	4 0 1 2 3 4	4 3 2 0 1	2 2 3			0 2 7 3	-
Dumbarton Br	0	2 0 5 7	0 1 2 3	C Z I 7	0 2 1 4 3	C 7 2 1 0	-
Average Rartus: Rowal to Nigha Press I	et merða) 0.0 1.0 2.0 3.0 4.0 0.0 1.7 1.7 2.7 4.0	3.5 1.6 0.5 3.6 1.0 4.0 3.0 0.7 1.3 1.0	0.0 2.5 4.0 2.5 1.0 0.0 1.0 2.3 3.3 3.3	0.0 2.6 2.0 2.6 3.6 0.0 3.0 2.0 2.7 2.3	0.0 1.8 1.6 4.0 3.0 0.0 1.1 1.7 3.7 3.0	0.0 0.0 0.1 0.0 0.0 0.0 0.0 0.1 0.0 0.0	0.0 2.0 0.0 1.7 1
Overall	0.0 1.4 1.8 2.8 4.0	3.8 2.4 0.8 2.2 1.0	0.0 1.8 3.0 3.0 2.4	0.0 2.8 2.0 2.8 2.8	0.0 1.6 1.6 3.8 3.0	0.0 1.6 1.6 3.2 3.2	0.0 1.0
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