# CHEMICAL AND BIOLOGICAL MEASURES OF SEDIMENT QUALITY IN McGRATH LAKE



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California Regional Water Quality Control Board, Los Angeles Region

Moss Landing Marine Laboratories

California Department of Fish and Game
Marine Pollution Studies Laboratory

University of California, Santa Cruz

Institute of Marine Sciences

## AUTHORS

Michele Jacobi, Russell Fairey, Cassandra Roberts, Eli Landrau, and James Downing
San Jose State University Foundation- Moss Landing Marine Laboratories

John Hunt, Brian Anderson, and Bryn Phillips
University of California Santa Cruz- Institute of Marine Sciences

Max Puckett
California Department of Fish and Game

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| | | |
|---|---|---|
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| | | |
|---|---|---|
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| Michele Jacobi | Eli Landrau | |

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| | |
|---|---|
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| | | |
|---|---|---|
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| | | |
|---|---|---|
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## LIST OF ABBREVIATIONS

| | |
|---|---|
| AA | Atomic Absorption |
| ASTM | American Society for Testing Materials |
| AVS | Acid Volatile Sulfide |
| BPTCP | Bay Protection and Toxic Cleanup Program |
| CDFG | California Department of Fish and Game |
| CH | Chlorinated Hydrocarbon |
| COC | Chain of Custody |
| COR | Chain of Records |
| EDL | Elevated Data Levels |
| ERL | Effects Range Low |
| ERM | Effects Range Median |
| EqP | Equilibrium Partitioning Coefficient |
| FAAS | Flame Atomic Absorption Spectroscopy |
| GC/ECD | Gas Chromatograph Electron Capture Detection |
| GFAAS | Graphite Furnace Atomic Absorption Spectroscopy |
| HCl | Hydrochloric Acid |
| HDPE | High-density Polyethylene |
| HMW PAH | High Molecular Weight Polynuclear Aromatic Hydrocarbons |
| $HNO_3$ | Nitric Acid |
| HPLC/SEC | High Performance Liquid Chromatography Size Exclusion |
| $H_2S$ | Hydrogen Sulfide |
| IDORG | Identification and Organizational Number |
| KCL | Potassium Chloride |
| $LC_{50}$ | Lethal Concentration (to 50 percent of test organisms) |
| LMW PAH | Low Molecular Weight Polynuclear Aromatic Hydrocarbons |
| MDL | Method Detection Limit |
| MDS | Multi-Dimensional Scaling |
| MLML | Moss Landing Marine Laboratories |
| MPSL | Marine Pollution Studies Laboratory |
| $NH_3$ | Ammonia |
| NIST | National Institute of Standards and Technology |
| NOAA | National Oceanic and Atmospheric Administration |
| NS&T | National Status and Trends Program |
| NOEC | No Observed Effect Concentration |
| PAH | Polynuclear Aromatic Hydrocarbons |
| PCB | Polychlorinated Biphenyl |
| PEL | Probable Effects Level |
| PPE | Porous Polyethylene |
| PVC | Polyvinyl Chloride |
| QA | Quality Assurance |
| QAPP | Quality Assurance Project Plan |
| QC | Quality Control |
| REF | Reference |

**List of Abbreviations (cont.)**

| | |
|---|---|
| RWQCB | Regional Water Quality Control Board |
| SPARC | Scientific Planning and Review Committee |
| SQC | Sediment Quality Criteria |
| SWRCB | State Water Resources Control Board |
| T | Temperature |
| TBT | Tributyltin |
| TFE | Tefzel Teflon® |
| TEL | Threshold Effects Level |
| TOC | Total Organic Carbon |
| TOF | Trace Organics Facility |
| TON | Total Organic Nitrogen |
| UCSC | University of California Santa Cruz |
| USEPA | U.S. Environmental Protection Agency |

Units
liter = 1 l
milliliter = 1 ml
microliter = 1 µl
gram = 1 g
milligram = 1 mg
microgram = 1 µg
nanogram = 1 ng
kilogram = 1 kg
1 part per million (ppm) = 1 mg/kg, 1 µg/g
1 part per billion (ppb) = 1 µg/kg, 1 ng/g
1 part per trillion (ppt) = 1 ng/kg

## INTRODUCTION

McGrath Lake is a coastal backdune lake and part of McGrath State Beach, which is located in the city of Ventura, in Ventura County. McGrath State Beach provides habitat for a variety of resident and migratory wildlife, including the endangered California Least Tern and the threatened Western Snowy Plover. Under the City of Oxnard's General Plan, McGrath State Beach has been designated a conservation and resource protection area. The adjacent Santa Clara River Estuary was designated as a State Natural Preserve in 1979. McGrath Lake is owned by the California Department of Parks and Recreation and is managed for low intensity uses, such as hiking and nature observation; however, the area immediately surrounding McGrath State Beach has a variety of industrial uses. There is an oil-related facility directly north of McGrath Lake, owned by Berry Petroleum Company, and an operational power plant to the south of the lake, run by Mandalay Power. To the east of McGrath Lake there are oilwells, park lands, and agricultural fields. Adjacent and to the west of McGrath Lake are coastal dunes and the Pacific ocean. McGrath Lake has no ocean outlet, although waves occasionally overwash the beach berm, and there have been unregulated breaches of the lake during flood conditions. The primary sources of water to the lake are irrigation and drainage runoff, groundwater, and rainfall (California Department of Parks and Recreation, 1979). The north end of the lake is held in private ownership, and in granting the park property to the State, the property owner retained the right to control McGrath Lake water levels within a specified ranged.

Historically, the land surrounding McGrath Lake was probably part of the Rancho Rio de Santa Clara (Schwartzberg and Moore, 1995). This area was used for raising cattle and sheep until the mid 1800's. During the late 1800's and early 1900's, crop and oil production began to occur in the land surrounding the Santa Clara River and persists today. In December 1993, there was a release of crude oil into McGrath Lake by the Berry Petroleum Company. Following this incident, the McGrath Trustee Council was established and designated with the responsibility of restoring natural resources affected by the oil release.

The purpose of this study was to provide a detailed characterization and assessment of McGrath Lake based upon physical characterization, water and sediment chemical analyses, toxicity tests, and benthic community analysis. This characterization was requested in response to the oil spill. It is further substantiated by Bay Protection and Toxic Cleanup Program (BPTCP) data, which indicated sediment samples from McGrath Lake had elevated levels of pesticides and metals (Anderson et al., 1998). This study was to determine if elevated contaminant levels have continued to be present in sediments and waters of McGrath Lake, and whether or not adverse biological effects are associated with identified contaminants. An initial reconnaissance survey of the lake occurred during July 1998. Data from this sampling effort were used to plan the second phase of sampling, which occurred in October 1998 and included more detailed analyses of samples. Results gained from this study will be used by the RWQCB and other parties, such as the McGrath

Lake Trustee Council, in decisions concerning management and restoration objectives for McGrath Lake.

## METHODS

### *Summary of Sampling Design*

An initial reconnaissance of the lake was performed to define physical characteristics, such as depth, sediment type, and basic water column parameters (dissolved oxygen, conductivity, pH, turbidity, etc.) in July 1998. The lake was subdivided by ten transects between the north and south ends of the lake, with each transect being approximately 75 meters apart. PVC stakes were placed at both ends of the transect line and five samples were taken at roughly equal distances along the transect line. Two additional stations were selected at locations along the main agricultural drainage, which empties into the northern end of the lake. A station also was selected where the agricultural drainage enters the lake, immediately adjacent to a diesel truck pump. For the remainder of the report the station nearest the diesel truck pump will be referred to as the pumphouse station. One additional station also was selected near the ocean berm where infrequent breaching occurs. A total of 54 stations were sampled during the reconnaissance survey, using an aluminum skiff as a sampling platform (Figure 1). Stations were located using GPS (Magellan NAV 50000 system), however, during this sampling event differentially corrected positions could not be obtained due to difficulties in obtaining a receiving signal. Sediment samples were collected for grain size and TOC analyses and water column profiles were conducted using a multi-parameter water quality data logger (Solomat, WP803). Upon completion of all other sampling, an initial screening for presence of resident fish was conducted. Fish surveys were performed along the western edge of the lake near transects N3 and M6 at two locations, using a 100 ft nylon net beach seine. Eight mosquito fish (*Gumusia* sp.) were captured, but no further analysis occurred.

After the reconnaissance survey was completed, detailed map profiles of the lake were prepared and used to select representative stations for a more detailed characterization of the lake. A subsequent sampling trip in October 1998 allowed for more in depth analysis of one station per transect. Agricultural drainage station # 1 and the pumphouse station also were sampled for more detailed characterization. A total of 12 stations were sampled during the characterization phase, using an inflatable zodiac as a sampling platform (Figure 1). An additional station was planned for groundwater sampling at a local well, however, access was not granted to the site and the sample was abandoned.

Detailed characterization of stations involved collecting four liters of surficial sediment (top 5 cm) to perform trace metal and trace organic chemical analyses, TOC analysis, grain size analysis, and sediment toxicity. In addition, three replicate cores of sediment were collected and sieved for benthic community analysis. Water quality profiles, similar to those collected during the reconnaissance survey, were recorded. Subsurface water samples were collected at five stations (one from the north, central and south end of the

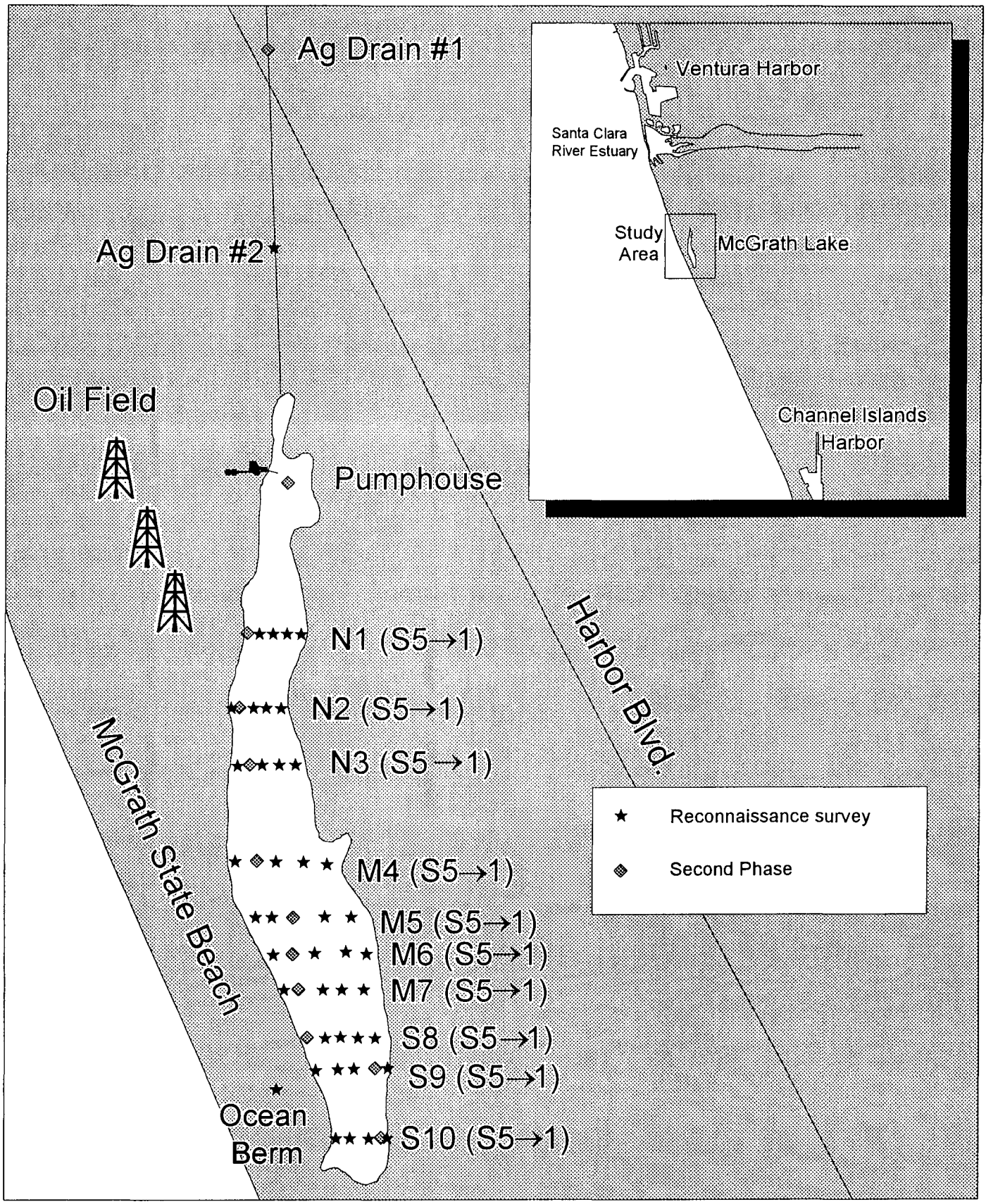


Figure 1. Overview of study area. During the reconnaissance survey, 54 stations were sampled along the trans lines and at various points around McGrath Lake. Twelve stations then were investigated further during the sec sampling phase.

lake, one at the agricultural drain and one at the pumphouse station) for nutrient analysis, trace organic and trace metal chemistry analyses and water column toxicity analysis.

At one station along transects 1, 2, 3, 5, 7, 9 & 10 (n=7) deep sediment cores were collected to the greatest depth possible. Two cores were taken at each selected station to obtain enough sediment volume for analyses. Cores were sub-sectioned at 30 cm depth intervals and sediment from each depth interval was homogenized. Each depth interval then was analyzed for TOC, trace metals, and trace organic compounds.

### *Summary of Sampling Methods*

#### Cleaning Procedures

All sampling equipment (i.e., containers, container liners, scoops, water collection bottles, and deep cores) was made from non-contaminating materials and was pre-cleaned and packaged protectively prior to entering the field. Sample collection gear and samples were handled only by personnel wearing non-contaminating polyethylene gloves. All sample collection equipment was cleaned by using the following sequential process:

Two-day soak and wash in Micro® detergent, three tap-water rinses, three deionized water rinses, a three-day soak in 10% HCl, three ASTM Type II Milli-Q® water rinses, air dry, three petroleum ether rinses, and air dry.

All cleaning after the Micro® detergent step was performed in a positive pressure "clean" room to prevent airborne contaminants from contacting sample collection equipment. Air supplied to the clean room was filtered.

Sample storage containers were cleaned in accordance with the type of analysis to be performed upon its contents. All containers were cleaned in a positive pressure "clean" room with filtered air to prevent airborne contaminants from contacting sample storage containers.

Plastic containers (HDPE or TFE) for trace metal analysis media (sediment, archive sediment, and subsurface water) were cleaned by: a two-day Micro® detergent soak, three tap-water rinses, three deionized water rinses, a three-day soak in 10% HCl or $HNO_3$, three Type II Milli-Q® water rinses, and air dry.

Glass containers for total organic carbon, grain size or synthetic organic analysis media (sediment, archive sediment, and subsurface water), and additional Teflon® sheeting cap-liners were cleaned by: a two-day Micro® detergent soak, three tap-water rinses, three deionized water rinses, a three-day soak in 10% HCl or $HNO_3$, three Type II Milli-Q® water rinses, air dry, three petroleum ether rinses, and air dry.

## Sediment Sample Collection

All sampling locations (latitude & longitude) were verified using a Magellan NAV 5000 Global Positioning System, and recorded in the field logbook. For the sediment sample, personnel sampled the station using polycarbonate cores (diver cores). Diver cores were 10 cm diameter and 30 cm in length. Samplers entered a station location from one end and sampled in one direction, so as to not disturb the sediment with their feet. Cores were taken to a depth of at least 15 centimeters. Sediment was extruded out of the top end of the core to the prescribed depth of 5 cm, removed with a polycarbonate spatula and deposited into a cleaned pre-labeled polycarbonate tub. Additional samples were taken with the same seawater rinsed core tube until the required total sample volume was attained. Between cores, the sediment sample in the container was covered with a Teflon® sheet, and the container covered with a lid and kept cool. When a sufficient amount of sediment was collected, the sample was covered with a Teflon® sheet assuring no air bubbles. A second, larger Teflon® sheet was placed over the top of the container to ensure an air tight seal, and nitrogen was vented into the container to purge it of oxygen.

## Deep Core Sediment Collection

Deep core sediment samples were taken using pre-cleaned 2 meter acrylic tubes. Samplers pushed deep cores into the sediment as deep as the surrounding sediments allowed (approximately .3 to 1.6 meters). Deep cores then were capped and returned to the shore for sectioning. The top five centimeters of mud was discarded from each core because a representative sample for that sediment layer already had been taken by diver core. Cores then were sectioned into 30 cm sections using a stainless steel hacksaw. Due to the varying depths in which cores penetrated, the deepest section was not always 30 cm in length. Sediment from each section was extruded out the core and placed into separate pre-labeled polycarbonate tubes. Samples then were covered with Teflon® and nitrogen was vented into the container to purge it of oxygen.

## Subsurface Water Sample Collection

Subsurface water samples were taken at representative stations throughout the lake and at the pumphouse and agricultural drainage stations. These samples were taken using a kayak, before any other activity in the lake. Air-filled collecting bottles were inverted and placed below the lake's surface (approximately 0.3 m when possible), triple rinsed, the bottles then were righted and allowed to fill completely with water. Samples were stored on ice and shipped to the appropriate laboratory for analysis.

## Benthic Sample Collection

Replicate benthic samples (n=3) were obtained from diver cores at predetermined stations. The coring device was 10 cm in diameter and 14 cm in height, enclosing a 0.0075 $m^2$ area. Corers were placed into sediment with minimum disruption of the surface sediments, capturing essentially all surface-active fauna as well as species living deeper in the sediment. Corers were pushed about 12 cm into the sediment and retrieved by digging

along one side, removing the corer and placing the intact sediment core into a PVC screening device. Sediment cores were sieved through a 0.5 mm screen and residues (e.g., organisms and remaining sediments) were rinsed into pre-labeled storage bags and preserved with a 10% formalin solution. After 3 to 4 days, samples were rinsed and transferred into 70% isopropyl alcohol and stored for future taxonomy and enumeration.

**Transport of Samples**

All sample containers were packed with enough ice to keep them at 4°C for 48 hours. Each container was sealed in large plastic bags closed and with a cable tie to prevent contact with other samples or ice or water. Ice chests then were driven back to the laboratory by the sampling crew or shipped overnight to the appropriate laboratory.

**Homogenization and Aliquoting of Samples**

All sample identification information (station numbers, etc.) was recorded on Chain of Custody (COC) and Chain of Record (COR) forms prior to homogenizing and aliquoting. A single container was placed on plastic sheeting while also remaining in original plastic bags. The sample was stirred with a polycarbonate stirring rod until mud appeared homogeneous.

All pre-labeled sample jars were filled using a clean Teflon® or polycarbonate scoop and stored in freezer/refrigerator (according to media/analysis) until analysis. The sediment sample was aliquoted into appropriate containers for trace metal analysis, organic analysis, and bioassay testing. Samples were placed in boxes sorted by analysis type. Sample containers for sediment bioassays were placed in a refrigerator (4°C) while sample containers for sediment chemistry (metals, organics, TOC and grain size) were stored in a freezer (-20°C).

**Chain of Records & Custody**

Chain-of-records documents were maintained for each station. Each form was a record of all sub-samples taken from each sample. IDORG (a unique identification number for only that sample), station numbers and station names, leg number (sample collection trip batch number), and date collected were included on each sheet. A Chain-of-Custody form accompanied every sample so that each person releasing or receiving a subsample signs and dates the form.

***Total Organic Carbon Analysis of Sediments***

**Summary of Methods**

Samples were received in the frozen state and allowed to thaw at room temperature. Source samples were gently stirred and sub-samples were removed with a stainless steel spatula and placed in labeled 20 ml polyethylene scintillation vials. Approximately 5 grams equivalent to dry weight of the wet sample was sub-sampled.

Sub-samples were treated with two, 5 ml additions of 0.5 N, reagent grade HCl to remove inorganic carbon ($CO^{-3}$), agitated, and centrifuged to a clear supernate. Some samples were retreated with HCl to remove residual inorganic carbon. The evolution of gas during HCl treatment indicates the direct presence of inorganic carbon ($CO^{-3}$). After HCl treatment and decanting, samples were washed with approximately 15 ml of deionized-distilled water, agitated, centrifuged to a clear supernate, and decanted. Two sample washings were required to remove weight determination and analysis interferences.

Prepared samples were placed in a 60° C convection oven and allowed to come to complete dryness (approximately 48 hrs.). Visual inspection of the dried sample before homogenization was used to ensure complete removal of carbonate containing materials (shell fragments). Two 61 mm (1/4") stainless steel solid balls were added to the dried sample, capped and agitated in a commercial available ball mill for three minutes to homogenize the dried sample.

A modification of the high temperature combustion method, utilizing a Weatstone bridge current differential was used in a commercially available instrument (Control Equipment Co., 440 Elemental Analyzer) to determine carbon and nitrogen concentrations. The manufactures suggested procedures were followed. The methods are comparable to the validation study of USEPA method MARPCPN I. Two to three aliquots of 5-10 mg of dried prepared sub-sample were used to determine carbon and nitrogen weight percent values. Calibration of the instrument was with known standards using Acetanilide or L-Cystine. Detection limits are 0.2 ug/mg carbon and 0.01 ug/mg nitrogen dry weight. The above methods and protocols are modifications of several published papers, reference procedures and analytical experimentation experience (Franson, 1981; Froelich, 1980; Hedges and Stern, 1983; MARPCPN I, 1992).

**Quality Control/Quality Assurance**

Quality control was tested by the analysis of National Research Council of Canada Marine Sediment Reference Material, BCSS-1 at the beginning and end of each sample analysis set (20-30 individual machine analyses). All analyzed values were within suggested criteria of $\pm$ 0.09% carbon (2.19% Average). Nitrogen was not reported on the standard data report, but was accepted at $\pm$ 0.008% nitrogen (0.195% Average) from the EPA study. Quality assurance was monitored by re-calibration of the instrument every twenty samples and by the analysis of a standard as an unknown and comparing known theoretical percentages with resultant analyzed percentages. Acceptable limits of standard unknowns were less than $\pm$ 2%. Duplicate or triplicate sample analysis variance (standard deviation/mean) greater than 7% was not accepted. Samples were rehomogenized and reanalyzed until the variance between individual runs fell below the acceptable limit of 7.0%.

*Grain Size Analysis of Sediments*

**Summary of Methods**

The procedure used combined wet and dry sieve techniques to determine particle size of sediment samples. Methods follow those of Folk (1974).

**Sample Splitting and Preparation**

Samples were thawed and thoroughly homogenized by stirring with a spatula. Spatulas were rinsed of all adhering sediment between samples. Size of the subsample for analysis was determined by the sand/silt ratio of the sample. During splitting, the sand/silt ratio was estimated and an appropriate sample weight was calculated. Subsamples were placed in clean, pre-weighed beakers. Debris was removed and any adhering sediment was washed into the beaker.

**Wet Sieve Analysis (separation of coarse and fine fraction)**

Beakers were placed in a drying oven and sediments were dried at less than 55°C until completely dry (approximately three days). Beakers were removed from drying oven and allowed to equilibrate to room temperature for a least a half-hour. Each beaker and its contents were weighed to the nearest 0.01 g. This weight minus the empty beaker weight was the total sample weight. Sediments in beakers were disaggregated using 100 ml of a dispersant solution in water (such as 50 g Calgon/L water), and the sample was stirred until completely mixed and all lumps disappeared. The amount and concentration of dispersant used was recorded on the data sheet for each sample. Sample beakers were placed in an ultrasonic cleaner for 15 minutes for disaggregation. Sediment dispersant slurry was poured into a 63 μm (ASTM #230, 4 phi) stainless steel or brass sieve in a large glass funnel suspended over a 1L hydrometer cylinder by a ring stand. All fine sediments were washed through the sieve with water. Fine sediments were captured in a 1L hydrometer cylinder. Coarse sediments remaining in sieve were collected and returned to the original sample beaker for quantification.

**Dry Sieve Analysis (coarse fraction)**

The coarse fraction was placed into a pre-weighed beaker, dried at 55-65°C, allowed to acclimate, and then weighed to 0.01 g. This weight, minus the empty beaker weight, was the coarse fraction weight. The coarse fraction was poured into the top sieve of a stack of ASTM sieves having the following sizes: No. 10 (2.0 mm), 18 (1.0 mm), 45 (0.354 mm), 60 (0.25 mm), 80 (0.177 mm), 120 (0.125 mm), and 170 (0.088 mm). The stack was placed on a mechanical shaker and shaken at medium intensity for 15 minutes. After shaking, each sieve was inverted onto a large piece of paper and tapped 5 times to free stuck particles. The sieve fractions were added cumulatively to a pre-tared weighing dish, and the cumulative weight after each addition determined to 0.01g. The sample was

returned to its original beaker, and saved until sample computations were completed and checked for errors.

### Analytical Procedures

Fractional weights and percentages for various particle size fractions were calculated. If only wet sieve analysis was used, weight of fine fraction was computed by subtracting coarse fraction from total sample weight, and percent fine composition was calculated using fine fraction and total sample weights. If dry sieve was employed as well, fractional weights and percentages for the sieve were calculated using custom software on a Macintosh computer. Calibration factors were stored in the computer.

## *Subsurface Nutrient Analysis*

### Analytical Procedures

BC Laboratories Inc. performed subsurface nutrient analysis on selected stations. Total phosphorous was analyzed using EPA method # 365.4. The sample was heated in the presence of sulfuric acid, $K_2SO_4$, and HgSO, for two and one half hours. The residue was cooled and diluted to 25 ml and placed on the Technicon AutoAnalyzer for phosphorous determination. Nitrogen and nitrate were analyzed using EPA method 353.2. This method allows for the determination of nitrite singly, or nitrite and nitrate combined in water. A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that was originally present plus the reduce nitrate) was determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form highly colored azo dye, which is measured colorimetrically. Separate, rather than combined nitrate-nitrite, values are readily obtained by carrying this procedure first with, and then without, the Cu-Cd reduction step.

## *Trace Organic Analysis (PCBs, Pesticides, and PAHs)*

### Summary of Methods

Trace organic analysis of samples were conducted by Battelle Laboratories. Methods are briefly described below and are summarized from Battelle's data report (1999).

### Water and Filter Sample Extraction

Five water samples were analyzed with this sample set. One sample (the Pumphouse station) was filtered (vacuum filtered through a combusted glass fiber filter), and the filter and filtrate processed and analyzed separately. The filter was processed in the same manner as a sediment (discussed in detail below): the sample was spiked with surrogate internal standards, shaken with methylene chloride three times with three aliquots of

solvent, and the extracts combined. From this point, the filter extract and the water extracts were treated identically. The water samples were processed as per Battelle SOP 5-200, *Water Extraction for Trace Level Semi-Volatile Organic Contaminant Analysis.* The volume of water associated with the sample was measured, the sample was added to a separatory funnel, spiked with surrogate internal standards, and an aliquot of methylene chloride was added. The sample was shaken manually, and the solvent eluted from the funnel. This extraction procedure was repeated twice more, with two additional aliquots of solvent. The extracts were combined and dried over sodium sulfate. Each extract was cleaned through an alumina chromatography column (F-20, 2% deactivated). The final extract was concentrated to approximately 1 ml, spiked with recovery internal standards (to calculate the recovery of the surrogate internal standards), and split into two fractions. One was analyzed for PAH by GC/MS, and the other fraction was solvent exchanged into hexane and analyzed for chlorinated hydrocarbons by GC/ECD. Sample data are reported in units of ng/L.

**Sediment Sample Extraction**

Battelle SOP 5-190, *Tissue and Sediment Extraction for Trace Level Semi-Volatile Organic Contaminants* was followed for all sediment sample analyses. This is the standard operating procedure for implementation of NOAA National Status and Trends Program (NOAA, 1993) methodologies for sediment sample preparation. Approximately 30-g of well-mixed sediment was weighed into a Teflon® extraction jar, spiked with the appropriate surrogate internal standards, combined with solvent (methylene chloride) and sodium sulfate, and shaken for 12 hours; the extract was decanted into an Erlenmeyer flask. An additional 5-g aliquot of sediment homogenate was removed for percent moisture determination. Another aliquot of methylene chloride was added to the sediment extraction vessel, the sample was shaken for 4 hours, and the resulting solvent extracts combined in the Erlenmeyer flask. A third extraction was performed for 0.5 hr, and the extracts combined with the first two in the flask. The total extract was dried over sodium sulfate, processed through a 20 g F20 (2% deactivated) alumina column, and concentrated to 900 µL using Kuderna-Danish and nitrogen evaporation techniques. The concentrated extract was further purified using size-exclusion HPLC, a procedure that removes common contaminants that interfere with instrumental analysis, including lipid and elemental sulfur. The post-HPLC extract was concentrated to approximately 1 ml under nitrogen and the recovery internal standards added to quantify extraction efficiency. One half of the extract was analyzed by GC/MS for PAH; the remaining extract was solvent-exchanged with isooctane for chlorinated hydrocarbon analysis by GC/ECD. All data are surrogate corrected and reported on a dry weight basis.

Activated copper was used to remove the excess sulfur from the sample extracts, despite the fact it causes degradation of certain pesticides of interest. The quality control data indicate that chlorpyrifos and methoxychlor were moderately effected by this procedure; from previous experience it is noted that ethion, dacthal, and oxadiazinon behave in the same manner as chlorpyrifos and methoxychlor, therefore these two target analytes may be considered representative compounds.

**PAH Analysis**

Sample extracts were analyzed using a Hewlett-Packard 5972 GC/MS operated in the selective ion monitoring (SIM) mode, following Battelle SOP 5-157, *Identification and Quantification of Polynuclear Aromatic Hydrocarbons by Gas Chromatography/Mass Spectrometry*. This is the SOP for implementation of the NOAA National Status and Trends Program methods (NOAA, 1993). The GC was fitted with a 60-m 0.25-mm i.d., 0.25 μm film thickness DB-5 capillary column. The oven conditions were: initial temperature of 40 °C, ramp rate 6°C/min to 290 °C, hold 40 min. The instrument was initially calibrated using a 7-level calibration. The initial calibration was checked approximately every 8 samples by analyzing a mid-range calibration standard. All samples were bracketed by "passing" calibration standards, as defined in Battelle's table of Data Quality Objectives.

**PCB/Pesticide Analysis**

Sample extracts were analyzed on two different Hewlett-Packard 5890 Series II GC/ECD, following Battelle SOP 5-128, *Identification and Quantification of Polychlorinated Biphenyls (By Congener and Aroclor) and Chlorinated Pesticides by Gas Chromatography/Electron Capture Detection*. This standard operating procedure for our implementation of the NOAA National Status and Trends Program methods (NOAA, 1993). The GC was fitted with a 60-m 0.25-mm i.d., 0.25 μm film thickness DB-5 capillary column. The oven conditions were: initial temperature of 60 °C, ramp rate 10 °C/min to 140 °C, ramp rate 0.9 °C/min to 220° C, ramp rate 5 °C/min to 290°C, hold 15 minutes. Extracts were analyzed by instruments operating in the dual column mode (for confirmatory analysis). Data were acquired using a X-Chrom™ data system. Instruments were calibrated for the extended list of PCB congeners, the NOAA/Status & Trends congeners, and pesticides. Gamma-chlordene and 4,4'-DDMS were unavailable from any chemical standards vendor, and therefore are not included in the instrument calibration or matrix spiking solutions. Additionally as discussed, selected pesticides were not available immediately upon receipt of the samples and therefore are not included in the MS solutions. They have been included however in the calibrations and therefore are quantified in the samples. The instruments were initially calibrated using 5-level calibrations. The initial calibrations were checked approximately every 8 samples by analyzing a mid-range calibration standard. All samples were bracketed by "passing" calibration standards, as defined in Battelle's table of Data Quality Objectives. Deviations were reviewed and justified, and are reported in Section C of Battelle's report.

***Trace Metal Analysis***

**Summary of Methods**

Trace metals analyses were conducted at the California Department of Fish and Game's Trace Metals Facility at Moss Landing, CA. Table 1 indicates the trace metals analyzed

and lists method detection limits for sediments and water. These methods were modifications of those described by Evans and Hanson (1993), as well as those developed by the CDFG (1990).

Table 1. **Trace Metal Detection Limits**

| Analytes | MDL µg/g dry Sediment | MDL µg/L wet Water |
|---|---|---|
| Silver | 0.002 | 0.008 |
| Aluminum | 1 | 0.05 |
| Arsenic | 0.1 | 0.1 |
| Cadmium | 0.002 | 0.002 |
| Copper | 0.003 | 0.003 |
| Chromium | 0.02 | 0.03 |
| Iron | 0.1 | 2.0 |
| Mercury | 0.03 | 0.00002 |
| Manganese | 0.05 | 0.003 |
| Nickel | 0.1 | 0.006 |
| Lead | 0.03 | 0.002 |
| Antimony | 0.1 | NA |
| Tin | 0.02 | NA |
| Selenium | 0.1 | NA |
| Zinc | 0.05 | 0.02 |

**Trace Metal Analysis of Sediment**

Sediment Digestion Procedures

One gram aliquot of sediment was placed in a pre-weighed Teflon® vessel, and one ml concentrated 4:1 nitric:perchloric acid mixture was added. Vessels were capped and heated in a vented oven at 130° C for four hours. Three ml of hydrofluoric acid were added to the vessel, recapped and returned to an oven overnight. Twenty ml of 2.5% boric acid were added to the vessel and placed in oven for an additional 8 hours. Weights of Teflon® vessels and solution were recorded, and solution was poured into 30 ml polyethylene bottles.

Sediment Atomic Absorption Methods

Samples were analyzed on either a Perkin-Elmer ELAN 6000 Inductively Coupled Plasma (ICP)-MS or a Perkin-Elmer Flame Model 2280 AA. Samples, blanks, and standards were prepared using clean techniques in a clean laboratory. Milli-Q® water (MQ) and ultra clean chemicals were used for all standard preparations. Blanks and standard reference material were analyzed with each set of samples for sediments and water. Mercury samples were analyzed on a Perkin-Elmer Flow Injection Mercury System (FIMS). Samples, blanks, and standards were prepared using MQ water and ultra clean chemicals inside a clean laboratory.

**Trace Metal Analysis of Water**

Evaporation Methods

Two hundred fifty ml Teflon® beakers are removed from acid bath and rinsed thoroughly in MQ water. The beaker then is filled with MQ and placed on a hot plate in a laminar-flow clean hood, where it is heated on low for 20 to 30 minutes. MQ then is discarded and the beaker is rinsed with MQ again, dried on the hot plate and then cooled prior to weighing. The sample bottle is inverted to homogenize the sample. An aliquot then is weighed into the Teflon® beaker. This is generally 250 g, unless there is a great deal of sediment evident in the sample bottle. A blank also is made, consisting of 10 ml MQ plus 1.25 ml Q-$HNO_3$. The beaker chosen for the blank is rotated among those available. Beakers are placed on a hot plate on low temperature in a clean-air, laminar-flow hood. The blank is placed in the hood immediately adjacent to the hot plates. Samples are heated until dry. This generally takes 40-48 hours. Following evaporation, 1 ml of concentrated Q-$HNO_3$ is added to each beaker to redissolve the residue. Then 9 ml MQ are added to each beaker. This solution is rolled around the walls of the beaker to ensure dissolution of all salts. The weight then is recorded for the concentrated sample. The density for each sample is calculated following the weighing of small aliquots of sample. The weight of the concentrated sample then is converted into a volume. Concentrated samples are decanted into 30 ml low density polyethylene bottles for analysis. The Teflon® beakers are rinsed in MQ, scrubbed with 2N $HNO_3$, rinsed again in MQ, and then placed in a 6N HCl acid bath. Beakers are subsequently soaked in a Q-$HNO_3$ acid bath prior to reuse.

AA Methods For Water

Samples were analyzed by flameless AA on a Perkin-Elmer Zeeman 5000 Atomic Absorption Spectrophotometer equipped with an HGA 500 graphite furnace. Due to high concentrations, a few samples were analyzed using flame AA on a Perkin-Elmer 603 AAS. Samples and standards were prepared in a laminar-flow clean bench inside the trace metal laboratory. To ensure accurate results the samples were analyzed using the stabilized-temperature platform technique. The characteristic mass for each element was computed to ensure the proper functioning of the Zeeman AA. Samples may be analyzed using a matrix modifier made up from ultra-clean chemicals. When no modifier is used, high-char temperatures allow interfering matrix components of the sample to be volatized prior to atomization. Single spike additions to samples also allow a check for recovery when standards are linear. Finally, the SLRS-3 river water standard reference material is evapoconcentrated and analyzed with each set of samples.

*Toxicity Testing*

**Summary of Methods**

All toxicity tests were conducted at the California Department of Fish and Game's Marine Pollution Studies Laboratory (MPSL) at Granite Canyon. Toxicity tests were conducted by personnel from the Institute of Marine Sciences, University of California, Santa Cruz.

**Sediment Samples**

Bedded sediment samples were transported to MPSL from the sample-processing laboratory at Moss Landing in ice chests at 4°C. Transport time was one hour. Samples were held at 4°C, and all tests were initiated within 14 days of sample collection, unless otherwise noted in the Quality Assurance section. All sediment samples were handled according to procedures described in ASTM (1992) and BPTCP Quality Assurance Project Plan (Stephenson et al., 1994). Samples were removed from refrigeration the day before the test, and loaded into test containers. Water quality was measured at the beginning and end of all tests. At these times, pH, temperature, salinity, total ammonia, and dissolved oxygen were measured in overlying water from all samples to verify that water quality criteria were within the limits defined for each test protocol. Samples of overlying water for hydrogen sulfide measurement were taken at the beginning and end of each toxicity test. Interstitial water sample measurements were taken at the beginning and at the end of test. Hydrogen sulfide samples were preserved with zinc acetate and stored in the dark until time of measurement.

Estuarine Amphipod Survival Tests

Solid-phase sediment sample toxicity was assessed using the 10-day amphipod survival toxicity test protocols outlined in EPA 1994. All *Eohaustorius estuarius* were obtained from Northwestern Aquatic Sciences in Yaquina Bay, Oregon. Animals were separated into groups of approximately 100 and placed in polyethylene boxes containing Yaquina Bay collection site sediment, then shipped on ice via overnight courier. Upon arrival at Granite Canyon, the *Eohaustorius* were acclimated to 20‰ (T=15°C). Once acclimated, the animals were held for an additional 48 hours prior to addition to the test containers.

Test containers were one liter glass beakers or jars containing two cm of sediment and filled to the 700 ml line with control seawater adjusted to the appropriate salinity using spring water or distilled well water. Test sediments were not sieved for indigenous organisms prior to testing although at the conclusion of the test, the presence of any predators was noted and recorded on the data sheet. Test sediment and overlying water were allowed to equilibrate for 24 hours, after which 20 amphipods were placed in each beaker along with control seawater to fill test containers to the one liter line. Test chambers were aerated gently and illuminated continuously at ambient laboratory light levels.

Five laboratory replicates of each sample were tested for ten days. A negative sediment control consisting of five lab replicates of Yaquina Bay home sediment for *Eohaustorius* was included with each sediment test. After ten days, the sediments were sieved through a 0.5 mm Nitex screen to recover the test animals, and the number of survivors was recorded for each replicate.

Positive control reference tests were conducted concurrently with each sediment test using cadmium chloride as a reference toxicant. For these tests, amphipod survival was recorded in three replicates of four cadmium concentrations after a 96 hour water-only

exposure. A negative seawater control consisting of one micron-filtered Granite Canyon seawater, diluted to the appropriate salinity was compared to all cadmium concentrations. Amphipod survival for each replicate was calculated as:

$$\frac{\text{Number of surviving amphipods}}{\text{Initial number of amphipods}} \quad X\ 100$$

**Subsurface Water Samples**

Subsurface water sample toxicity was assessed using the mysid, *Neomysis mercedis* and followed protocols outlined by the EPA's acute test methods (EPA 1993). Juvenile *Neomysis* were exposed to subsurface water samples for 96 hours. Mysids were obtained from Brezina and Associates on November 3, 1998. Mysid juveniles were greater than 4 days old at test initiation. Five mysid juveniles were added to 200 ml of test solution in each of five replicate beakers. Mysids were counted daily and fed newly hatched *Artemia* twice per day. Test solutions were renewed 50% at 48 hours. The test was conducted at 17 ± 2 °C. with 16-h light/8 h dark photoperiod.

**Measurement of Ammonia and Hydrogen Sulfide**

Total ammonia concentrations were measured using an Orion Model 95-12 Ammonia Electrode. The concentration of unionized ammonia was derived from the concentration of total ammonia using the following equation (Whitfield 1974, 1978):

$$[NH_3] = [\text{total ammonia}] \times ((1 + \text{antilog}(pK_a^\circ - pH))^{-1}),$$

where $pK_a^\circ$ is the stoichiometric acidic hydrolysis constant for the test temperature and salinity. Values for $pK_a^\circ$were experimentally derived by Khoo et al. (1977). Method detection limit for total ammonia was 0.1 mg/L.

Total sulfide concentrations were measured on a spectrophotometer using a colorimetric method (Phillips et al. 1997). The concentration of hydrogen sulfide was derived from the concentration of total sulfide by using the following equation (ASCE 1989):

$$[H_2S] = [S^{2-}] \times (1 - ((1 + \text{antilog}(pK_a^\circ - pH))^{-1})),$$

where temperature and salinity dependent $pK_a^\circ$ values were taken from Savenko (1977). The method detection limit for total sulfide was 0.1 mg/L for the electrode method, and 0.01 mg/L for the colorimetric method. Values and corresponding detection limits for unionized ammonia and hydrogen sulfide were an order of magnitude lower than those for total ammonia and total sulfide, respectively. Care was taken with all sulfide and ammonia samples to minimize volatilization by keeping water quality sample containers capped tightly until analysis.

**Statistical Analysis of Toxicity Test Data**

Samples were defined as significantly more toxic than laboratory controls if the following criteria were met: 1) a separate variance t-test determined there was a significant difference ($\alpha<0.05$) in mean toxicity test organism response (e.g., percent survival) between the sample and the laboratory control and 2) mean organism response in the toxicity test was lower than a certain percentage of the control value, as determined using the 90th percentile Minimum Significant Difference (MSD).

Statistical significance in t-tests is determined by dividing an expression of the difference between sample and control by an expression of the variance among replicates. We used a "separate variance" t-test that adjusted the degrees of freedom to account for variance heterogeneity among samples. If the difference between sample and control is large relative to the variance among replicates, then the difference is determined to be significant. In many cases, however, low between-replicate variance will cause a comparison to be considered significant, even though the magnitude of the difference can be small. The magnitude of difference that can be identified as significant is termed the Minimum Significant Difference (MSD), which is dependent on the selected alpha level, the level of between-replicate variation, and the number of replicates specific to the experiment. With the number of replicates and alpha level held constant, the MSD varies with the degree of between-replicate variation. The "detectable difference" inherent to the toxicity test protocol can be determined by identifying the magnitude of difference that can be detected by the protocol 90% of the time (Schimmel et al., 1994; Thursby and Schlekat, 1993). This is equivalent to setting the level of statistical power at 0.90 for these comparisons. This is accomplished by determining the MSD for each t-test conducted, ranking them in ascending order, and identifying the 90th percentile MSD, the MSD that is larger than or equal to 90% of the MSD values generated. For *Eohaustorius* a MSD of 25 has been calculated, therefore a sample must have survivorship of less than 75% of the control response to be considered toxic. There has been no MSD calculated for *Neomysis*, therefore a sample was considered toxic if it was less than 80% of the control response (Thursby and Schlekat, 1993)

**Toxicity Test Acceptability and Evaluation**

Quality Assurance/Quality Control (QA/QC) guidelines, for the toxicity tests used in the BPTCP project, are summarized in the BPTCP Quality Assurance Project Plan (Stephenson et al., 1994). Test acceptability criteria from published protocols were evaluated for all tests. Quality assurance checklists were compiled that noted compliance for all tests with each of these criteria.

Evaluation codes were assigned to each deviation from QA/QC guidelines, and can be summarized as follows:
-3: sample has minor exceedences of QA criteria that were unlikely to affect assessments.
-9: not analyzed

It is recommended if assessments are made that are especially sensitive or critical, that the QA evaluations be consulted before using the data. Test data judged to be unacceptable are not reported, and samples from unacceptable tests are retested if necessary.

### *Benthic Community Analysis*

#### Summary of Methods

Each catalogued sample was processed individually in the laboratory to obtain an accurate assessment of species diversity and abundance. All macroinvertebrates were sorted from residues under a dissecting microscope, identified to lowest possible taxon, and counted. Laboratory processing of benthic cores consists of both rough and fine sorting. Initial sorting separates animals into large taxonomic groups such as polychaetes, crustaceans, mollusks and other (e.g., phoronids). Bound laboratory logbooks were maintained and used to record number of samples processed by each technician, as well as results of any sample resorts, if necessary. Sorters were required to sign and date a Milestone Progress Checksheet for each replicate sample processed. Specimens of similar taxonomic groups were placed in vials and labeled internally and externally with project, date collected, station information, and IDORG. In-house senior taxonomists and outside specialists processed and verified the accuracy of species identification and enumeration. An archived voucher specimen collection was established at this time.

## RESULTS AND DISCUSSION

Tabulated data for all physical, chemical, toxicological, and benthic analyses are presented in Appendices C, D, E, and F. The summary of data presented in the following results section was based on analyses of the full data set and is intended to present findings of chemical, biological, and toxicological significance in McGrath Lake.

### *Physical Characterization*

The reconnaissance survey of McGrath Lake in July 1998 found the lake to be 900 m in length and 140 m at its widest point; however, historically the lake has been known to overflow its boundaries and even flood Harbor Boulevard. It should be noted that the depth of McGrath Lake can change dramatically depending on water depth adjustments, controlled by pumping stations, or by rainfall. These large fluctuations in water depth make a clear definition of McGrath Lake's bathymetry difficult. During the reconnaissance sampling trip the lake's depth was measured at 50 stations, along 10 transect lines. Figure 2 shows a contour map of McGrath Lake's bathymetry. Contour lines for the depth gradient may be skewed slightly because of the way the lake was sampled (only along transect lines), especially in the deeper portion of the lake. A more randomized sampling

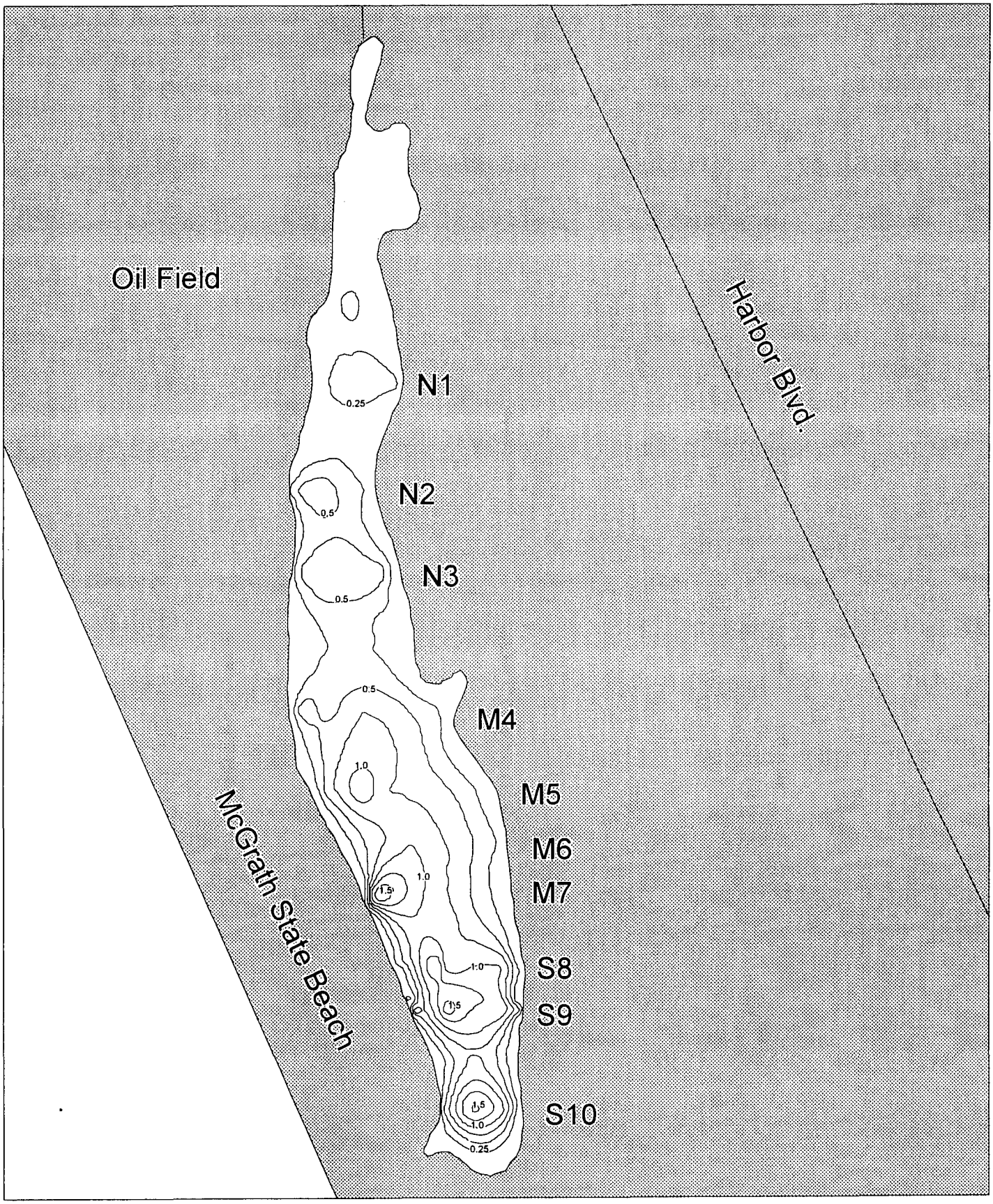


Figure 2. Bathymetry map of McGrath Lake based on the 51 stations sampled during the reconnaissance survey. Isobaths are at 0.25 m intervals with a maximum of 1.5 m depth.

design would have most likely provided a smoother depth profile of the lake. Despite this sampling artifact, McGrath Lake had an average depth of just over 0.6 m, with the lake's deepest point being 1.5 m. The southern portion of the lake tended to be deeper than the northern end of the lake and had an average depth of 0.9 m. The northern end of the lake probably was slightly shallower because of increased sedimentation rates due to runoff from the agricultural drainage, however sedimentation rates were not measured during this study.

Total organic carbon is of interest in this environment because sites with lower TOC values tend to allow chemical compounds to be more bioavailable to surrounding organisms (Di Toro et al., 1991) and pollutants may be of greater biological significance. TOC was measured at 53 stations in and around McGrath Lake with values ranging from 0.34 to 10.68 percent dry weight (Figure 3, Appendix D). A sediment sample could not be taken at station S10S1 due to excess detrital matter. TOC values had a tendency to be greatest in the central portion of the lake, with lesser values at the southern and northern extremes of the lake. The agricultural drainage sites, as well as the ocean berm site, had TOC values below one percent dry weight. Stations with greater TOC values have an increased binding capacity for chemical compounds (Di Toro et al. 1991), thus stations with greater TOC values, within a given transect, were chosen for a more detailed analysis during the second phase of sampling. The second sampling phase indicated TOC levels, at the selected stations, dropped approximately 50%. This change in TOC values may be attributed to several factors. During the reconnaissance trip a hand held sediment grab was used to collect sediment, rather than diver cores that were used during the second sampling phase. It is possible that the sediment grab samples, from the reconnaissance trip, had a greater concentration of TOC because the sediment depth sampled was shallower and had more detrital matter. Because there are notable differences in the total organic nitrogen (TON) concentrations, as well as TOC, the lower TOC values obtained in October can be attributed partially to differences between the two sampling methods. Subsequent laboratory analysis of the disparity between TOC values for the first and second sampling event indicated an abnormally high concentration of inorganic carbon (carbonates) in McGrath Lake sediments. The source of carbonates is unknown and may warrant future investigation. Varying TOC values also may be due to fluctuations in organic input into the lake. The lake is surrounded heavily by Toule rush (*Scirpus* spp.), as well as willow thickets (*Salix* spp.), and other vegetation. Input from decaying plant matter may increase TOC content considerably and may vary seasonally. It is interesting to note that when sampling the pumphouse station, people were observed removing brush from that end of the lake. Presumably because the dead plant material would clog the diesel truck's pump and thus it was removed, in turn the pumphouse station had relatively low TOC values.

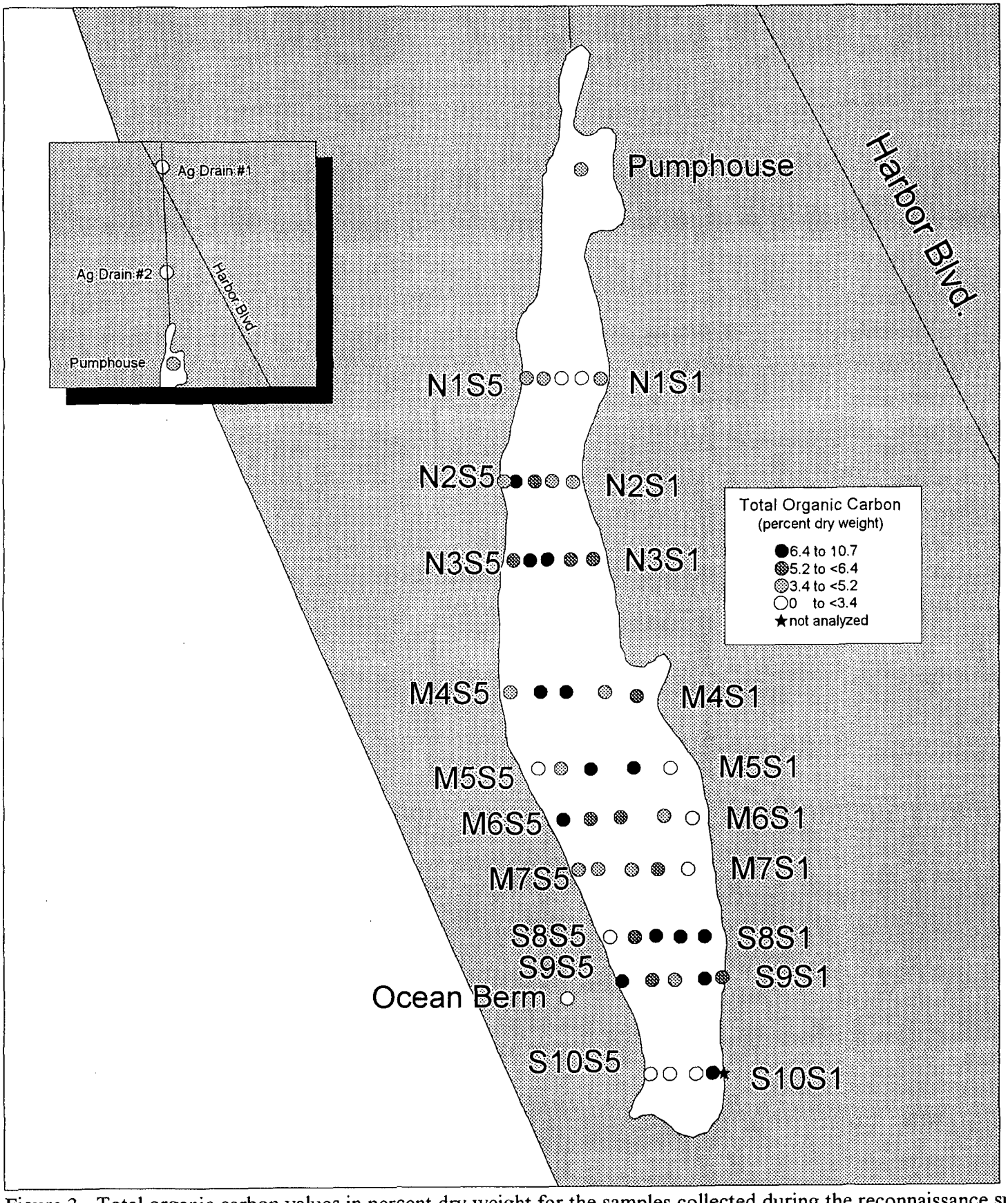


Figure 3. Total organic carbon values in percent dry weight for the samples collected during the reconnaissance surv of McGrath Lake.

Grain size was measured at 53 stations in and around McGrath Lake, with the majority of the lake having a relatively high degree of percent fine grain size (Figure 4, Appendix D). Grain size in the northern end of the lake ranged between 75-100 percent fines (% silt + % clay). Stations nearest the edge of the lake, as well as those at the southern extreme of the lake, tended to have a greater percentage fine sand rather than silt or clay. These differences in grain size may be caused by higher sedimentation rates in the northern end of the lake due to agricultural drainage and pumping actions. Those stations closer to the edge of the lake could have coarser sediment, possibly due to sand being blown in or deposited from the surrounding beach area. Grain size at the ocean berm station was predominately fine sand with almost no silt or clay like particles. The pumphouse station, which also may receive a high degree of sedimentation from the agricultural drainage, had a considerably greater percentage of silt and clay particles; however please note sedimentation rates were not calculated during this study and may be of interest in future investigations. Direct effects of grain size are difficult to assess because many factors co-vary with grain size, such as organic content, bacteria quantity, and quality and meiofaunal populations (Dale, 1974). Chemicals are known to be removed from solution by adsorption to particulates and that removal is a function of surface area; in sediments surface area increases with decreasing grain size and increasing particle angularity and/ or texture (Ott, 1986). Therefore, finer sediment within McGrath Lake may have greater chemical concentration, due to adsorption properties.

**Water Quality**

Basic water quality parameters, such as salinity, dissolved oxygen, turbidity, pH, and temperature were measure at 54 stations around McGrath Lake using a Solomat WP803 (Appendix B, Section III). Salinity within the lake ranged between 2.6 and 5.3 ‰ in shallower water and 4.08 and 24.30 ‰ in deeper waters. The greater salinity values occurred in the deeper portion of the lake between transects M4 and S8. There appeared to be a salt wedge existing between surface and deeper waters near the west end of the lake, with differences between surface and depth salinities as great as 19 ‰. This salinity stratification may have been a result of low circulation within the lake near the time of the reconnaissance survey. During the second phase of sampling this salinity gradient was not as distinct, and the greatest difference between surface and deeper waters was only 9 ‰. Circulation within the lake was probably greater during the second phase of sampling because water had been pumping into the lake for several days prior to the sampling event. Dissolved oxygen also was measured within the lake and ranged from 7.17 to 10.12 ppm during the reconnaissance survey, and 8.85 and 15.76 ppm during the second phase of sampling. There was little change in dissolved oxygen content with depth. Again these higher values during the second phase of sampling could be related to increased water

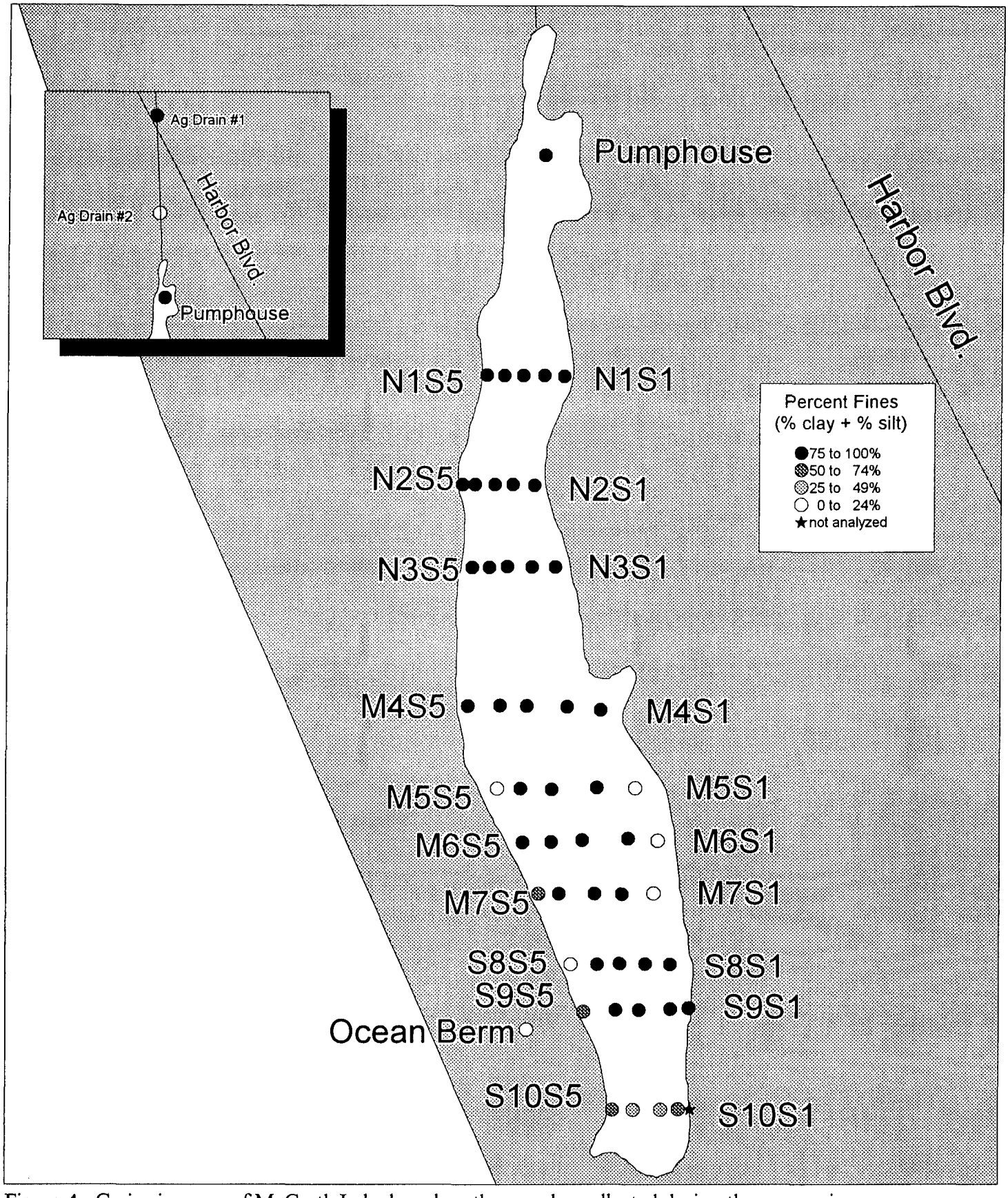


Figure 4. Grain size map of McGrath Lake based on the samples collected during the reconnaissance survey.

circulation. These values also may be due to increased algal photosynthesis during daylight hours. Percent dissolved oxygen saturation levels were consistently above 100% throughout the lake and were mostly above the calibration range of the Solomat instrument (values ranged between 120-902 %). Turbidity levels within the lake were relatively low with values ranging between 17.7 and 62.7 NTU. Turbidity was slightly lower at the south end of the lake, this was most likely due to decreased water movement in this portion of the lake. Mean water temperature within the lake during the reconnaissance trip in July was 24.8°C. The lake was slightly cooler during the second phase of sampling in October with a mean temperature of 19.5°C. The pH levels within the lake were alkaline and ranged between 8.24 and 9.39 during both phases of sampling.

**Subsurface Water Nutrient Analysis**

Nutrient samples were taken at five stations, which included the north, middle, and southern portions of McGrath Lake, as well as one sample at the pumphouse station and the agricultural drainage site. Nutrient concentration values are shown in Table 2. Nitrate concentrations were greatest at the agricultural drainage and at the pumphouse station; however, nitrate concentrations decreased at stations within the lake. Nitrite values displayed the opposite trend. The lowest nitrite values were found at the agricultural drainage and the pumphouse, with greater values of approximately 5.3 uM found throughout the lake. Phosphate values were greatest at the pumphouse station (9.1 uM) but were considerable less throughout the remainder of the lake. Irrigation runoff is McGrath Lake's primary source of water for McGrath Lake. Nitrogen and phosphorus often are present in agricultural drainage outflows, primarily due to the addition of fertilizers (Evans et al., 1995). These nutrients within estuarine systems are extremely complex and may strongly affect the delicate balance of undesirable algal blooms and more desirable flora (Evans et al. 1995). Water bodies that receive excess nutrient levels are more susceptible to eutrophication, however, the determination of acceptable nutrient levels is extremely difficult to assess. Acceptable nutrient levels depend on the size of the waterbody, the physical, biological, and chemical processes occurring within the waterbody, and the number of nutrient sources entering the waterbody (Tetra Tech, 1997). Despite these constraints nitrate values in McGrath Lake were comparable to similar agricultural areas, with high nutrient inputs. For example, the greatest nitrate value sampled in the Tembladero Slough, in Monterey county, had comparable nitrate values of 1745 uM. However, Tembladero Slough had considerably greater phosphate concentrations of 15.8 uM (Downing et al. 1998).

Table 2. Summary of Nutrient Data.

| STANUM | STATION | NITRATE uM | NITRITE uM | PHOSPHATE uM |
|---|---|---|---|---|
| 45024.0 | McGrath Lake Estuary-N2S4 | 1725.8 | 5.7 | 5.5 |
| 45053.0 | McGrath Lake Estuary-M5S3 | 1854.8 | 5.0 | 6.3 |
| 45092.0 | McGrath Lake Estuary-S9S2 | 1774.2 | 5.2 | 6.0 |
| 45003.0 | McGrath Lake Estuary-Pumphouse | 2548.4 | 2.6 | 9.1 |
| 45001.0 | McGrath Lake Estuary-Ag Drain | 3322.6 | 1.3 | 6.6 |

**Chemical Specific Screening Values**

Bioavailability is the key to understanding the relationship between sediment chemistry and biological impacts. However, using toxic identification evaluations (TIE's), bioaccumulation analyses, or other specialized methods to evaluate bioavailability were not possible during this limited study. In order to assess samples for their potential to impact biological resources, we compared sediment chemical concentrations to published guideline values derived from studies of approximately one thousand samples collected nationwide. These studies have used empirical observations of large data sets containing matching chemistry and biological data to provide guidance for evaluating the probability that measured contaminant concentrations may contribute to observed biological effects (MacDonald, 1994a,b; Long et al. 1995). While the reported guideline values were derived from sediments containing mixture of chemicals, they were calculated individually for each chemical. Their application may be confounded in sediments where biological responses are affected by synergistic or antagonistic interactions among multiple compounds by unmeasured or unidentified compounds, or by unconsidered physical factors. The following paragraphs provide a brief description of how these guideline values were calculated.

The National Status and Trends Program has used chemical and toxicological evidence from a number of modeling, field and laboratory studies to determine ranges of chemical concentrations which are rarely, sometimes, or usually associated with toxicity (Long and Morgan, 1992). Evaluation of available data (Long et al.,1995) has led to identification of three ranges in concentration for each chemical:

1) Minimal Effects Range: The range in concentration over which toxic effects are rarely observed;

2) Possible Effects Range: The range in concentrations over which toxic effects are occasionally observed;

3) Probable-Effects Range: The range in chemical concentrations over which toxic effects are frequently or always observed.

Two slightly different methods were used to determine these chemical ranges. One method developed by NOAA (Long and Morgan, 1990; Long et al., 1995) used chemical

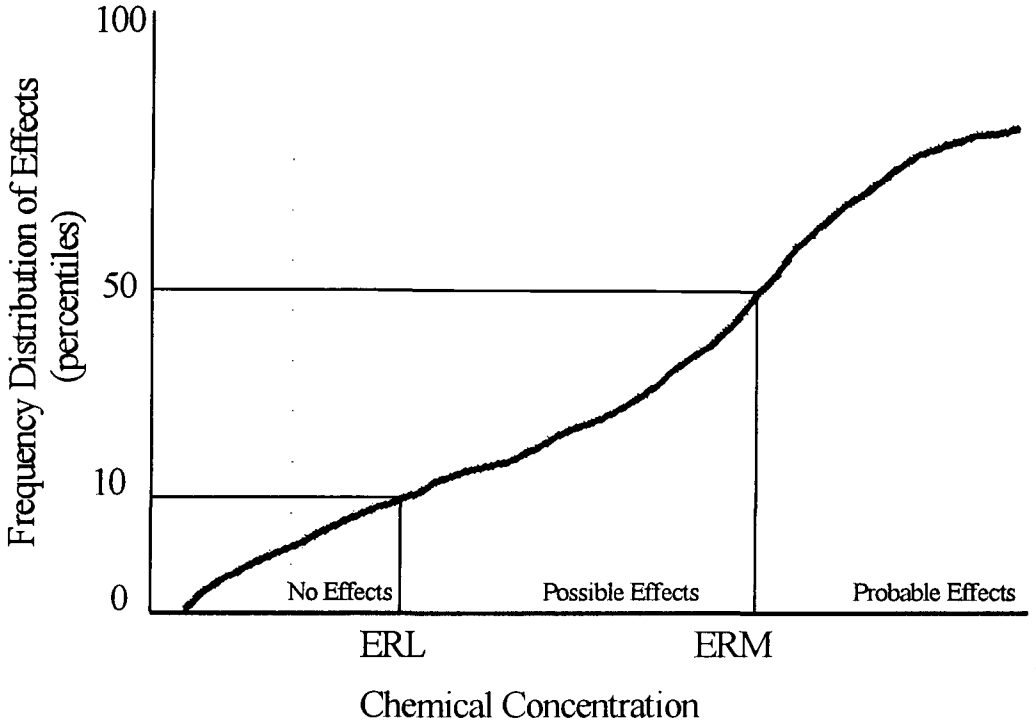


Figure 5. Conceptual outline of the relationships between the no effects, possible effects and probable effects ranges in chemical concentrations (from Long and MacDonald 1992).

data which were associated with a toxic biological effect. These data were used to determine the lower 10th percentile of ranked data, where the chemical level was associated with an effect (Effects Range-Low, or ERL). Sediment samples, in which all chemical concentrations were below the 30 ERL values, were not expected to be toxic. The Effects Range-Median (ERM) reflects the 50th percentile of ranked data and represents the level above which effects are expected to occur. Effects are expected to occur occasionally when chemical concentrations fall between the ERL and ERM (Figure 5). The probability of toxicity was expected to increase with the number and degree of exceedences of the ERM values.

Another method identifies ranges using chemical concentration data associated with both toxic biological effects and no observed effects (MacDonald, 1992; MacDonald, 1994a,b; MacDonald et al., 1996). The ranges are identified as TEL (Threshold Effects Level) and the PEL (Probable Effects Level). TEL values were derived by taking the geometric mean of the 50th percentile of the "no effects" data and the 15th percentile of the "effects" data. The PEL values were derived by taking the geometric mean of the 85th percentile of the "no effects" data and the 50th percentile of the "effects" data. Although different percentiles were used for these two methods, they are in close agreement, usually within a factor of 2. Values reported for both methods are shown in Table 3. Neither of these methods is advocated over the use of the other in this report.

Table 3. Comparisons of Sediment Quality Guideline Values Developed by the State of Florida and NOAA.

| | State of Florida (1) | | NOAA(2) | |
|---|---|---|---|---|
| Substance | TEL | PEL | ERL | ERM |
| **Organics (ng/g- dry weight)** | | | | |
| Total PCBs | 21.550 | 188.79 | 22.70 | 180.0 |
| PAHs | | | | |
| Acenaphthene | 6.710 | 88.90 | 16.00 | 500.0 |
| Acenaphthylene | 5.870 | 127.89 | 44.00 | 640.0 |
| Anthracene | 46.850 | 245.00 | 85.30 | 1100.0 |
| Fluorene | 21.170 | 144.35 | 19.00 | 540.0 |
| 2-methylnaphthalene | 20.210 | 201.28 | 70.00 | 670.0 |
| Naphthalene | 34.570 | 390.64 | 160.00 | 2100.0 |
| Phenanthrene | 86.680 | 543.53 | 240.00 | 1500.0 |
| Total LMW-PAHs | 311.700 | 1442.00 | 552.00 | 3160.0 |
| Benz(a)anthracene | 74.830 | 692.53 | 261.00 | 1600.0 |
| Benzo(a)pyrene | 88.810 | 763.22 | 430.00 | 1600.0 |
| Chrysene | 107.710 | 845.98 | 384.00 | 2800.0 |
| Dibenz(a,h)anthr acene | 6.220 | 134.61 | 63.40 | 260.0 |
| Fluoranthene | 112.820 | 1493.54 | 600.00 | 5100.0 |
| Pyrene | 152.660 | 1397.60 | 665.00 | 2600.0 |
| Total HMW-PAHs | 655.340 | 6676.14 | 1700.00 | 9600.0 |
| Total PAHs | 1684.060 | 16770.54 | 4022.00 | 44792.0 |
| Pesticides | | | | |
| p,p'-DDE | 2.070 | 374.17 | 2.20 | 27.0 |
| p,p'-DDT | 1.190 | 4.77 | n/a | n/a |
| Total DDT | 3.890 | 51.70 | 1.58 | 46.1 |
| Lindane | 0.320 | 0.99 | n/a | n/a |
| Chlordane | 2.260 | 4.79 | 2.00 | 6.0 |
| Dieldrin | 0.715 | 4.30 | n/a | 8.0 |
| Endrin | n/a | n/a | n/a | 45.0 |
| **Metals (μg/g-dry weight)** | | | | |
| Arsenic | 7.240 | 41.60 | 8.20 | 70.0 |
| Antimony | n/a | n/a | 2.00 | 25.0 |
| Cadmium | 0.676 | 4.21 | 1.20 | 9.6 |
| Chromium | 52.300 | 160.40 | 81.00 | 370.0 |
| Copper | 18.700 | 108.20 | 34.00 | 270.0 |
| Lead | 30.240 | 112.18 | 46.70 | 218.0 |
| Mercury | 0.130 | 0.70 | 0.15 | 0.7 |
| Nickel | 15.900 | 42.80 | 20.90 | 51.6 |
| Silver | 0.733 | 1.77 | 1.00 | 3.7 |
| Zinc | 124.000 | 271.00 | 150.00 | 410.0 |

(1) D.D. MacDonald, 1994a,b; (2) Long et al. 1995 & Long and Morgan, 1990

A cautionary note should be included; the degree of confidence which MacDonald (1994a,b) and Long et al. (1995) had in their respective guidelines varied considerably among chemicals. They express low confidence in the values derived for nickel, mercury, DDTs, chlordane, dieldrin, and endrin. When more data become available regarding these chemicals and their potential effects, their guidelines may be revised, probably increasing for some substances. Due to low confidence in guideline values, in the case of DDT, the guideline value of 100 um/g organic carbon (OC)was used (Swartz et al.,1994). This value was normalized to organic carbon, to which DDT strongly binds, therefore this TOC normalized value may be more reflective of DDT bioavailability in the environment.

In order to evaluate those chemicals for which no guideline values have been calculated, individual chemical concentrations were compared to the range of chemical concentrations collected by the Bay Protection and Toxic Cleanup Program. This database contains approximately 120 analytes measured in sediments throughout California's bays and estuaries. Based upon the number of samples analyzed for a specific chemical, and the number of samples that exceeded the method detection limit, the $90^{th}$ and $95^{th}$ percentiles were calculated for each chemical using the range of samples above the MDL (Table 4). These percentiles then were used to compare individual chemical concentrations relative to the range of concentrations throughout California.

Table 4. Individual Chemical Screening Values for the Bay Protection Toxic Cleanup Program (units are reported as used in appendices).

| Chemical Name | MDL | # Analyzed | # above MDL | Highest Value | 90% Threshold | 95% Threshold | ERM Guideline Value |
|---|---|---|---|---|---|---|---|
| Aluminum | 1 | 603 | 603 | 165,000 | 83,000 | 101,000 | n/a |
| Antimony | 0.1 | 603 | 603 | 52.8 | 3.35 | 5.35 | 25 |
| Arsenic | 0.1 | 544 | 544 | 1140 | 21.2 | 26 | 70 |
| Cadmium | 0.002 | 603 | 603 | 27.9 | 1.76 | 2.67 | 9.6 |
| Chromium | 0.02 | 603 | 603 | 860 | 212 | 250 | 370 |
| Copper | 0.003 | 603 | 603 | 7,800 | 300 | 400 | 270 |
| Iron | 0.1 | 603 | 603 | 336,300 | 55,300 | 59,900 | n/a |
| Lead | 0.03 | 603 | 603 | 2100 | 120 | 171 | 218 |
| Manganese | 0.05 | 603 | 603 | 1190 | 630 | 682 | n/a |
| Mercury | 0.03 | 603 | 603 | 9.14 | 0.969 | 1.54 | 0.7 |
| Nickel | 0.1 | 550 | 550 | 167 | 88 | 109 | 51.6 |
| Silver | 0.002 | 603 | 603 | 35.7 | 1.58 | 2.22 | 3.7 |
| Selenium | 0.1 | 544 | 386 | 35.7 | 1.09 | 1.9 | n/a |
| Tin | 0.02 | 603 | 603 | 92.9 | 9.03 | 12 | n/a |
| Zinc | 0.05 | 603 | 603 | 6,000 | 490 | 630 | 410 |
| Aldrin | 0.5 | 621 | 22 | 8.2 | 4.7 | 8.2 | n/a |
| Chloropyrifos | 1 | 444 | 130 | 78 | 28 | 44.4 | n/a |
| Total Chlordane | 3 | 612 | 403 | 246 | 44.57 | 69.5 | 6 |
| Dacthal | 0.2 | 465 | 59 | 25.2 | 7.51 | 19 | n/a |
| Total DDT | 5.4 | 621 | 507 | 3,569 | 235.5 | 471.9 | 46.1, 100/OC |
| p',p'-Dichlorobenzophenone | 3 | 465 | 46 | 63.3 | 30.6 | 35.2 | n/a |
| Dieldrin | 0.5 | 618 | 210 | 62.6 | 11.7 | 16.8 | 8 |
| Endosulfan I | 0.5 | 606 | 17 | 19.6 | 13.4 | 19.6 | n/a |
| Endosulfan II | 1 | 606 | 59 | 59.8 | 10.4 | 13.8 | n/a |
| Endosulfan Sulfate | 2 | 606 | 40 | 163 | 21 | 45.6 | n/a |
| Endrin | 2 | 618 | 15 | 21.8 | 16.4 | 21.8 | 45 |
| Ethion | 2 | 69 | 4 | 36.4 | 36.4 | 36.4 | n/a |
| alpha-HCH | 0.2 | 465 | 14 | 292 | 26.1 | 292 | n/a |
| beta-HCH | 1 | 465 | 6 | 56.8 | 56.8 | 56.8 | n/a |
| gamma-HCH (Lindane) | 0.2 | 618 | 43 | 8.4 | 2.82 | 8.24 | 0.99 (PEL) |
| delta-HCH | 0.5 | 465 | 11 | 99.4 | 14.4 | 99.4 | n/a |
| Heptachlor | 0.5 | 621 | 58 | 15.8 | 4.5 | 7.3 | n/a |
| Heptachlor Epoxide | 0.5 | 618 | 27 | 17.8 | 2.5 | 3.1 | n/a |
| Hexachlorobenzene | 0.2 | 621 | 174 | 59.7 | 3.63 | 7.07 | n/a |
| Methoxychlor | 1.5 | 606 | 60 | 131 | 55.3 | 78.6 | n/a |
| Mirex | 0.5 | 620 | 25 | 103 | 2.6 | 3.74 | n/a |
| Oxadiazon | 6 | 465 | 12 | 114 | 45.8 | 114 | n/a |
| Oxychlordane | 0.5 | 465 | 37 | 30.3 | 10.7 | 12.3 | n/a |
| Toxaphene | 50 | 609 | 10 | 15,700 | 3,200 | 15,700 | n/a |
| Tributyltin | 0.003 | 555 | 555 | 6.21 | 0.422 | 0.724 | n/a |
| Total PCB | 9 | 684 | 628 | 19,901 | 497 | 865 | 180 |
| Acenapthene | 5 | 624 | 320 | 1,350 | 140 | 272 | 500 |
| 2-Methylnapthalene | 5 | 624 | 446 | 15,700 | 131 | 243 | 670 |
| Benzo[a]pyrene | 5 | 628 | 610 | 47,300 | 1660 | 2720 | 1600 |
| Dibenz[a,h]anthracene | 5 | 628 | 498 | 15,500 | 343 | 541 | 260 |
| LMW PAHs | 60 | 624 | 473 | 92,097 | 2,585 | 4,253 | 3,160 |
| HMW PAHs | 60 | 628 | 606 | 225,740 | 15,727 | 24,473 | 9,600 |
| Total PAHs | 60 | 628 | 628 | 227,801 | 17,107 | 27,485 | 44,792 |
| Total Organic Carbon | n/a | 686 | 686 | 26.8 | 3 | 4.01 | n/a |
| Grain Size | n/a | 689 | n/a | 100 | 98.16 | 99.6 | n/a |
| ERM Summary Quotient | n/a | 546 | n/a | 3.94 | 1.01 | 1.3 | n/a |
| PEL Summary Quotient | n/a | 553 | n/a | 7.8 | 1.52 | 1.95 | n/a |

*Primary Chemicals of Concern*

Results from chemical analyses of sediments in McGrath Lake are shown in Appendix C. It is interesting to note, despite the oil spill in 1993 Polycyclic aromatic hydrocarbons (PAHs) within McGrath Lake were generally low. There were no ERL or TEL exceedences for individual PAHs, low or high molecular weight PAHs, or for total PAHs. Instead selenium, manganese, total PCBs, and several pesticides (including chlordane, DDT, dieldrin, lindane, and endosulfan I ) most often were found to exceed sediment quality guidelines, or the BPTCP's 90$^{th}$ and 95$^{th}$ percentiles. These chemicals are described in detail below.

Selenium is a naturally occurring trace element that is unevenly distributed throughout the earth's crust. Natural weathering of rocks and soils is accelerated by crop irrigation and artificial drainage of saline or selenium rich soils and therefore it may result in high concentrations of selenium in drainage waters from agricultural fields (Johns et al. 1988). Selenium contamination of agricultural soils and drainage waters in the San Joaquin valley of California have been known to cause elevated mortality rates and deformities in many migratory waterfowl and are the major source of selenium contamination for fish (Losi and Frankenberger, 1997; Saiki et al., 1992). Selenium also is a by product of crude oil refinement and is used in photographic emulsions, as an additive for pigments in plastics, paints, enamels, and rubber, as an oil antioxidant, and is used in insecticides and fungicides (Adams and Johnson, 1981; Johns et al 1988). Sediment selenium concentrations within McGrath Lake ranged between 0.50 and 1.93 ppm. There are no ERM or PEL values established for selenium, however, selenium is considered a potential chemical of concern because all surface sediment samples within the lake were above the BPTCP's 90$^{th}$ percentile. Selenium values were lower at the pumphouse station and agricultural drainage, having values of 0.96 and 0.310 respectively.

Manganese is a naturally occurring trace element found in many types of rock formations and its chemical derivatives have several industrial uses. Manganese chloride is used in animal feed and in the production of dry cell batteries; manganese sulfate is used in ceramics glazes and in fertilizers and fungicides; potassium permanganate is used as an oxidizing agent, disinfectant, metal cleaner, and as a preservative for fresh flowers and fruits (Ward, 1999). Despite the fact that current sediment guideline values do not exist for manganese, sediment concentrations in McGrath Lake were above the BPTCP's 90$^{th}$ or 95$^{th}$ percentiles at all but one station. Although concentrations varied considerably, ranging between 446 and 1340 ppm, elevated levels were prevalent throughout the lake thus it is a potential chemical of concern.

Polychlorinated biphenyls or PCBs refers to a group of 209 individual congeners, based on substitution of the biphenyl molecule with varying numbers of chlorine atoms (Davis et al. 1999). Due to their resistance to electrical, thermal, and chemical processes, PCBs were used in a wide variety of applications including electrical transformers and capacitors, hydraulic fluids, and plasticizers, since their initial commercial production in 1929

(Brinkman and de Kok, 1980). In 1979, increasing concerns regarding PCB toxicity, bioaccumulation potential, and their resistance to degradation, resulted in a ban of PCBs implemented by the U.S. EPA. The ban prohibited the manufacturing, processing, commercial distribution, and use of PCBs, except in totally enclosed applications; despite these restrictions, a significant amount of PCBs may still be in use in industrial equipment (Rice and O'keefe, 1995). Concentrations of total PCBs (sum of 18 congeners- see Appendix C- Section III) in surface sediments exceeded ERM sediment quality guidelines of 180 ppb at eight of the 10 transect stations. PCB concentrations had a tendency to decrease at the southern end of the lake and also decreased with depth (Figure 6). Both the pumphouse and agriculture drainage stations were below sediment quality guideline values. However, because PCBs exceed ERM guideline values at many stations they are considered a potential chemical of concern. Subsurface water concentrations of PCBs also exceeded the U.S. EPA's ambient water quality guideline, for 24 hour exposure, of 30 ppt at every station sample. The greatest value was 236.624 ppt and was found at the pumphouse's unfiltered water sample.

Chlordane is a chlorinated organic pesticide, which was used extensively as a broad spectrum insecticide in structural and agricultural applications for termite and insect control (Shigenaka, 1989). Chlordane production began in the late 1940s, however, concerns regarding environmental persistence and human health impacts caused the chemical to be restricted starting in 1974, and commercial use was cancelled by the U.S. EPA in 1988 (Howard, 1991). Because of its long term effectiveness, chlordane was used widely throughout the United States. Unfortunately, it is resistant to chemical and biological degradation and has become pervasive in both terrestrial and aquatic ecosystems, with a half life of 10 to 20 years (Rostag, 1997). Surface sediment samples in McGrath Lake were always above the ERM guideline value of 6 ppb and also always above the BPTCP 95$^{th}$ percentile of 69.5 ppb, ranging from 457.14 to 815.96 ppb (136 x the ERM) (Figure 7). Only the pumphouse and agricultural drainage stations were not above the BPTCP 95$^{th}$ percentile however, they were above the ERM guideline with values of 15.05 and 18.99 respectively. Chlordane concentrations tended to decrease with core depth due to chemical and biological degradation. However, they were often above the BPTCP 90$^{th}$ percentile, even at 60cm in depth (Figure 8). Elevated concentrations in surface sediments of McGrath Lake probably are related to terrestrial runoff of soil bound chlordane, and is enhanced due to chlordane's insolubility in water. Concentrations of chlordane within water samples exceeded the U.S. EPA's ambient water quality guideline, for 24 hour exposure, of 1.9 ppt at all stations, except for the pumphouse station.

Like chlordane, DDT is an organochlorine insecticide that was used extensively in structural and agricultural applications from the 1940s until it was banned in the mid 1970s. DDT is persistent in the environment and has a half-life between 3 and 30 years depending on environmental conditions (Lichtenstein et al., 1971; Edwards, 1973). DDT has a low solubility in water and high solubility in lipids, therefore it tends to accumulate in tissues of aquatic organisms and magnify in concentration up the food chain (Howard, 1991).

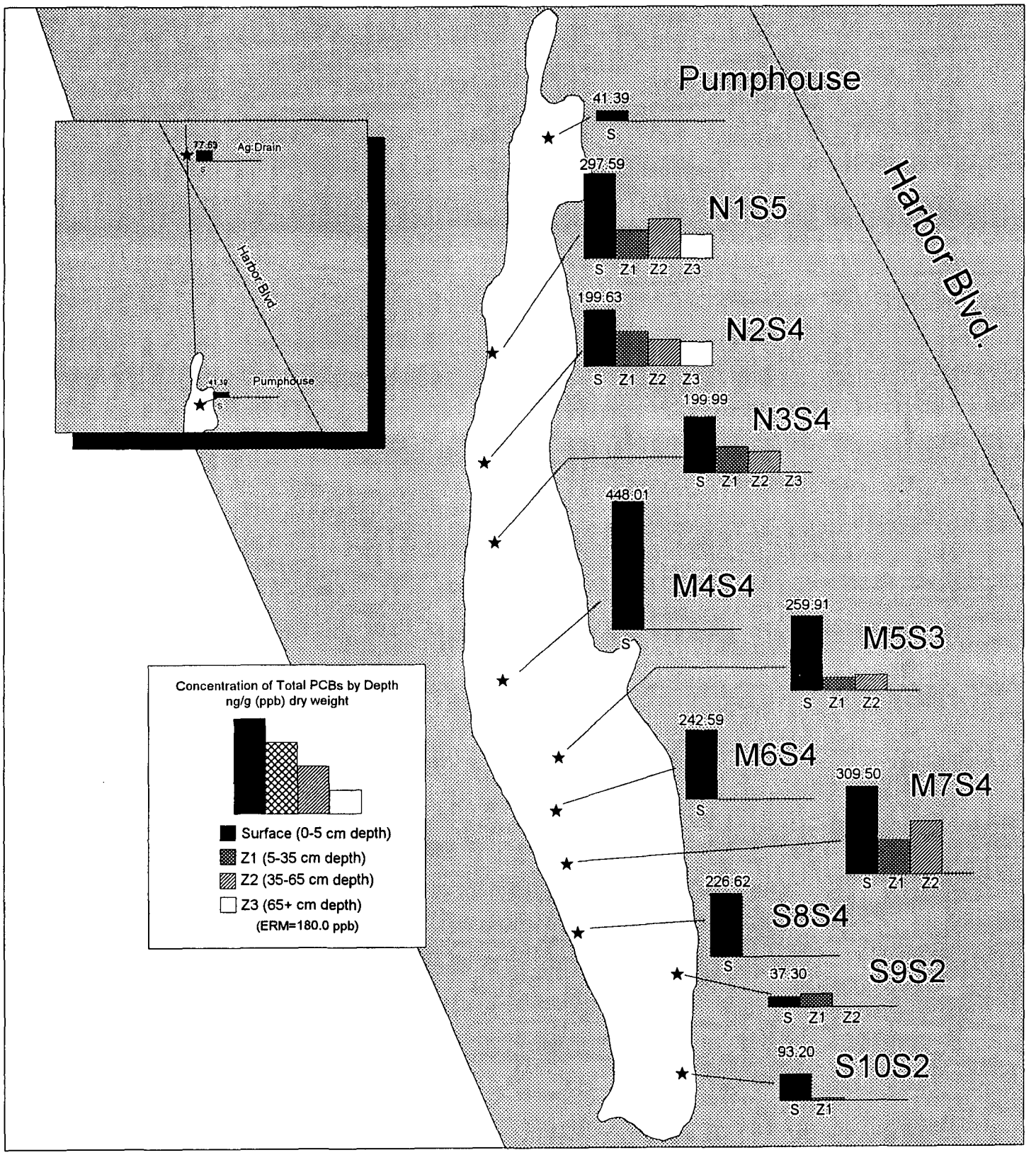


Figure 6. Concentration of total PCBs, during the second phase of sampling, in both surface sediments and at the seven stations for which cores were taken. The deepest depth for a particular core may vary depending on penetration depth of the core.

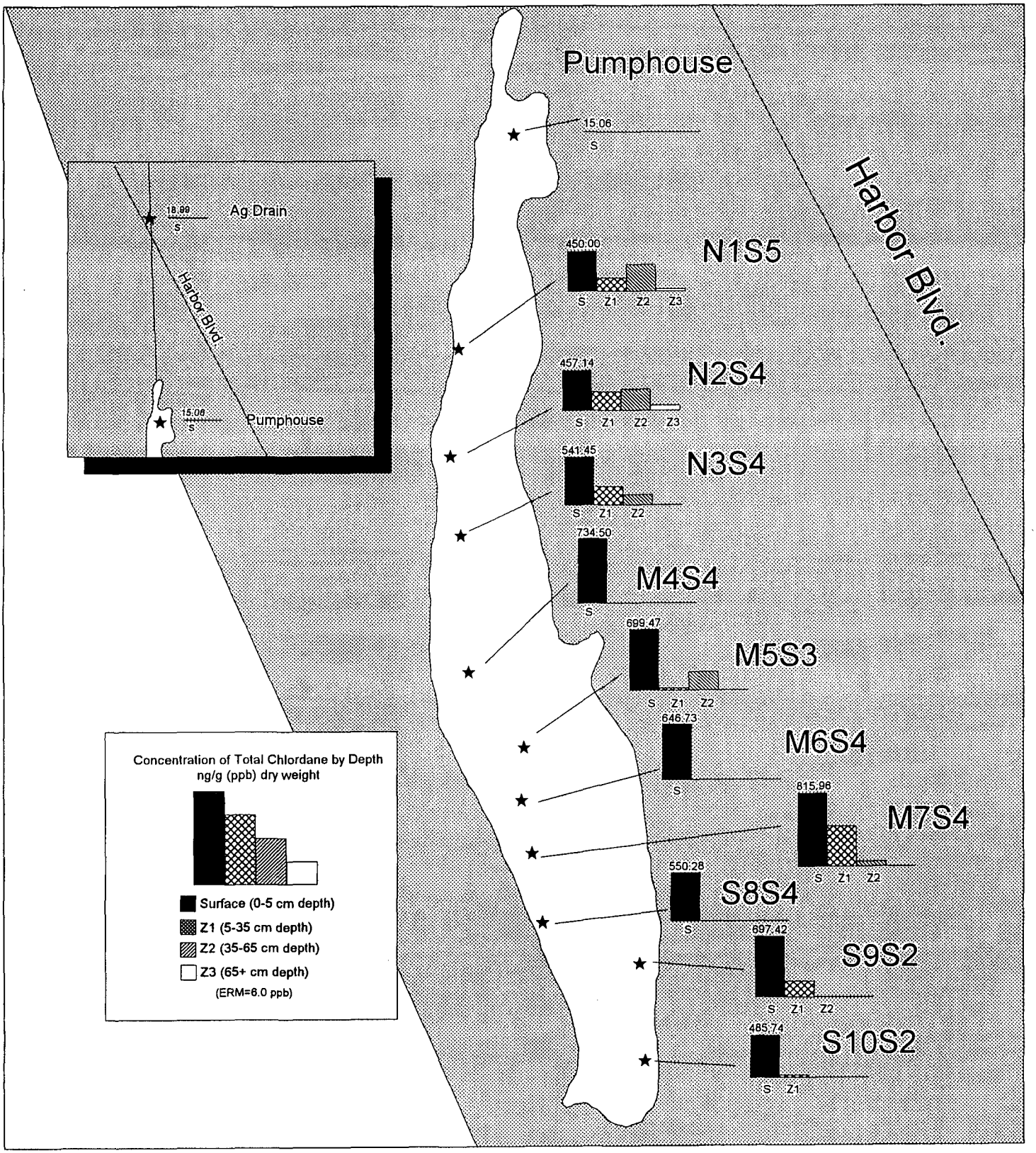


Figure 7. Concentration of chlordane during the second phase of sampling, in surface sediments and at the seven stations for which cores were taken. The deepest depth for a particular core may vary depending on penetration depth of the core.

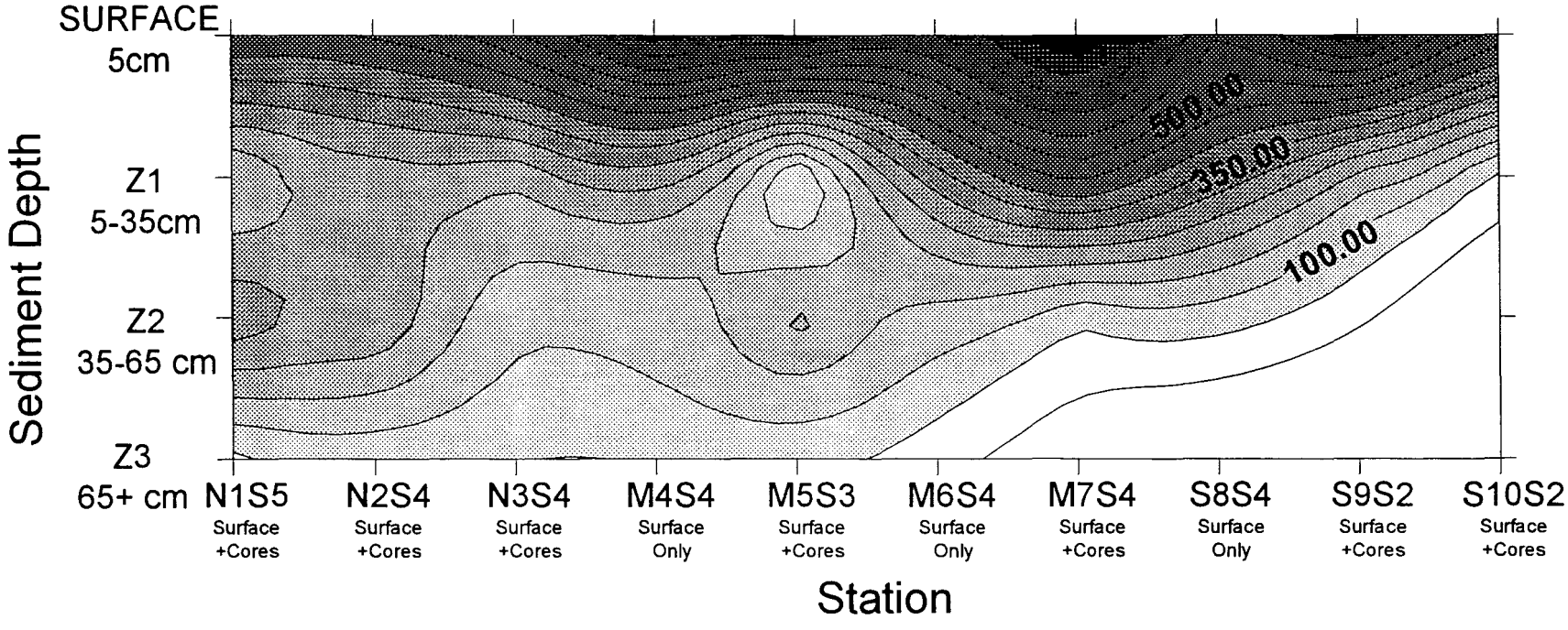


Figure 8. Contour plot of surface and subsurface chlordane concentration (ng/g dry weight) along the line extending from stations N1S5 to S10S2.

DDT concentrations within McGrath Lake were some of the highest in the state, ranging between 3487.8 and 1368.66 ppb in surface sediments; the BPTCP's 95 $^{th}$ percentile for the state is 471.9 ppb. These results concur with previous BPTCP data for McGrath Lake in 1993 and 1996, which also found DDT concentrations in surface sediments above the 95 $^{th}$ percentile (Anderson et al. 1998). Concentrations of DDT tended to decrease with depth, but were always above the BPTCP's 95 $^{th}$ percentile (Figure 9). The only exception to this trend was the southern most core's deeper sections, but these values were still above the DDT ERM of 46.1 ppb. As DDT degrades in the environment it is metabolized first to DDD and then to DDE. The ratio of the parent compound DDT to its metabolites is an indication of DDT weathering and microbial degradation (Pham et al., 1993; Venkatesan et al., 1996). Most of the DDT within McGrath Lake appears to be weathered, having ratios of parent DDT to its metabolites always less than one (Figure 10). Subsurface core samples had even lower DDT to metabolite ratios indicating that deeper sediments were undergoing the weathering or degradation process for longer time periods. However, considering the extent of elevated concentrations of DDT within the lake, the breakdown of DDT to its metabolites could take many years. DDT concentrations in water samples exceeded the U.S. EPA's ambient water quality guideline, for 24 hour exposure, of 1 ppt limit at all stations sampled and were greatest at the agricultural drainage station, which had 140.59 ppt DDT.

Dieldrin is an organochlorine insecticide that was used for termite control and citrus, corn, and cotton crops. Restrictions for dieldrin applications began in 1974 and it was completely banned, even for termite control, in 1987 (USEPA, 1995). Dieldrin is known to persist in soils for long periods of time due to slow photodegradation and will not undergo hydrolysis or appreciable degradation (Howard, 1991). Once dieldrin is released in surface waters (primarily due to agricultural runoff), it binds strongly to sediments and may bio-concentrate in fish and other species (Howard, 1991). Dieldrin is considered a potential chemical of concern because concentration levels within McGrath Lake surface sediments ranged between 14.50 and 38.10 ppb; all of which exceeded the PEL guideline value of 4.3 ppb and the BPTCP 90$^{th}$ percentile of 11.7 ppb (Figure 11). Lower dieldrin concentrations of 5.74 and 5.94 ppb respectively were found at the pumphouse and agricultural drainage stations, but these stations still exceeded dieldrin's PEL guideline value. Dieldrin concentrations tended to decrease with sediment depth, especially in the southern portion of the lake. However, it should be noted that at some stations dieldrin levels exceeded PEL values even at depths greater than 65 cm. Historical BPTCP data for 1993 and 1996 indicated that surface sediments in McGrath Lake exceeded the BPTCP's 95$^{th}$ percentile for the state during both years. Elevated levels of dieldrin also were seen in one subsurface water sample, taken in the middle portion of the lake, which had a concentration of 14.3 ppb. This sample exceeded the U.S. EPA's ambient water quality guideline, for 24 hour exposure, of 1.9 ppt. All other subsurface water stations were below detection limits for dieldrin.

Lindane is used primarily as an insecticide on hardwood logs and lumber, seeds, fruits, vegetables, hardwood forests, existing structures, and livestock and pets (for external

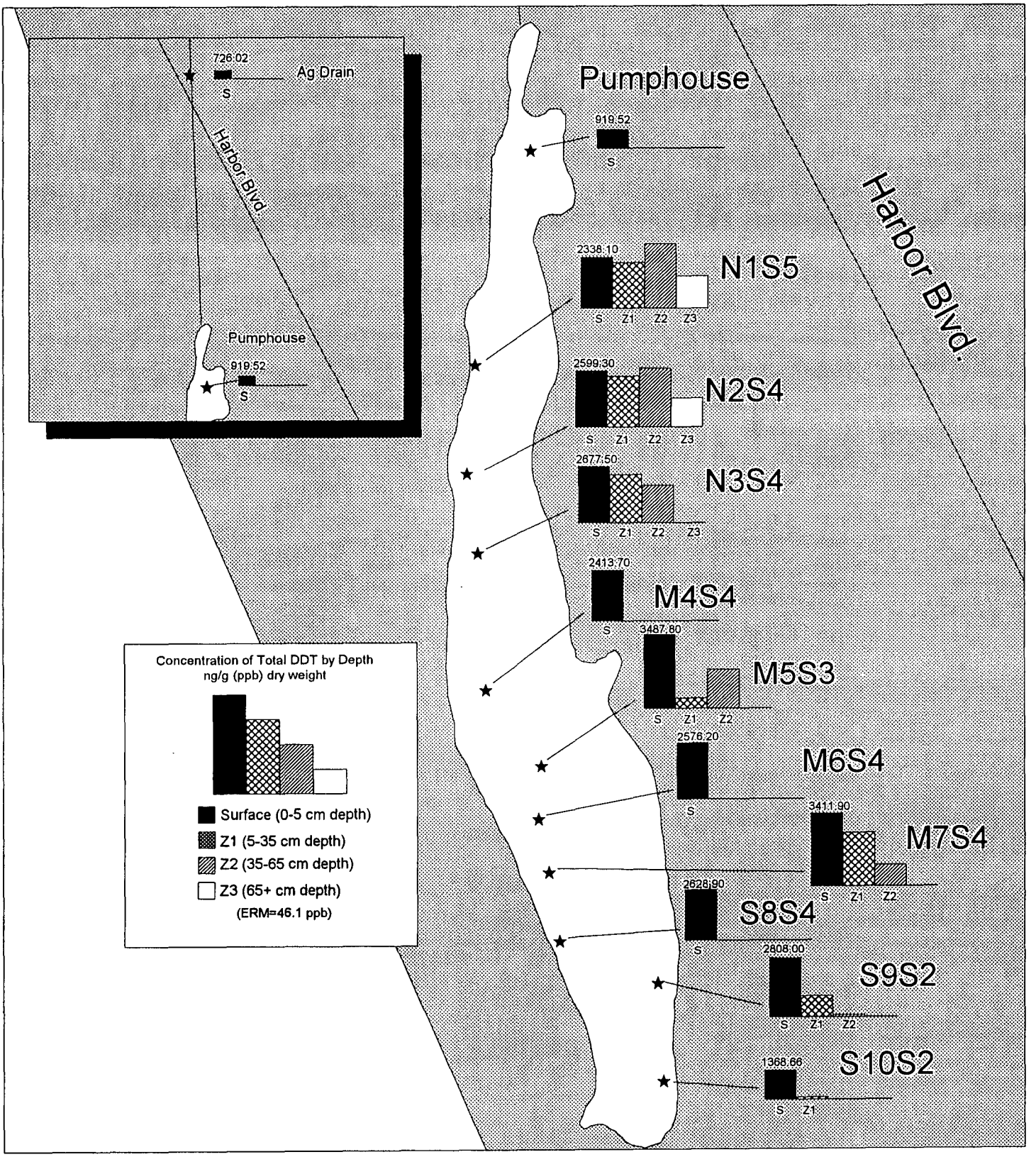


Figure 9. Concentration of total DDT, during the second phase of sampling, in both surface sediments and at the seven stations for which cores were taken. The deepest depth for a particular core may vary depending on penetration depth of the core.

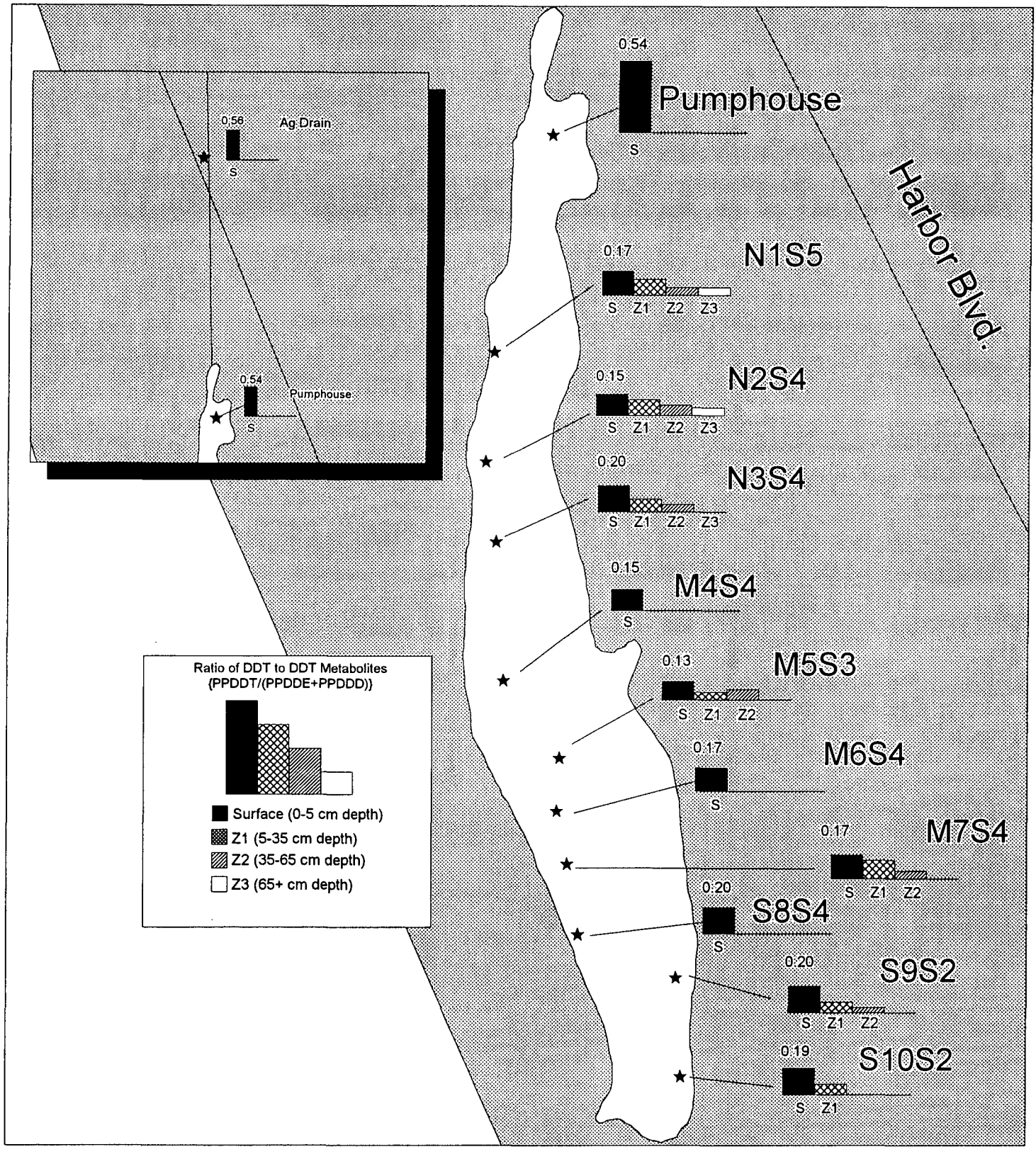


Figure 10. Ratio of DDT to metabolites (P'P'DDT/{(P'P'DDE+P'P'DDD)}, during the second phase of sampling, in both surface sediments and at stations for which cores were taken. The deepest depth for a particular core may vary depending on penetration.

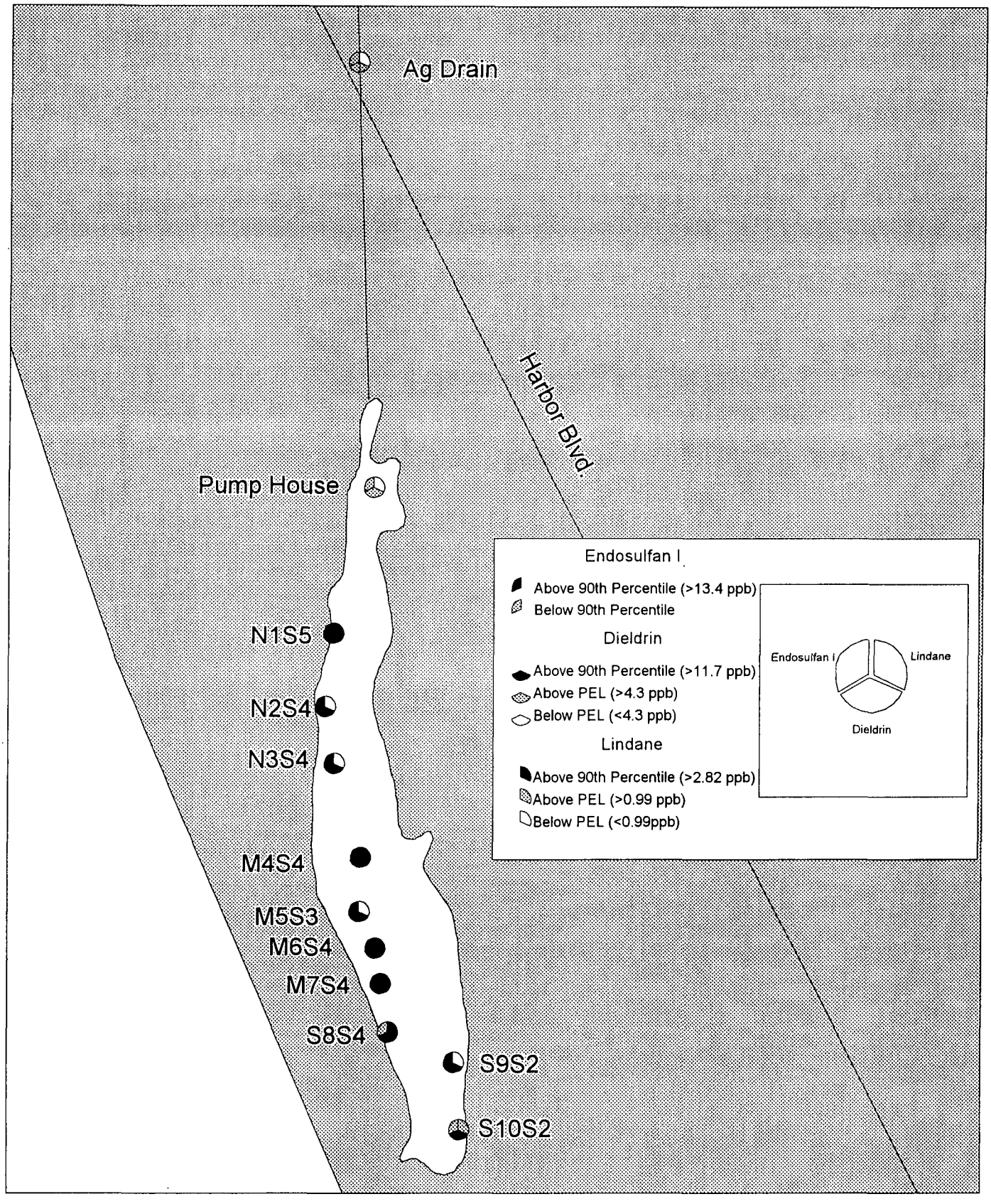


Figure 11. Pesticide concentrations in surface sediments from the second phase of sampling. Levels are compared to sediment quality guideline values and/or the 90th percentile of values from the BPTCP. No sediment quality guideline values have been derived for Endosulfan I.

parasite control). Since 1985, many uses of lindane have been banned or restricted because it is classified as a probable/ possible human carcinogen. Lindane concentrations within McGrath Lake ranged from below detection limits to 7.94 ppb. Several stations exceeded the PEL of 0.99 ppb and the BPTCP's 90th percentile value of 2.82 ppb (Figure 11), thus it is considered a potential chemical of concern. Unlike many other pesticides measured in McGrath Lake, there were instances in which lindane concentrations were actually greater at depth relative to core samples. Lindane is very stable in both freshwater and marine environments and is resistant to photodegradation (EXTOXNET-PIP, 1999). Lindane was not detected at the pumphouse station and or the agricultural drainage station.

Endosulfan I is a chlorinated hydrocarbon that acts as a poison to a wide variety of insects and mites upon contact (EXTOXNET-PIP, 1999). It can be used as a wood preservative, however, it is primarily used on food crops such as coffee, fruits, vegetables, rice, cereals and other grains (EXTOXNET-PIP, 1999). Although no ERM or PEL sediment quality guideline values have been establish for endosulfan I, it is considered a potential chemical of concern because it exceeded the BPTCP's $90^{th}$ and $95^{th}$ percentiles (13.4 and 19.6 respectively) in nearly all surface samples taken within McGrath Lake (Figure 11). Values ranged between 7.3 and 28 ppb in surface samples within the lake. Values tended to decrease with depth and concentrations were lower in the south end of the lake. Endosulfan I concentrations were lower at the pumphouse station and at the agricultural drainage station, having values of 3.260 and 3.77 ppb respectively. In addition to elevated levels found during this study, BPTCP data taken in 1993 and 1996 also showed endosulfan I values, within McGrath Lake, to exceed the $90^{th}$ and $95^{th}$ percentile for the state.

As observed in Figure 11, sediment concentrations of pesticides, as well as TOC concentrations (Figure 3), are greater in the main body of the lake compared to the northern end, where the agricultural drainage enters the lake and water flow is enhanced. Chemical analyses of filtered and unfiltered water samples, at the pumphouse, indicate a significant portion of trace metals and trace organics are bound to particles suspended in the water column. It is suspected that the broad main body of the lake, where flow rates are reduce, is acting as a settling trap for suspended particles and the associated bound chemicals. This could account for the observed spatial distribution of pesticides in sediments.

***Toxicity Analysis***

During the second phase of sampling, sediment toxicity tests were performed on samples from 12 stations, using the estuarine amphipod *Eohaustorius estuarius*. Because this species tolerates salinity variations from 0 to 34 ‰, it was selected as the most appropriate test species for the mixed salinity environment of McGrath Lake. Subsurface water toxicity tests were performed on samples from five stations, using the mysid shrimp *Neomysis mercedis*, another euryhaline species. A summary of toxicity test results are shown in Table 5 and results are further detailed in Appendix E. Eleven of the 12 sediment samples were found to be toxic to *E. estuarius* and survival ranged between 7

and 85 percent. As discussed earlier, some pesticide concentrations were extremely elevated in the sediment samples tested, exceeding national sediment quality guidelines and state specific 90$^{th}$ and 95$^{th}$ percentiles. It is suspected that pesticides play a major role in the observed toxicity to amphipods. The magnitude of toxic response in the southern portion of the lake was slightly less than at the northern portion of the lake, although no clear spatial pattern was obvious for sediment toxicity. Elevated levels of interstitial hydrogen sulfide (2.8882 mg/L) may have been a factor in toxicity at station M7S4, however, hydrogen sulfide and unionized ammonia levels did not appear elevated at the remaining 10 stations that also were found to be toxic. The pumphouse and agricultural drainage stations had extremely low survival with values of 20 and 7 percent respectively. These two stations also were the only two sites found to be toxic during subsurface water tests with *N. mercedis*. Chemical analysis of water at these two stations indicated exceedences of EPA water quality criteria for copper, (4.9 ppb), DDT (1 ppt), and total PCBs ( 30 ppt). It is plausible that one or more of these chemicals played a role in the observed water column toxicity.

Table 5. Summary of Toxicity Results

| STANUM | STATION | SEDIMENT | | SUBSURFACE WATER | |
|---|---|---|---|---|---|
| | | *Eohaustorius estuarius* | | *Neomysis mercedis* | |
| | | Toxicity | % Survival | Toxicity | % Survival |
| 45015.0 | McGrath Lake Estuary-N1S5 | T | 61 | | |
| 45024.0 | McGrath Lake Estuary-N2S4 | T | 70 | NT | 96 |
| 45034.0 | McGrath Lake Estuary-N3S4 | T | 41 | | |
| 45044.0 | McGrath Lake Estuary-M4S4 | T | 57 | | |
| 45053.0 | McGrath Lake Estuary-M5S3 | T | 65 | NT | 96 |
| 45064.0 | McGrath Lake Estuary-M6S4 | T | 57 | | |
| 45074.0 | McGrath Lake Estuary-M7S4 | T | 34 | | |
| 45084.0 | McGrath Lake Estuary-S8S4 | T | 43 | | |
| 45092.0 | McGrath Lake Estuary-S9S2 | T | 74 | NT | 92 |
| 45102.0 | McGrath Lake Estuary-S10S2 | NT | 85 | | |
| 45003.0 | McGrath Lake Estuary-Pumphouse | T | 7 | T | 12 |
| 45001.0 | McGrath Lake Estuary-Ag Drain | T | 20 | T | 24 |

### *Benthic Community Analysis*

Benthic community analysis was performed on 12 stations during the second phase of sampling; one along each of the transect lines, one at the pumphouse station, and one at the agricultural drainage. A summary of benthic community data is shown in Appendix F. Results indicated that McGrath Lake has a very depopurated benthic community. The total number of species, at each station, ranged between one and five, and total number of individual ranging between 4 and 710. Insect larvae, of the family Chironomidae, were found at every station except those stations sampled along transects 7 and 8. Areas dominated by insect larvae such as Chironomidae generally are indicative of a degraded

benthic community (Karr et al. 1998). Stations from transects 7 and 8 were unique compared to the rest of the lake's benthic communities. These two stations were located in the deeper portion of the lake, where salinity values were more than twice as great as the shallower portions of the lake. These elevated salinities probably made for intolerable conditions for insect larvae and resulted in these stations having the lowest number of individuals, 4 and 29 respectively. Besides insect larvae Oligochaetes and Ostracod crustaceans also were found at several stations within McGrath Lake. However, overall numbers for these species were low indicating a degraded benthic state.

## SUMMARY CONCLUSIONS

Results from this study indicate that McGrath Lake had a shallow, brackish water environment with a high percentage of fine sediments. The primary concern of this study was assessing persistent crude oil residuals from the 1993 oil spill and any resultant ecological effects from this release. Study results indicate PAHs have degraded rapidly and pose little risk to the ecology of the lake, however, chlorinated pesticides in both the sediments and waters of McGrath Lake are an obvious concern. Chemicals of primary concern within McGrath Lake were selenium, manganese, total PCBs, and the pesticides chlordane, DDT, dieldrin, lindane and endosulfan I. All of these compounds were above sediment quality guideline values and many surface sediment samples were greater in chemical concentrations than 95% of the samples collected statewide, by the BPTCP. Chemical concentrations tended to decrease with sediment depth, however, the primary chemicals of concern still often exceeded sediment guideline values even at depths of 60 cm. Nutrient concentrations within the lake are elevated, but comparable to other water bodies with similar agricultural inputs, such as the Tembladero Slough. It appears McGrath Lake act as a sink for adjacent agricultural inputs (Anderson et al. 1998) and has some of the greatest concentrations of pesticides measured by the BPTCP. The benthic communities at all stations were depopurated and indicated degraded benthic conditions. Fluctuations in salinities, as well as chemical contamination, may play a factor in the low number of species and individuals observed during this study. Although the pumphouse and agricultural drainage stations generally had lower chemical concentrations then the stations within McGrath Lake, these two stations demonstrated the greatest degree of toxicity in both amphipod and mysid shrimp bioassays.

### *Recommendations*

The current study was designed to assess contaminant concentrations and associated biological effects within McGrath Lake. Elevated levels of previously banned chlorinated pesticides, such as chlordane and DDT, in association with elevated nutrient levels, suggest that agricultural activities play a major role in the depressed ecology of McGrath Lake. It is prudent to further investigate the role that agricultural chemicals play in the observed toxicity and degraded benthic communities of McGrath Lake. The current study targeted a limited list of pesticides for identification and quantification. Most of the

targeted pesticides were from banned chlorinated pesticide category lists; our target analytes did not include many current use pesticides, such as those found in the organophosphate or carbamate categories. It is possible one or more of these unmeasured pesticides are the cause of observed biological effects. Future chemical analyses at McGrath Lake should include an expanded analyte list for current use pesticides, herbicides and surfactants. In addition, toxicity identification evaluations (TIE) should be used to link the observed toxicity in bioassays with specific measured chemicals in sediments and the water column.

Chlorinated hydrocarbons are known for their ability to bioaccumulate in the fatty tissues of higher trophic level organisms. An investigation of tissue bioaccumulation should be considered for the protection of any higher trophic level resident species or endangered species found using the McGrath Lake area.

Although the current study was designed to assess contamination within McGrath Lake, results indicated a clear need to assess contamination and ecological effects caused by the discharge of McGrath Lake waters to the marine environment. Samples from the pumphouse station, at the northern end of the lake, were highly toxic in both sediment and water exposures. This station is located within several meters of the intake pipe for the pump that regulates the lake level. Water, suspended sediments, and associated contaminants are pumped from this location, for approximately 100 meters, across the dunes through a pipe, and then discharged into the beach zone. An investigation of the toxicity, bioaccumulative potential and fate of this discharge water is strongly recommended using appropriately sensitive marine species and analyses. Initial water samples from this discharge location have been taken and data results are pending.

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