

## **APPENDIX 3**

### **BENTHIC SEDIMENTS PROGRAM**

The Benthic Sediments Program consists of a semiannual quantitative survey of the benthic macrofauna of the Palos Verdes shelf coupled with a survey of the physical/chemical characteristics of the shelf's surficial sediments (top two cm.).

In 2005, benthic sediment sampling was conducted in winter (January) and in summer (July). As stipulated by the Los Angeles Region RWQCB, during the winter survey 18 of the 44 offshore stations were sampled. During the summer survey, all 44 stations were sampled with five replicates collected at three sites (OC, 3C and 8C). Sample analyses of both surveys included infauna, grain size, pore-water sulfides, redox potential, TOC, and organic nitrogen at all sites and replicates. Sampling site latitude and longitude is included in Appendix 1, pages 8 and 9.

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## SURVEY METHODS

**POSITIONING AND NAVIGATION:** Positioning on station is accomplished by means of a Differential Global Position Satellite (DGPS) navigation system confirmed by fathometer and two to three axis visual ranges. The vessel is dynamically maintained on station during deployment and recovery of sampling gear.

**SAMPLING EQUIPMENT:** Benthic sampling was conducted from aboard the Districts' 20 meter monitoring vessel, the R/V *OCEAN SENTINEL*. The benthic sediments for this program are collected by means of a tandem-rigged modified 0.1 m<sup>2</sup> Van Veen grab. This device consists of two modified 0.1 m<sup>2</sup> Van Veen grabs paired on a single hinge shaft. This arrangement allows the collection of paired samples, one for infaunal analysis, the other for the analysis of sediment physical/ chemical parameters. The two grabs are separated on the shaft by approximately 15 cm.

**SAMPLE COLLECTION:** Once on station, the tandem Van Veen grab is deployed and lowered by means of a davit and hydrographic winch. When the grab is approximately 10 meters above the bottom, the speed of descent is increased to assure maximal penetration into the sediments. Upon retrieval, the contained sample in each grab is inspected to determine acceptability. Acceptable samples are those in which penetration exceeds 10 cm and with little or no evidence of surface disturbance due to washing or slumping. Both samples in the pair must be judged acceptable for either to be accepted. Upon acceptance, a qualitative description is made of sediment type and color. The apparent presence or absence of hydrogen sulfide odor in the sediments and its qualitative intensity (trace, moderate, or strong) are determined by exposing the subsurface sediments to the nose. These data, along with the sampling date, station name, station depth, penetration depth, and sediment temperature are recorded on field log sheets.

**INFAUNAL SAMPLING:** After the sediments are described, the contents of the grab containing sediments to be used for infaunal analysis are emptied into a large tray. Any sediments remaining in the grab are washed by hose into the tray. The sediment is then transferred from the tray onto a specially designed washing table and washed with a gentle spray of seawater. All wash-waters used during sample handling are filtered through fine screens to prevent contamination of sample by surface-water organisms. As the sediment is washed, it flows down the length of the washing table and into a screen box where it passes through the 1.0 mm mesh limiting screen used in this study. The material (debris, coarse sediments, and organisms) retained upon this screen is then carefully collected into a labeled sample jar. The material is exposed to a MgSO<sub>4</sub> relaxant solution for a period of 30 minutes. The sample is then fixed with a 10% solution of buffered formalin and stored in plastic crates for return to the Marine Biology Lab (MBL) for subsequent analysis.

**PHYSICAL/CHEMICAL SAMPLING:** After the sediments are described, the grab containing the sediments to be used for physical/chemical analysis is sub-sampled. All analyses are conducted on the surficial sediments, defined in this study as the top 2 cm of the sediment in the grab.

Sub-sampling for pore-water sulfides and redox potential is accomplished by means of a syringe calibrated to remove a 35 mm diameter core of the top 2 cm of sediment. This core is transferred into a cylinder-and-piston device that allows the removal of pore-water in the absence of oxygen by

compressing the sediments under low hydraulic pressure. As pore-water is forced from the sediment it passes through both a coarse paper filter and fine syringe filter into a plastic collection syringe. This device and pore-water extraction technique is partially described in Kalil, 1974. The collected pore-water is analyzed immediately on-board ship for sulfides, redox potential, and pH using potentiometric techniques. Redox potential is measured using a platinum redox electrode. Sulfides are determined by means silver/silver sulfide indicator electrode. A double junction reference electrode is used in both analyses. The sulfide analytical procedure is detailed later in this appendix.

After sub-sampling for pore-water sulfides, four sub-samples of surficial sediment are collected for surface sediment texture and chemistry. Single 125 ml samples are collected for analysis of grain size and for TOC/organic nitrogen and 250 ml samples are collected for metals and for organic priority pollutants. All contaminant samples are collected in pre-cleaned glass containers with TFE-lined lids.

Reference: Kalil, Emil K. 1974. Rapid Pore Water Analysis For Sediments Adjacent To Reactor Discharges *IN*: Proceedings of the 1974 International Atomic Energy Symposium On Environmental Surveillance Around Nuclear Installations. Warsaw, Poland. IAEA-SM-180/37

## **INFAUNAL SAMPLE ANALYSIS METHODS**

**SAMPLE PREPARATION:** Upon return to the MBL, the samples are logged into a sample record. The samples are then prepared for subsequent biomass determination and taxonomic analysis. This preparation is a two part process consisting of (1) washing and preserving the sample, and (2) sorting the sample.

### Washing and Preservation.

#### **A. General**

The purpose of the washing and preservation of the samples upon return to the lab is to remove the fixative (formalin) and replace it with preservative (ethanol). The removal of formalin is necessary for two reasons. Formalin will become increasingly acidic over time and prolonged exposure will damage organisms with calcareous structures (e.g. shelled molluscs). Therefore, following adequate time for fixation to take place (no more than several days), the formalin must be replaced with a preservative suitable for long-term storage. Also, formalin is a noxious, potentially dangerous chemical; its replacement by ethanol makes the subsequent handling of the sample safer. Other benefits of the washing process are the removal of excess silt from mudballs that may have broken down during fixation and, in some cases, the opportunity to separate the bulk of organisms in a sample from the inorganic debris through a flotation process.

#### **B. Procedure**

- 1) Samples are to remain in buffered 10% formalin a minimum of two days and a maximum of

one week.

- 2) Prior to washing, the volume of the material contained in a sample (excluding the fixative) is to be estimated to the nearest 25 ml (nearest 100 ml for samples >1000 ml) and the volume entered into the Benthic Sample Sorting Record.
- 3) If the sample is contained in more than a single container, the number of containers is to be noted in the Benthic Sample Sorting Record. A notation is not required for single container samples.
- 4) Under the fume hood, the fixative is to be decanted through a screen sieve into the sink in which water is freely running. The screen sieve is to be no more than 1/2 the mesh size of the limiting screen specified for the study (e.g. the Districts' usual limiting screen is 1.0 mm and requires the use of a 0.5 mm washing screen).
- 5) After decanting the formalin, the sample jar is to be refilled with water, recapped, agitated by swirling, and the entire sample washed into the sieve.
- 6) The sample is to be gently washed on the sieve with tap water to remove all formalin and, if present, fine silt. Screen and sample may be swished briefly in a pan of water.
- 7) Using a spatula and wash bottle of 70% ethanol, the sample is to be returned to the sample container, topped with 70% ethanol, recapped, and returned to the sample shelf to await sorting.
- 8) FLOTATION. If a sample is primarily coarse sand, subsequent sorting can be greatly facilitated if inorganic material in the sample is separated from the lighter organic debris and organisms by the flotation technique.
  - a) After washing the formalin from the sample, the material is spread out in a shallow pan and covered with of water.
  - b) The sample is gently agitated to allow the lighter organic debris and organisms to separate from the sand.
  - c) The water is then decanted off through the screen sieve and the process repeated several times.
  - d) The material collected in the sieve is removed by means of spatula and wash bottle of 70% ethanol into a small wide-mouth jar, along with a label recording the sample name, and topped with 70% ethanol.
  - e) Together with the jar containing the floated fraction, the balance of the sample material is returned to the original sample container. The container is topped off with preservative and returned to the sample shelf to await sorting.

- f) Large volume samples may have to be floated in several repeated steps. However, all floated material is to be collected into a single, labeled jar.

### Sample Sorting

#### A. General

Sorting is the process by which the organisms in a benthic sample are removed from the organic and inorganic residues that compose the sediments and sorted into broad taxonomic categories for subsequent taxonomic analysis. Sorting is an exacting and time consuming task that requires close attention for prolonged periods. Despite its demands, it is essential to the success of the entire survey effort that sorting be done both accurately and efficiently. Besides the basic procedure below, a Benthic Infaunal Sorting Guide has been prepared to provide guidance to sorters.

#### B. Procedure

- 1) A single sample is selected from the sample storage shelf. The samples are to be selected in the sequence listed in the Benthic Sample Sorting Record. There are few exceptions to this sequence. Therefore the next available sorter works on the next available sample.
- 2) The sorter "checks" the sample out by initialing and dating the Benthic Sample Sorting Record. The Sample now becomes the responsibility of the sorter. No sharing or splitting of the sample among sorters is permitted without specific instructions. In the case of samples composed of multiple containers, all containers are to be sorted by the responsible sorter.
- 3) A portion or all of the sample is transferred to a large diameter (150 mm) petri dish. The amount of material in a dish is to be limited to a single layer. Several dishes are typically needed to hold the material in a sample.
- 4) Each dish is to be labeled with the sample name by means of white labeling tape and a black marking pen.
- 5) Each dish is to be filled with enough 70% ethanol to cover all the material. Sorting is to be done over alcohol (with the lab supervisor's permission, persons sensitive to alcohol vapor may sort over water).
- 6) Samples are to be sorted under a dissecting microscope into two wide-mouth jars, each of which bears a label with the station name and inventory number (1 of 2, 2 of 2). Samples that contain an unusually large organism may require a third jar. All jars are to be filled with preservative.
- 7) The organisms removed from the sample are to be sorted into seven taxa lots as follows:

Annelida	Mollusca
Arthropoda	Nemertea
Echiura	Other Phyla (a collective multi-phylum lot)
Echinodermata	

- 8) Each taxa lot is to be separately contained as follows: Annelida are to be loose in the first jar (1 of 2); all others into appropriately sized shell vials, filled with preservative, cotton stoppered, and placed in the second jar (2 of 2).

Upon completion of each dish the sorter is to initial the tape to designate its completion. Upon completion of the entire sample all the material and sorted organisms are to be turned over to the person performing sorting QA/QC.

The completion date and number of hours required to sort the entire sample are to be entered in the Benthic Sample Sorting Record.

**SORTING QA/QC:** All sorters are provided, in addition to the procedure above, a nine page Benthic Infaunal Sorting Guide which expands upon the procedure and provides various detailed instructions and guidance on the handling of different sample and organism types.

All samples are subject to a 100% re-sort as a QC measure. This re-sort is performed by experienced staff specifically assigned to this task. Staff performing sorting QC do not participate in the original sorting of the samples. If the re-sort reveals inadequate sorting (<95% of the organisms removed) the sample is returned to the responsible sorter and remedial instruction provided.

**BIOMASS ESTIMATION:** After the sample has passed sorting QC, the biomass is estimated from the wet-weight of each of the seven taxa lots in the sample. A wide plastic weigh-boat modified with a fine (<0.5 mm) mesh bottom is tared on a top-loading analytical balance. After the organisms to be weighed are placed in this weigh boat, it is set on absorbent paper and allowed to air-dry for a measured 5 minutes. The gross weight is then measured to the nearest 0.01 gm and the net weight (biomass) of the organisms determined and recorded to the nearest 0.1 gm.

**TAXONOMIC ANALYSIS:** Once the biomass has been estimated the sample is turned over to the taxonomists for identification and enumeration. All organisms are identified to the lowest practicable taxon, usually the species level. Data are recorded on sample data sheets designed for this purpose. Each data sheet has recorded on it the sample name, sample date, sediment description, depth, date of identification, and the name of the taxonomist(s) performing the analysis. During the process of identification the organisms within each sample are sorted into taxa and sample lots as detailed in the following curatorial procedures:

#### A. Materials:

##### 1) Preserving Fluid

- a) All infaunal samples are to be stored in 70% to 75% non-denatured Ethanol.

- b) In making up Ethanol solution use D.I. water as dilutant.

100% Ethanol is to be used for "topping" archived samples that have lost preservative due to evaporation.

## 2) Containers & Closures

- a) Only glass containers are to be used for the storage of Sample Lots.

- b) Sample Lots are to be stored in the following glassware (and closures):

Round wide-mouth jars in 32, 16, 8, & 4 oz. sizes (polypropylene lids fitted with 2 mm thick polyethylene liners).

Round, tall form, wide mouth jars in 2 oz size ("Polyseal" style caps).

- c) Taxa Lots are to be stored within the Sample Lot jars in the following glassware (and closures):

Glass shell vials in 6, 4, 3, 2, 1, 1/2 dram sizes (stoppered with cotton)

Other containers, such as 1 oz tall form jars, screw cap vials, no. 1 & 3 capsule vials, snap cap vials (plastic or glass), may be used if glass shell vials are not adequate.

## 3) Labels

- a) All labels used within containers are to be made from 100% linen paper (e.g. Byron Weston Linen Record, 40# weight).

- b) Labels to be attached to the exterior of Sample Lot containers are to be made from adhesive labels of appropriate size.

## 4) Writing Implements

Labels are to be filled out using soft to medium pencil (e.g. #2 & #3 or leads B & HB) or indelible ink (e.g. Higgins Eternal). If ink is used, the label must be allowed to dry completely before immersion.

### B. Procedure:

#### 1) Taxa Lots

- a) The material within a sample is to be sorted into the following taxa lots:

Polychaete (by families)	Oligochaeta	Hirudinea
Bivalvia	Gastropoda	Moll. Misc.
Gammaridea	Ostracoda	Decapoda

Arthro. Misc.  
Cnidaria  
Echiura  
Brachiopoda

Ophiurans  
Polycladida  
Sipuncula  
Hemichordata

Echino. Misc.  
Nemertea  
Phoronida  
Chordata

If other taxa are encountered they should be sorted into taxa lots at the Phylum level.

- b) The Taxa Lot vial is to be of sufficient size to contain the organism(s) without undue crowding or flexure.
- c) Each Taxa Lot is to be accompanied by a label stating taxa name and, on reverse, the complete sample name. The complete sample name is a compound name formed from the Survey designation, the Station name, and (if replicate samples were collected) the Replicate number (e.g. F3B3, 0187-5A, 0888-6C5).

## 2) Sample Lots

- a) Taxa Lots from a sample are to be stored in a two jar Sample Lot (three jars may be used if sample contains an unusually large specimen), one jar containing the Annelid Taxa Lots, the other(s) containing all other Taxa Lots.
- b) Sample Lot containers are to be of sufficient size to allow easy access to the Taxa Lot vials and adequate headroom to assure the vials do not impede lid closure and are completely submerged in preservative.
- c) Sample Lots are to be labeled with both a label inside and an adhesive label on top of lid.
- d) Sample Lot labels to be placed inside of container are to be sized to the container so as to be easily visible.
- e) Labels on and inside Sample Lots are to state the Sample Name. The complete sample name is a compound name made up of the Survey name, Station name, and (if replicate samples were collected) the Replicate number (e.g. G7B2, 0185-0A, 0888-1C4).
- f) In addition, for inventory purposes, the labels shall indicate which of the two (or more) Sample Lot jars it is and how many jars make up the Sample Lot. This is to be indicated by the notation 1 of 2 or 2 of 2, etc. This inventory number is to be clearly set off from the Sample Name so as to avoid confusion. The jar containing the Annelid lots is to always be the first of the jars indicated by the inventory number.

**TAXONOMY QA/QC:** All identifications are reviewed by the laboratory supervisor or a taxonomist other than the original identifier. Differences of opinion are resolved by the laboratory supervisor. Taxa that require further study are assigned to a taxonomist for review.



A voucher collection of specimens of all species encountered in the course of Districts' surveys is maintained in the lab. An extensive reference collection is also maintained, containing specimens of many local species, as well as species extralimital to our study area but which may be encountered within California waters.

The Districts' taxonomists are active participants in the Southern California Association of Marine Invertebrate Taxonomists and maintain active contacts with taxonomists throughout the region and internationally.

All samples collected during the course of benthic surveys are retained in archives at the MBL. This material is maintained under the curatorial guidelines detailed above. These archived samples are periodically reviewed and provide a large collection of material for the resolution of taxonomic problems. Based upon these reviews, the results of past surveys are emended to assure the consistency of identifications over the long (30+ yr) course of the Districts' infaunal study.

## **PHYSICAL/CHEMICAL SAMPLE ANALYSIS METHODS**

### **PROCEDURES FOR ANALYSIS OF PORE-WATER SULFIDES BY MEANS OF SULFIDE SELECTIVE ELECTRODE**

#### **1. Chemicals**

- 1.1 Sodium sulfide 9 H<sub>2</sub>O (MW 240.2)
- 1.2 Lead perchlorate 95% (MW 406.1)
- 1.3 Ascorbic acid (MW 176.12)
- 1.4 Disodium EDTA ((Ethylenedinitrilo)tetraacetic acid disodium salt) (MW 372.24)
- 1.5 Sodium hydroxide (MW 40.00)

#### **2. Reagent Preparation**

- 2.1 Approx. 0.1M lead perchlorate standard solution- 2 liters
  - 2.1.1 Dissolve approx. 90-100g lead perchlorate in 2 liters deionized water (concentrated perchloric acid may have to be added dropwise in order to dissolve the lead salt).
  - 2.1.2 Analyze lead perchlorate solution by atomic absorption (0.1M=  $2.07 \times 10^4$  ppm - dilute 1:20,000 to prepare approx. 1 ppm atomic absorption sample).

Warning: Lead perchlorate crystals may explode upon heating or percussion. Lead perchlorate is indefinitely stable in aqueous solution in the absence of strong reducing

agents. Do not heat such solutions to dryness. Similar precautions must also be taken with perchloric acid.

- 2.1.3 Lead perchlorate solution may also be standardized with primary standard EDTA using xylenol orange indicator (E.W. Baumann, Anal. Chem., 46, 1345 (1974)).

## 2.2 Sulfide Anti-Oxidant Buffer (SAOB)

- 2.2.1 Place approx. 2000 mL water and a 2 inch stirring bar in a large, narrow-mouth screw cap plastic bottle. (Use fresh, filtered seawater for marine samples.)
- 2.2.2 Bubble nitrogen through the water with a gas dispersion tube while stirring in order to deaerate it. (Deaeration is complete in 15-20 minutes).
- 2.2.3 Add 500 mL of this deaerated water and a 2 inch stirring bar to a 1000 mL volumetric flask. (Adjust volumes to meet the needs of the analysis.)
- 2.2.4 Using a wide-mouth powder funnel, add 80 g sodium hydroxide to the volumetric flask as the solution is stirred. (The solution will become very hot during the dissolution process, so do not stopper the flask.)
- 2.2.5 Blow nitrogen into the headspace of the flask to prevent reabsorption of oxygen while the solution is stirring.
- 2.2.6 Continue stirring until the solution has cooled.

NOTE: If deaerated seawater is used to prepare SAOB, the solution will turn cloudy with a white precipitate of magnesium hydroxide after the addition of sodium hydroxide. This precipitate will not dissolve and will not affect the analysis.

- 2.2.7 Add 67 g disodium EDTA to the solution and continue stirring solution while flushing headspace with nitrogen.
- 2.2.8 Quickly add 35 g ascorbic acid to the stirred flask and resume nitrogen flushing.

NOTE: After ascorbic acid dissolves in a basic solution, it will react with even trace amounts of oxygen. At this stage it is especially necessary that the SAOB solution be kept under a blanket of nitrogen. As oxygen reacts with the ascorbate, the solution will turn very dark brown. This reaction is promoted by heat so it is important that the solution be cooled down before the addition of ascorbic acid (cool to room temperature).

- 2.2.9 Add deaerated water to the stirred solution to take volume up to 1000 mL.

2.2.10 Wrap the volumetric flask stopper with one layer of teflon tape.

2.2.11 After the flask headspace has been thoroughly flushed with nitrogen, stopper the flask (teflon tape will provide a more air-tight seal and will prevent the ground glass stopper from freezing up when exposed to the highly basic SAOB).

2.2.12 Store SAOB solution in a refrigerator in order to preserve it. The solution should be clear to pale yellow-brown in color. It should be discarded when it turns dark brown. With the proper precautions, this solution will remain useable for weeks or even months.

### 2.3 Sulfide standards

#### 2.3.1 Prepare saturated sulfide solution

- a.) Place approx. 150 mL deaerated deionized water in a small, wide-mouth screw-cap plastic bottle.
- b.) Add approx. 100 g sodium sulfide to the water and stir until the solution is saturated. (A saturated solution is about 2M or 64,000 ppm in  $S_2$ .)
- c.) Cap the bottle and store in cool place.

Warning: Sodium sulfide crystals may explode upon rapid heating or percussion. Sodium sulfide crystals and solutions are strongly alkaline and corrosive.

#### 2.3.2 Prepare stock standard

- a.) Add 500 mL SAOB to 1000 mL volumetric flask.
- b.) Flush headspace of flask with nitrogen.
- c.) Pipet 20 mL of saturated sulfide solution into flask and stir.
- d.) Add deaerated water (ocean water for marine samples) to make up volume to 1 liter.
- e.) Concentration of this standard will be approximately 0.04M or 1300 ppm.
- f.) Always flush headspace of SAOB container with nitrogen after use.

#### 2.3.3 Preparation of serial dilution standards

- a.) To make 1:10 serial dilutions, pipet 10 mL standard into a 100 mL volumetric flask containing 45 mL SAOB. Dilute to the mark with deaerated water (seawater for marine samples). (Note: these are air sensitive)
- b.) To make 1:100 serial dilutions, pipet 1 mL standard into a 100 mL volumetric flask containing 50 mL SAOB. Dilute to the mark with deaerated water (seawater for marine samples). (Note: these are air sensitive)

#### 2.3.4 Preparation of blank

Make up blank consisting of 50 mL SAOB and 50 mL deaerated water (seawater for marine samples) (Note: this solution is air sensitive)

#### 2.3.5 Stability of standards

- a.) The stock standard should be stored in the same manner as the SAOB.
- b.) When properly protected from oxygen, the stock standard will be stable for at least a week.
- c.) It is recommended that the sulfide stock solution be restandardized or discarded every week.
- d.) Discard the sulfide stock solution if it exhibits a dark brown color indicating it has been air oxidized.
- e.) Serial dilution standards should be prepared daily.

### 3. Sulfide Analysis Procedures

#### 3.1 Standardization of sulfide stock standard.

- 3.1.1 Pipet 50 mL stock standard into 100 mL beaker.
- 3.1.2 Fill 25 mL buret with lead perchlorate standard.
- 3.1.3 Rinse both the double junction reference electrode and the silver/silver sulfide electrode with water.
- 3.1.4 Immerse electrodes in 100 mL beaker containing sulfide standard.
- 3.1.5 Attach electrodes to pH/millivolt meter.
- 3.1.6 Set meter to read millivolts and magnetically stir the standard.

- 3.1.7 The initial meter reading should be on the order of -600 to -800 millivolts.
- 3.1.8 Potentiometrically titrate the sulfide standard with the lead perchlorate standard. Take readings every 10mV if possible.
- 3.1.9 The potentiometric end point should occur after the addition of about 18 mL of titrant (this corresponds to a millivolt change of about 150-200 millivolts).
- 3.1.10 Use the following equations to calculate the concentrations of the sulfide stock standard:

$$C_S = C_{Pb} V_{Pb} / V_S \quad (1)$$

$$C'_S = (3.4 \times 10^4) C_S \quad (2)$$

where:  $C_S$  = molar concentration of sulfide stock standard

$C_{Pb}$  = molar concentration of lead perchlorate standard

$V_S$  = volume of sulfide stock standard titrated (50 mL)

$V_{Pb}$  = volume of lead perchlorate titrant added

$C'_S$  = ppm H<sub>2</sub>S concentration of sulfide stock standard

### 3.2 Standard curve for sulfide analysis

- 3.2.1 Rinse double junction reference and silver/silver sulfide electrodes with water.
- 3.2.2 Have four sulfide standards made up in the range of 0.1-1000 ppm sulfide. (Standards on the order of 0.1, 1.0, 10, and 100 ppm should be sufficient). Two standards may be used when the sample concentrations are expected to fall within a limited range.
- 3.2.3 Immerse electrodes in blank solution and magnetically stir several minutes.
- 3.2.4 Record millivolt reading for blank after it has stabilized.
- 3.2.5 Immerse electrodes in least concentrated sulfide standard.
- 3.2.6 Stir solution and record millivolt readings when it has stabilized.
- 3.2.7 Rinse and dry electrodes before repeating this procedure on the mid-range standard, and then the most concentrated standard.

3.2.8 The operation of the sulfide electrode is based on the following Nernstian relationship:

$$E = E_0 + A \log C_S \quad (3)$$

where: E = meter millivolt reading

A = electrode slope (approx. -29 mV)

C<sub>S</sub> = concentration of hydrogen sulfide

E<sub>0</sub> = electrochemical potential of 1M sulfide solution

3.2.9 Make up a linear calibration curve by plotting E versus log C<sub>S</sub>. If electrode slope is not in the range of 29 mV or is nonlinear, it will be necessary to recalibrate.

3.2.10 Low concentrations of sulfide (0.003-0.03 ppm) may not follow the linear relationship given in Equation 3. It is suggested that a separate nonlinear calibration curve be made up for low sulfide standards. More points must be taken for this curve.

3.2.11 The silver/silver sulfide electrode should be stored in "blank" solution prior to its use with low sulfide standards.

3.2.12 Recalibrate the electrodes every two hours. This may involve checking one standard to correct for electrode potential drift or checking several standards to correct for changes in electrode slope.

3.2.13 Ideally, the millivolt meter should be read to 0.1mV. If the millivolt meter only reads to 1 mV, then an 8% (plus or minus) relative error must be accepted.

### 3.3 Analysis of sulfide in water samples

3.3.1 Place a measured volume of sample in an appropriate container.

3.3.2 Add an equal volume of SAOB to the sample and stir.

3.3.3 Be sure sulfide electrode is thoroughly rinsed, especially after use in more concentrated solutions. It is best to store electrode in distilled water or blank SAOB solution between runs.

3.3.4 Immerse electrodes in sample solution.

3.3.5 Record the millivolt reading when it has stabilized.

3.3.6 Rinse electrodes and repeat the procedure with the remaining samples.

3.3.7 Use the following equation to determine the sulfide concentrations in the samples:

$$S = (2)(10^{\log C'_s}) = 2 C'_s \quad (4)$$

where:  $S$  = hydrogen sulfide concentration in the sample

$\log C'_s$  = quantity corresponding to the sample millivolt reading on the standard calibration curve

$C'_s$  = hydrogen sulfide concentration of sample after two-fold dilution with SAOB

Table A3.1 LACSD Sediment Chemistry Analytical Methods

Method <sup>(1)</sup>	Description	RL <sup>(2)</sup>	Unit of Measure
SM 2540B	Total Solids <sup>(3)</sup>		%
SM 2540B	% Moisture <sup>(3)</sup>		%
EPA 9010B/9014	Total Cyanide	0.3	mg/kg CN
SM 4500-Norg B	Organic Nitrogen	29	mg/kg N
SM 5220B	Total COD <sup>(3)</sup>		% O
EPA 410.2	Total Organic Carbon <sup>(3)</sup>		% C

(1) SM is Standard Methods for the Examination of Water and Wastewater

EPA is the Environmental Protection Agency Methods for Chemical Analysis of Water and Wastes

(2) The Reporting Limit (RL) is the lowest point on the calibration curve times all applicable factors including sample size, final volume, dilution factor and % moisture. The values above do not reflect these factors since they vary from sample to sample.

## **SEDIMENT GRAIN SIZE:**

MEC Analytical Systems, Inc.

### **1.0 SCOPE**

Percentages of gravel, sand, silt, and clay components and weights of phi fractions of the sediment sample will be determined.

### **2.0 EQUIPMENT**

- 8 oz. numbered (lettered) plastic deflocculent bottles.
- .025N (38.25 g per 15 liters deionized water) sodium hexametaphosphate (deflocculent).
- 63  $\mu$ m sieve.
- Stainless steel evaporating dish.
- Preweighed and numbered Coors dishes.
- Numbered 1000 ml graduated cylinders.
- Watchglasses to cover graduated cylinders.
- 3" sections of pipe (used to weigh down 1000 ml graduated cylinders in water bath).
- Plunging device (for agitating silt and clay solution).
- 25 ml Lowy Automatic Pipette with markings at 7, 8, 10, and 20 cm.
- Preweighed and numbered 50 ml beakers.
- 24°C water bath.
- Drying Oven (Required Range <50°C).
- Series of sieves with increasingly finer meshes, with a pan at the bottom and lid at the top.
- Sieve shaker.
- American Scientific Products digital electronic balance (Model Z-400-DR).

### **3.0 PROCEDURE**

#### **3.1 Initial Treatment**

- 1 Take samples out of refrigerated storage.
- 2 Center and calibrate balance (refer to SOP EQP023). Record calibration and approval in Balance Log Book.
- 3 Mix wet sample thoroughly in its container. Weigh 40 gm wet sediment immediately (while still homogeneous) into 8 oz. deflocculent bottles.
- 4 Record sample I.D. and analyzed by, date, sieve size for sand/silt-clay separation, and deflocculent bottle number on a grain size keypunch sheet.



- 5 Add approximately 150 ml of sodium hexametaphosphate (deflocculent) to the sediment in the deflocculent bottle. Shake bottles and leave overnight.
- 6 Place the 63  $\mu\text{m}$  screen in evaporating dish in order to catch all wash water.
- 7 Transfer the sample from the bottle to a sieve using a squirt bottle with deflocculent solution.
- 8 Wash the remaining silt and clay through the sieve (using light finger pressure and squirt bottle).
- 9 Wash the bottom of the sieve periodically to remove adhering particles.
- 10 Wash sand remaining in the sieve with deionized water to remove excess sodium hexametaphosphate and salts.
- 11 Carefully concentrate sand against bottom lip of sieve with squirt bottle. Scrape sand and wash into a numbered Coors dish. Record the sand dish number on grain size keypunch data sheets.
- 12 Leave sand to settle.
- 13 Dry sand in the oven at  $<50^{\circ}\text{C}$ . Record the oven temperature in the oven log and maintain at the required temperature,  $\pm 2^{\circ}\text{C}$  at the operating range of  $32\text{--}300^{\circ}\text{C}$ . If the temperature is found to be out-of-control during analysis, void the results of that analysis. Repeat the analysis after the oven has stabilized for 8 hours.
- 14 Transfer the silt/clay solution from evaporating dish to a numbered 1000 ml graduated cylinder, filled to 1000 ml with deflocculent solution.
- 15 Record the cylinder numbers on grain size keypunch data sheets.

### 3.2 Sieve Analysis for Sand

- 1 Center and calibrate the balance (refer to SOP EQP023). Record calibration and approval in the balance log book.
- 2 Weigh Coors dish with sample; record weight on grain size keypunch data sheet. Transfer sand from the Coors dish to the top sieve in the sieve stack. Record the weight of the dish.

- 3 Shake the sieve stack gently to break-up aggregated sediment on the top 1-3 sieves.
- 4 Place the sieve stack in the sieve shaker and shake for 10 minutes.
- 5 Starting with the top sieve, invert each sieve on a large piece of paper and rap firmly on the table top to remove all sand.
- 6 Examine particles on successive sieves and record notes in comments section of grain size keypunch data sheet if shells, aggregates, twigs, metal, etc., are present.
- 7 Tare the empty weight of the plastic weighing dish (dish wt. = 0.000 gm).
- 8 Transfer sand to tared plastic dish on balance, and record the cumulative weight for each successive sieve on grain size keypunch data sheets. The difference in the successive cumulative weights is the contribution of each phi size.

### 3.3 Pipette Analysis for Silt-Clay Fraction

- 1 Record cylinder numbers and batch numbers on grain size keypunch data sheets.
- 2 Record beaker numbers on the grain size keypunch data sheet.
- 3 Place numbered graduated cylinders in a water bath approximately 24°C (up to 10 cylinders at a time). Record the water bath temperature on grain size keypunch sheets.
- 4 Agitate each sample for one minute with the plunger, and take six 25 ml aliquots from each cylinder at different depths and different times. Plunging times, withdrawal times, and withdrawal depths are provided on a chart.
- 5 Transfer aliquots to numbered 50 ml beakers. Calculations (Part 3.4 below) give the weight contributed for each size.
- 6 Dry beakers in oven overnight at <100°C and then weigh.
- 7 Record beaker weight with dried sediment and empty beaker weight on grain size keypunch data sheets.
- 8 Track samples on laboratory tracking log sheet for grain size samples.

### 3.4 Calculations

1 Total Sand = (weight of Coors dish + sand) - weight of Coors dish.

2 Weight of silt and clay fractions = (weight of silt and clay + beaker) - weight of beaker.

Multiply this weight by 40.08 to obtain the total weight in 1000 ml.

( 25 ml / 1000 ml = 1/40 ;

0.08 is a correct factor because the pipette does not deliver exactly 25 ml at 24°C).

From this subtract .3825 grams (the weight of sodium hexametaphosphate in 150 ml of a .025N solution).

Total weight of silt and clay - ([wt. of beaker containing dry silt-clay - wt. of beaker] x 40.08) -.3825 gms.

3 Total sand + total silt-clay = total sample weight.

4 
$$\frac{\text{Total sand}}{\text{Total sample weight}} = \% \text{ sand}$$

5 
$$\frac{\text{Total silt-clay}}{\text{Total sample weight}} = \% \text{ silt and clay}$$

6 Enter data into a computer to calculate individual and cumulative percents, median and mean grain size, and grain size distribution moments.

### 4.0 PERSONNEL

A laboratory technician will perform grain size analysis.

### 5.0 QUALITY ASSURANCE REQUIREMENTS

Quality control procedures for grain size analyses will consist of visual inspection of all screens and equipment prior to analysis and strictly following the standard grain size protocol. In addition,

1 Duplicate analyses will be conducted for 10% of the samples. Percentages will be plotted for all phi values. Outliers will be checked (for presence of large shells, etc.). Analyses will be re-run when values vary significantly.

2 A reference standard will be routinely analyzed with each batch of 1-7 samples. Percentages will be plotted for all phi values; results will be compared against a cumulative plot of previous values. Outliers will be

checked, and analyses will be re-run when values fall out of the expected range.

Any defect in a screen or piece of equipment will be reported to the laboratory manager, and a corrective action report will be filed.

Raw data will be reviewed before entering into grain size analysis program. Any errors in recording or calculations will be reported, and appropriate corrective action will be taken.

## **DESCRIPTION of DATA FILES**

All data from the Benthic Sediments surveys collected during 2005 are provided on the CD accompanying this report. The following descriptions explain the formatting of each of the data files covering the Benthic Sediments data. Data files are in comma separated value file (.CSV) format. Each file begins with a header row providing the field names for the data records. A brief definition of each field name is provided below. The term “sample” is a generic one, which, in the Benthic Sediments program, acts as a synonym for an individual benthic sediment grab at a specific site.

Following the header row the data records begin. Data values can be either alpha, alphanumeric characters or numeric. Any missing data values appear as “,” (*i.e.*, nothing between the commas). The last data value is not followed by a comma.

### **FILE 1: BENTHIC INFAUNAL ABUNDANCE**

*Number of Data Records (excluding header row) = 7216*

#### **Header Row Field Definitions:**

**Survey:** Name of survey during which sample was collected. Benthic surveys are sampled in Summer and Winter.

**Site:** Identifies specific site from which sample collected

**Replicate:** Identifies position in sequence of replicate samples

**Species:** Name of species to which data record applies (may be a higher taxonomic category)

**Abundance\_Qualifier:** Qualifies value reported in Abundance field

**Abundance:** Number of individual(s) of the taxon reported in the record

**Data\_Quality:** Quality rating of the data. A= High quality data for use without qualification; B = Questionable data quality that may be used but see metadata for qualifications; C= Highly questionable data, do not use, see metadata for explanation.; D= unknown data quality

**Phylum:** Taxonomic phylum to which taxon reported in record belongs

**Class:** Taxonomic class to which taxon reported in record belongs

**Order:** Taxonomic order to which taxon reported in record belongs

**Family:** Taxonomic family to which taxon reported in record belongs

**Sampling\_Date:** Date on which sample was taken in the field in M/D/YYYY

**Sampling\_Depth:** Depth at which sample was taken

**Units\_Depth:** Unit of measurement for depth; M=meter  
**Sampling\_Latitude:** Latitude in decimal degrees where sample taken (positive =N)  
**Sampling\_Longitude:** Longitude in decimal degrees where sample taken (negative=W)  
**Sampling\_Gear:** Gear used to collect sample; TVV=tandem Van Veen  
**Screen\_Mesh:** Mesh size (in millimeter) used in screening benthic infaunal samples  
**Sample\_Comments:** Comments about the sample

## **FILE 2: BENTHIC INFAUNAL BIOMASS**

*Number of Data Records (excluding header row) = 474*

### **Header Row Field Definitions:**

**Survey:** Name of survey during which sample was collected. Benthic surveys are sampled in Summer and Winter.  
**Site:** Identifies specific site from which sample collected  
**Replicate:** Identifies position in sequence of replicate samples  
**Biomass\_Group:** Biomass is evaluated for 7 major groups; 6 are at the phylum level (Annelida, Mollusca, Arthropoda, Nemertea, Echiura, Echinodermata) and the last is a collective "Other" of all other phyla  
**Biomass\_Qualifier:** Qualifies value reported in Biomass field  
**Biomass:** Total wet-weight biomass for biomass group reported  
**Biomass\_Units:** Unit of measurement for biomass; G=gram  
**Data\_Quality:** Quality rating of the data. A= High quality data for use without qualification; B = Questionable data quality that may be used but see metadata for qualifications; C= Highly questionable data, do not use, see metadata for explanation.; D= unknown data quality  
**Outlier\_Flag:** Indicates there is a taxon contributing biomass to the sample that was not included in the Biomass value for the Biomass Group; outlier biomass is noted separately in the record; Y=Yes, N=No  
**Outlier\_Species:** Identity at the species level of the biomass outlier  
**Outlier\_Abundance:** Number of individuals of the biomass outlier taxon  
**Outlier\_Biomass\_Qualifier:** Qualifies value reported in Outlier Biomass field  
**Outlier\_Biomass:** Total wet-weight biomass for Biomass Outlier Species reported  
**Outlier\_Biomass\_Units:** Unit of measurement for outlier biomass; G=grams  
**Sampling\_Date:** Date on which sample was taken in the field in M/D/YYYY  
**Sampling\_Depth:** Depth at which sample was taken  
**Units\_Depth:** Unit of measurement for depth; M=meter  
**Sampling\_Latitude:** Latitude in decimal degrees where sample taken (positive =N)  
**Sampling\_Longitude:** Longitude in decimal degrees where sample taken (negative=W)  
**Sampling\_Gear:** Gear used to collect sample; TVV=tandem Van Veen  
**Screen\_Mesh:** Mesh size (in millimeter) used in screening benthic infaunal samples  
**Sample\_Comments:** Comments about the sample

## **FILE 3: SEDIMENT SCREENING**

*Number of Data Records (excluding header row) =306*

### **Header Row Field Definitions:**

**Survey:** Name of survey during which sample was collected. Benthic surveys are sampled in Summer and Winter.

**Site:** Identifies specific site from which sample collected

**Replicate:** Identifies position in sequence of replicate samples

**Screenings\_Volume:** Volume of screened material retained on sieve after sample washed in lab

**Volume\_Units:** Unit of measurement for screenings volume; ML=milliliter

**Screening\_Item:** Description of identifiable item making up material retained on sieve

**Abundance\_Designation:** Qualitative amount of screening item in the record; 3=Abundant, 2=Common, 1=Rare

**Sampling\_Date:** Date on which sample was taken in the field in M/D/YYYY

**Sampling\_Depth:** Depth at which sample was taken

**Units\_Depth:** Unit of measurement for depth; M=meter

**Sampling\_Latitude:** Latitude in decimal degrees where sample taken (positive =N)

**Sampling\_Longitude:** Longitude in decimal degrees where sample taken (negative=W)

**Sampling\_Gear:** Gear used to collect sample; TVV=tandem Van Veen

**Screen\_Mesh:** Mesh size (in millimeter) used in screening benthic infaunal samples

**Sample\_Comments:** Comments about the sample

#### **FILE 4: SEDIMENT DESCRIPTION**

*Number of Data Records (excluding header row) = 225*

##### **Header Row Field Definitions:**

**Survey:** Name of survey during which sample was collected. Benthic surveys are sampled in Summer and Winter.

**Site:** Identifies specific site from which sample collected

**Replicate:** Identifies position in sequence of replicate samples

**Penetration:** Estimated depth of penetration of sampler into the seafloor

**Penetration\_Units:** Units of measurement for penetration; CM=centimeter

**Surface\_Sed\_Color:** Qualitative description of sample sediment color in upper 1-2 cm layer

**Subsurface\_Sed\_Color:** Qualitative description of sample sediment color below 2 cm layer

**Surface\_Sed\_Type:** Qualitative description of sample sediment type in upper 1-2 cm layer

**Subsurface\_Sed\_Type:** Qualitative description of sample sediment type below 2 cm layer

**Sediment\_Temperature:** Temperature of subsurface sediments using thermometer inserted into lowest layer of sample

**Temperature\_Units:** Unit of measurement for temperature; C=centigrade degrees

**Sediment\_Odor:** Qualitative assessment of sediment odor

**Sampling\_Date:** Date on which sample was taken in the field in M/D/YYYY

**Sampling\_Depth:** Depth at which sample was taken

**Units\_Depth:** Unit of measurement for depth; M=meter

**Sampling\_Latitude:** Latitude in decimal degrees where sample taken (positive =N)

**Sampling\_Longitude:** Longitude in decimal degrees where sample taken (negative=W)

**Sampling\_Gear:** Gear used to collect sample; TVV=tandem Van Veen

**Sample\_Comments:** Comments about the sample

## **FILE 5: SEDIMENT CHEMISTRY**

*Number of Data Records (excluding header row) =600*

### **Header Row Field Definitions:**

**Survey:** Name of survey during which sample was collected. Benthic surveys are sampled in Summer and Winter

**Site:** Identifies specific site from which sample collected

**Replicate:** Identifies position in sequence of replicate samples

**Test\_Material:** Type or nature of material composing the sample (e.g. sediment, pore water)

**Parameter Group:** A grouping mechanism to categorize sediment chemistry parameters.

There are 5 parameter groups:

Phys, N, C, S– physical characteristics, Nitrogen, Carbon, Sulfide parameters

TICH- Total Identifiable Chlorinated Hydrocarbons

PAH- Polycyclic Aromatic Hydrocarbons

Metals- heavy metals

P Pollutants- priority pollutants (not covered in above categories)

**Parameter:** Name of chemistry parameter for which results are reported

**Qualifier:** Qualifies value reported in Results field

**Result:** Analytical result

**Result\_Units:** Units associated with the reported result

**Sampling\_Basis:** Identifies whether reported result was analyzed as wet or dry weight

**Data\_Quality:** Quality rating of the data. A= High quality data for use without qualification; B = Questionable data quality that may be used but see metadata for qualifications; C= Highly questionable data, do not use, see metadata for explanation.; D= unknown data quality

**Sampling\_Date:** Date on which sample was taken in the field in M/D/YYYY

**Sampling\_Depth:** Depth at which sample was taken

**Units\_Depth:** Unit of measurement for depth; M=meter

**Sampling\_Latitude:** Latitude in decimal degrees where sample taken (positive =N)

**Sampling\_Longitude:** Longitude in decimal degrees where sample taken (negative=W)

**Sampling\_Gear:** Gear used to collect sample; TVV=tandem Van Veen

**Sample\_Comments:** Analyst's comments about the sample

## **FILE 6: SEDIMENT GRAIN SIZE**

*Number of Data Records (excluding header row) = 2637*

### **Header Row Field Definitions:**

**Survey:** Name of survey during which sample was collected. Benthic surveys are sampled in Summer and Winter.

**Site:** Identifies specific site from which sample collected

**Replicate:** Identifies position in sequence of replicate samples

**Parameter:** Name of grain size parameter for which results are reported

**Qualifier:** Qualifies value reported in Results field; NR=not reached, EX=extrapolated

**Result:** Analytical result

**Result\_Units:** Units associated with the reported result

**Analysis\_Method:** Identifies the approved method for analysis; GS-1=Sieve Pipette, Plumb 1981

**Analysis\_Date:** Date the analysis was performed

**Data\_Quality:** Quality rating of the data. A= High quality data for use without qualification; B = Questionable data quality that may be used but see metadata for qualifications; C= Highly questionable data, do not use, see metadata for explanation; D= unknown data quality

**Sampling\_Date:** Date on which sample was taken in the field in M/D/YYYY

**Sampling\_Depth:** Depth at which sample was taken

**Units\_Depth:** Unit of measurement for depth; M=meter

**Sampling\_Latitude:** Latitude in decimal degrees where sample taken (positive =N)

**Sampling\_Longitude:** Longitude in decimal degrees where sample taken (negative=W)

**Sampling\_Gear:** Gear used to collect sample; TVV=tandem Van Veen

**Sample\_Comments:** Analyst's comments about the sample