Field Sampling Manual for the Regional Monitoring Program for Trace Substances

Prepared

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1 Program Overview

1.1 **RMP** Rationale

The Sacramento-San Joaquin Delta and the San Francisco Bay (together known as the Estuary) make up the West Coast's largest estuary. The watershed that drains into the 1,600 mi² Estuary comprises over 40% of California's surface area. The Estuary is in close proximity to and highly affected by both a highly urbanized landscape and the rich agricultural areas of the Central Valley. Urban runoff, agricultural runoff, treated wastewater, and dredging activities all introduce contaminants to estuarine waters.

Scientists have been conducting research and monitoring activities on the Estuary for decades. Until the early 1990s, these activities were typically geared for a specific need, limited in coverage, and failed to provide an overall picture of the Estuary's condition. In addition, sampling methods used by different studies were rarely comparable.

The San Francisco Bay Regional Water Quality Control Board (Regional Board) is the state agency responsible for implementing and overseeing water quality programs for the San Francisco Estuary. The Regional Board realized the need for comprehensive long-term monitoring and established the Regional Monitoring Program for Trace Substances (RMP) in 1992 in an effort to fulfill that need. In addition to the Regional Board, two other entities help determine the focus and operations of the RMP: the permit holders from eighty-three public and private organizations that discharge treated wastewater, cooling water, or urban runoff, and the San Francisco Estuary Institute (SFEI) which is responsible for implementation of the RMP.

The RMP regularly monitors contaminant concentrations in water, sediments, and fish and shellfish tissue in the Estuary. This contaminant monitoring allows the Regional Board to evaluate the effectiveness of its water quality programs in its overarching goal of protecting the beneficial uses of the Estuary.

1.2 RMP Objectives

The RMP's overall goal is to provide data and interpretation that helps to address certain of the Regional Board's information needs. These efforts fall under five major objectives:

- Describe patterns and trends in contaminant concentration and distribution.
- Describe general sources and loadings of contamination to the Estuary.
- Measure contaminant effect on selected parts of the Estuary ecosystem.
- Compare monitoring information to relevant water quality objectives and other guidelines.
- Synthesize and distribute information from a range of sources to present a more complete picture of the sources, distribution, fates, and effects of contaminants in the Estuary ecosystem.

1.3 RMP Organization and Management

The organization diagrams for water, sediment and bioaccumulation sampling are shown in Appendix A, Figures 2, 3 and 4, respectively. Responsibilities for each cruise are as follows:

For water sampling, Applied Marine Sciences (AMS) is responsible for drafting the sample cruise plan in accordance with the goals of SFEI and the Steering Committee (representatives of the permit holders), conducting CTD casts, collecting samples for water toxicity, and overall cruise management. The University of California, Santa Cruz (UCSC) is responsible for trace elements (also referred to as trace metals) water sample collection and analysis/reporting of trace elements and cognates data. UCSC also collects samples for analysis of As and Se that are shipped by AMS for analysis and reporting by Brooks Rand, Ltd. (BRL). Hg and MeHg are analyzed by the University of Maryland (UMCES). The University of Utah (UU) is responsible for collecting, analyzing and reporting all trace organics water samples. The Union Sanitary District (USD) provides hardness data for the sampled stations and Pacific EcoRisk Laboratory (PERL) runs toxicity tests. The *R/V David Johnston*, a UCSC-operated vessel, is the vessel used for conducting this sampling.

For sediment sampling, AMS is responsible for generating the cruise plan in accordance with the goals of SFEI and the Steering Committee. AMS is also responsible for sample collection, sample processing, pore water analysis of pH and ammonia, CTD profiling, and sample distribution. SFEI is responsible for assisting with sample collection and processing in the field and for overall data compilation and analysis. The Bay Area Dischargers Authority (BADA) is responsible for analysis and reporting of trace organics and trace elements samples, only As and Se are analyzed and reported by Brooks Rand, Ltd. (BRL). The Marine Pollution Studies Laboratory (MPSL) is responsible for analysis and reporting of sediment toxicity, hydrogen sulfide, total sulfides, and ammonia. UCSC is responsible for analysis and reporting of Hg and MeHg samples, as well as analysis of a subset of sediment samples using HF extraction for trace elements. The City and County of San Francisco is responsible for collection of benthic infauna samples, analysis, and reporting of the results, as well as HF extraction and reporting of trace elements.

For bioaccumulation sampling, AMS is responsible for generating the cruise plan in accordance with the goals of SFEI and the Steering Committee. AMS is also responsible for acquisition of all bivalves prior to the cruises; sample deployment, maintenance and retrieval via SCUBA diving; homogenization of bivalve samples for analysis of trace elements; survival rates, condition index, growth, and gonad index analysis; and additionally, vessel supply and operations for the Davis Point and Napa River site (BD40 and BD50). The vessel used for all RMP sites, except Davis Point, is the *R/V Questuary*, supplied and operated by the Romberg Tiburon Center. BADA is responsible for analysis and reporting of tissue trace elements and trace organic intercalibration samples. GERG is responsible for homogenizing trace organics samples, as well as analyzing and reporting trace organics. BRL is responsible for analysis and reporting of Se. SFEI is responsible for overall data compilation and analysis.

The principal investigators of the RMP are listed in Table 1.

Contractor	Affiliation
Prime Contractors	Dr. Bob Spies and Dr. Andy Gunther Applied Marine Sciences (AMS), Inc.,
	Livermore, CA
Trace Element Chemistry	Dr. Russ Flegal, UC Santa Cruz (UCSC), CA ; Dr. Rick Manson, Brooks-
	Rand, Ltd., (BRL) Seattle, WA
Trace Organic Chemistry	Dr. Terry Wade, Texas A&M University (GERG), TX; Dr. Walter Jarman,
	University of Utah, CA
Water Toxicity Testing	Dr. Scott Ogle Pacific Eco-Risk Laboratories (PERL), Martinez CA
Sediment Toxicity Testing	Mr. John Hunt and Mr. Brian Anderson Marine Pollution Studies Lab
	(MPSL), Granite Canyon, CA
Bagged Bivalve Sampling	Dr. Andy Gunther, AMS, Livermore, CA
USGS Water Quality	Dr. James Cloern, US Geological Survey (USGS), Menlo Park, CA
USGS Sediment Transport	Dr. David Schoellhamer, USGS, Sacramento, CA
Fish Tissue Sampling and Analysis	Dr. Jay Davis, San Francisco Estuary Institute (SFEI), Richmond, CA
Estuary Interface Pilot Study	Dr. Rainer Hoenicke, SFEI, Richmond, CA

Table 1. Principal Investigators of the RMP.

1.3.1 Telephone and E-mail Contact List

The telephone numbers and e-mail contacts of RMP investigators and staff are presented in Table 2.

Last	First	Affiliation	Position	Phone	E-mail
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Table 2. Telephone and e-mail contacts for RMP researchers and staff.

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McGann	Mary	United States Geological Service	Foraminifer Project Contact	650-329-4979 mmcgann@octopus.wr.usgs.gov
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2 Cruise Scheduling

Beginning in 2000, the sampling frequency of all matrices (water, sediment, and tissue) was adjusted to reflect some of the re-design recommendations from the five-year review process. Water cruises are conducted two times a year (wet and dry season), and sediment and bivalve sampling was reduced to once per year during the dry season only. Fish tissue sampling is taking place on a three-year cycle.

2.1 Water

The typical water cruise activity schedule assumes that an average of 1.5 hours is required for sampling each station and that the survey vessel is capable of maintaining a minimum cruising speed between stations of 7 knots. Actual survey times will vary depending on weather and sampling conditions. A typical cruise schedule is presented in Table 3.

Table 3. Water cruise activity schedule.

Day	Activity Schedule
Day 1	Mobilize gear on vessel R/V David Johnston at the Emeryville Marina. Conduct safety briefing and depart for South Bay sites. Sample Oyster Point, San Bruno Shoal, Coyote Creek, Redwood Creek, and South Bay. Transit to Redwood City.
Day 2	Mobilize gear on vessel R/V David Johnston. Depart Redwood City, sample Dumbarton Bridge, San Jose, and Sunnyvale sites. Transit to Emeryville Marina.
Day 3	Mobilize gear on vessel R/V David Johnston. Depart Emeryville Marina, sample Yerba Buena Island, Alameda, Golden Gate and Richardson Bay sites. Transit to Emeryville Marina.
Day 4	Mobilize gear on vessel R/V David Johnston. Depart Emeryville Marina, sample Red Rock and Point Isabel sites. Transit to Emeryville Marina. As and Se samples are shipped to Brooks Rand.
Day 5	R/V David Johnston transits to Martinez Marina. No crew is required.
Day 6	Mobilize gear on vessel R/V David Johnston. Depart Martinez Marina, sample Davis Point, Pinole Point, San Pablo Bay, and Petaluma River sites. Transit to Martinez Marina.
Day 7	Mobilize gear on vessel R/V David Johnston. Depart Martinez Marina, sample Honker Bay, Napa river, and Pacheco Creek sites. Transit to Martinez Marina.
Day 8	Mobilize gear on vessel R/V David Johnston. Depart Martinez Marina, sample Grizzly Bay, Sacramento, and San Joaquin River sites. Transit to Martinez Marina and demobilize gear off vessel.
Day 9	Sample watershed sites at Standish Dam (Coyote Creek) and South Bay Yacht Club (Guadalupe River). As and Se samples are shipped to Brooks Rand.

2.2 Sediment

The typical sediment cruise activity schedule assumes that sampling requires approximately 0.25 hours/grab/site, and that the survey vessel is capable of maintaining a cruising speed of 7 knots between stations during which time benthic samples are processed. A typical sediment cruise schedule is presented in Table 4.

Table 4. Sediment cruise activity schedule.

Day	Activity Schedule
Day 1	Mobilize gear on vessel R/V David Johnston, conduct safety briefing at the Martinez Marina. Depart for Grizzly Bay.
	Sample at Grizzly Bay, Honker Bay, Sacramento River, San Joaquin River, and Pacheco Creek. Drop off crew at Martinez Marina and shuttle cars to Vallejo. Vessel transits to Vallejo Marina.
	Demobilize gear at Vallejo Marina. Load benthic sampling gear onto vessel. All chemistry and toxicity samples will be stored on ice aboard the vessel.
Day 2	Mobilize gear on vessel R/V David Johnston at the Vallejo Marina. Benthic sampling crew member joins the rest of the sampling crew. Depart for Napa River.
	Sample at Napa River, Davis Point, Petaluma River, San Pablo Bay, Pinole Point, and Red Rock. Vessel transits to the Emeryville Marina.
	Demobilize gear at the Emeryville Marina. Toxicity samples are stored on wet ice aboard the vessel. Pore water samples are stored in a light-proof container. Trace elements, trace organics, Hg and MeHg and cognate samples are stored on dry ice aboard the vessel. Benthic samples are removed from the vessel by CCSF.
	The crew shuttles back to Vallejo to retrieve their cars.
Day 3	Mobilize gear on vessel R/V David Johnston at the Emeryville Marina. Depart for Point Isabel.
	Sample at Point Isabel, Richardson Bay, Horseshoe Bay, and Yerba Buena Island. Vessel transits back to Emeryville.
	Demobilize gear at Emeryville Marina. All chemistry and toxicity samples will be stored on ice aboard the vessel.
Day 4	Mobilize gear on vessel R/V David Johnson at the Emeryville Marina. Depart for Alameda.
	Sample at Alameda, Oyster Point, San Bruno Shoal, Redwood Creek, and South Bay. Vessel transits to Redwood City USGS dock.
	Demobilize gear at Redwood City. All chemistry and toxicity samples will be stored on ice aboard the vessel.
Day 5	Mobilize gear on vessel R/V David Johnston at the Redwood City USGS dock. Depart for Dumbarton Bridge.
	Sample at Dumbarton Bridge, San Jose, Sunnyvale and Coyote Creek. Vessel transits to Emeryville.
	Demobilize gear at Emeryville Marina. All toxicity and pore water samples are picked up at the vessel by a representative from MPSL. Trace metal and organic samples are picked up at the vessel by a BADA representative. As and Se samples for BRL are transferred to AMS for shipment the following day.
Day 6	Sample Standish Dam and Guadalupe River. Send all remaining samples to the proper analytical laboratories.

2.3 Bioaccumulation

Bioaccumulation cruises are conducted for deployment of bivalves, maintenance of bivalves approximately 50 days after deployment, and retrieval of bivalves approximately 100 days after deployment. The typical bioaccumulation deployment cruise activity schedule assumes that dive operations require approximately 0.5 hours on site and that the diver support vessel is capable of maintaining a cruising speed of 12 knots between sites. A typical bioaccumulation cruise schedule is presented in Table 5.

Table 5. Bioaccumulation cruise activity schedule.

Day	Activity
Day 1	Approximately 7-14 days prior to the start of a deployment cruise, oysters (<i>C. gigas</i>) are obtained from a commercial grower located in Tomales Bay. Oysters are transferred from the grower's tanks into mesh bags and placed into a holding tank at the Bodega Marine Lab (BML). Normally during the same day, mussels (<i>M. californianus</i>) are collected during low tides from Bodega Head, Sonoma County. Mussels are transferred into mesh bags and also placed into a holding tank at BML. The holding tank at the BML is constantly flushed with filtered seawater at ambient ocean temperatures. Bivalves are kept in holding tanks no less than 24 hours and no longer than 14 days prior to deployment.
Day 2	All bivalves are retrieved from the holding tank at the BML. (This task occurs within 2-14 days after bivalves are collected)
Day 3	Mobilize gear on vessel M.E. II, conduct safety briefing at Martinez Marina. Deploy bivalves at Davis Point. Demobilize gear at Martinez Marina.
Day 4	Mobilize gear on vessel R/V Questuary, conduct safety briefing at Emeryville Marina. Deploy bivalves at Yerba Buena Island, Alameda, Redwood Creek, Dumbarton Bridge and Coyote Creek. Demobilize gear at Emeryville Marina, refill SCUBA tanks as necessary.
Day 5	Mobilize gear on vessel R/V Questuary, Emeryville Marina. Deploy bivalves at Horseshoe Bay, Red Rock, Pinole Point, San Pablo Bay, Petaluma River, and Napa River. Demobilize gear at Martinez Marina.
Day 6	Mobilize gear on vessel R/V Questuary, Martinez Marina. Conduct clam harvesting operations at Sacramento River and San Joaquin River as needed and return to Emeryville Marina. Demobilize gear.

2.4 Site Data

As one objective of the RMP is to determine seasonal and annual trends in chemical and biological water quality, it is important to maintain sample sites that are as far as possible from the influence of major contaminant sources. In this way, temporal and spatial variability in analytical data can be interpreted without the confounding influence of variable contaminant input from nearby sources. This criterion requires that stations be located in places of higher dilution, such as close to the major channels in each embayment. As the program is adjusted to reflect evolving management questions, the number of sampling sites and locations may change periodically, while maintaining a basic set of long-term sites.

Another objective of the RMP is to determine the spatial distribution of contamination in the Estuary. This requires that stations be located throughout the Estuary, from the extreme South Bay all the way up the northern reach of the Estuary to the mouths of the Sacramento and San Joaquin rivers. This also requires that samples be collected approximately the same time each year, so that data may be compared over several years during the same seasonal period.

Site selection is also influenced by those stations monitored in the Estuary during the pilot phase of the RMP, conducted by the Regional Board from 1989 through 1992. Locating RMP sample sites at or near pilot sites provides a larger database that is directly comparable to the data collected during the pilot program. This is because many of the analytical and sampling methods that were used in the pilot phase of the program have been adopted for use in the current RMP.

Finally, many sample sites are chosen due to methodological requirements in the field. For example, normal water sampling operations requires the vessel to remain at a site for at least an hour without the engines running. This means that stations cannot be located in a vessel traffic lane, which is a frequent use of estuarine channels. Such feasibility requirements have been addressed in the pilot program, and this knowledge was applied in selecting the sampling sites for the RMP.

It is the responsibility of the vessel captain to ensure that the vessel reaches and maintains the proper location for each sample site. It is the responsibility of the cruise manager to verify the accuracy of sample site coordinates and to record the coordinates in a cruise logbook. This logbook contains the time of arrival, time of departure, latitude and longitude (measured from vessel's global positioning system) and general sea conditions if outside the normal range of conditions for the station being sampled. Sampling coordinates are checked throughout sampling to ensure that the anchor has not dragged. For sediment sampling, coordinates are recorded for each replicate grab at each sampling location. The site names, codes and coordinates for all RMP sample locations (water, sediment and bioaccumulation deployments and collections) are listed in Table 6.

Site Name	Code	Sample Matrix	Measurements Made	Sample Events	La	titude	Lon	gitude
					deg	min	deg	min
Coyote Creek	BA10	water	Q,M,O	2	37	28.20'	122	03.80'
	BA10	sediment	Q,M,O,T,P	1	37	28.20'	122	03.80'
	BA10	bioaccumulation	M,O,C	1	37	28.19'	122	03.83'
South Bay	BA20	water	Q,M	2	37	29.69'	122	05.34'
	BA21	sediment	Q,M,O,T,P	1	37	29.64'	122	05.25'
Dumbarton Bridge	BA30	water	Q,M,O,T	2	37	30.90'	122	08.11'
	BA30	sediment	Q,M,O,P	1	37	30.87'	122	08.08'
	BA30	bioaccumulation	M,O,C	1	37	30.80'	122	08.08'
Redwood Creek	BA40	water	Q,M,O	2	37	33.67'	122	12.57'
	BA41	sediment	Q,M,O,T,P	1	37	33.67'	122	12.62'
	BA40	bioaccumulation	M,O,C	1	37	32.82'	122	11.70'
San Bruno Shoal	BB15	water	Q,M	2	37	37.00'	122	17.00'
	BB15	sediment	Q,M,O,T,P	1	37	37.00'	122	17.00'
Oyster Point	BB30	water	Q,M	2	37	40.20'	122	19.75'
	BB30	sediment	Q,M,O,P	1	37	40.21'	122	19.77'
Alameda	BB70	water	Q,M,O	2	37	44.66'	122	19.30'
	BB70	sediment	Q,M,O,T,P	1	37	44.84'	122	19.40'
	BB71	bioaccumulation	M,O,C	1	37	41.73'	122	20.38'
Yerba Buena	BC10	water	Q,M,O	2	37	49.36'	122	20.96'
Island	BC11	sediment	Q,M,O,T,P	1	37	49.44'	122	20.93'
	BC10	bioaccumulation	M,O,C	1	37	49.12'	122	20.95
Golden Gate	BC20*	water	0,M,O	2				
Horseshoe Bay	BC21	sediment	O.M.O.T.P	1	37	49.98'	122	28.43'
Tionseshee Duy	BC21 BC21	bioaccumulation	M,O,C	1	37	49.87'	122	28.65'
Richardson Bay	BC30	water	Q,M	2	37	51.81'	122	28.66'
······	BC32	sediment	Q,M,O,P	1	37	51.82'	122	28.72'
Point Isabel	BC41	water	O.M	2	37	53.30'	122	20.55'
	BC41	sediment	Q,M,O,P	1	37	53.34'	122	20.55'

Table 6. Site name, codes and coordinates of RMP sample locations.

Site Name	Code	Sample Matrix	Measurements Made	Sample Events	La	titude	Lon	gitude
Red Rock	BC60 BC60 BC61	water sediment bioaccumulation	Q,M,O Q,M,O,T,P M,O,C	2 1 1	deg 37 37 37	min 55.00' 55.00' 55.70'	deg 122 122 122	min 26.00' 25.97' 28.13'
Petaluma River	BD15	water	Q,M,O	2	38	06.66'	122	29.00'
	BD15	sediment	Q,M,O,P	2	38	06.66'	122	29.00'
	BD15	bioaccumulation	M,O,C	1	38	06.77'	122	30.05'
San Pablo Bay	BD20	water	Q,M,O	2	38	02.92'	122	25.19'
	BD22	sediment	Q,M,O,P	2	38	02.86'	122	25.24'
	BD20	bioaccumulation	M,O,C	1	38	02.72'	122	25.71'
Pinole Point	BD30	water	Q,M,O,T	2	38	01.48'	122	21.65'
	BD31	sediment	Q,M,O,P	1	38	01.49'	122	21.71'
	BD30	bioaccumulation	M,O,C	1	38	01.00'	122	22.05'
Davis Point	BD40	water	Q,M,O	2	38	03.12'	122	16.62'
	BD41	sediment	Q,M,O,T,P	2	38	03.11'	122	16.65'
	BD40	bioaccumulation	M,O,C	1	38	03.26'	122	15'.63
Napa River	BD50	water	Q,M,O	2	38	05.79'	122	15.61'
	BD50	sediment	Q,M,O,T,P	2	38	05.79'	122	15.61'
	BD50	bioaccumulation	M,O,C	1	38	04.84'	122	14.82'
Pacheco Creek	BF10	water	Q,M	2	38	03.09'	122	05.80'
	BF10	sediment	Q,M,O,P	1	38	02.85'	122	05.66'
Grizzly Bay	BF20 BF21 BF20	water sediment bioaccumulation	Q,M,O,T Q,M,O,T,P No deployment.	2 1	38 38 38	06.96' 06.97' 06.49'	122 122 122	02.31' 02.35' 03.37'
Honker Bay	BF40	water	Q,M	2	38	04.00'	121	56.00'
	BF40	sediment	Q,M,O,P	1	38	04.00'	121	56.00'
Sacramento River	BG20	water	Q,M,O	2	38	03.56'	121	48.59'
	BG20	sediment	Q,M,O,T,P	1	38	03.36'	121	48.63'
	BG20	bioaccumulation	M,O,C	1	38	03'.58	121	47.50'
San Joaquin River	BG30	water	Q,M,O	2	38	01.40'	121	48.45'
	BG30	sediment	Q,M,O,T,P	1	38	01.36'	121	48.44'
	BG30	bioaccumulation	M,O,C	1	38	01.27'	121	48.32'
San Jose	C-3-0	water	Q,M,T,O	2	37	27.85'	122	01.60'
	C-3-0	sediment	Q,M,O,P,T	1	37	27.72'	121	58.53'
Sunnyvale	C-1-3	water	Q,M,T	2	37	26.08'	122	00.64'
	C-1-3	sediment	Q,M,O,P	1	37	26.13'	122	00.67'

Table 6 notes:

Abbreviation	Notes
*	Location dependent on salinity
Q	Water and/or sediment quality
0	Trace organics
С	Bivalve condition index
М	Trace elements
Т	Toxicity
Р	Porewater chemistry

3 Sampling Methods

3.1 Water Sampling

3.1.1 Overview and Objectives

Water sampling for the RMP consists of sampling 26 stations in the Estuary, including two watershed sites located in the South Bay. A cruise normally requires seven to eight working days to complete, including one day for the vessel to transit between ports in Emeryville and Martinez. Water samples are collected in the total (unfiltered) and dissolved (filtered) fraction twice each year. Samples are collected for the analysis of trace elements, trace organics and toxicity. In addition, ship-board measurements of general water quality are taken, including conductivity/temperature/depth (CTD) profiling of the water column. The objective of water CTD profiling is to measure conductivity, temperature, salinity, optical backscatterance, dissolved oxygen and depth in the water column over the duration while water chemistry samples are being collected and as a water column profile at the completion of chemistry sampling.

The University of California, Santa Cruz (UCSC) performs analysis of total and dissolved trace elements and conducts direct measurements of trace elements on the particulate fraction retained on the filters, and ship-board water quality measurements. The University of Utah (UU) performs analysis of total and dissolved organics. Brooks Rand Ltd. (BRL) analyzes arsenic and selenium. The University of Maryland (UMCES) performs Hg and MeHg analysis. The Union Sanitary District (USD) is responsible for hardness data. In addition, Pacific Eco-Risk Laboratories (PERL) performs toxicity analysis. Except for preparation of samples and ship-board measurements of water quality parameters, all samples are processed in the laboratory after the cruise.

The objectives of the water cruise are:

- Collect water samples from 26 sites for analysis of total and dissolved trace elements.
- Collect water samples from 17 sites for analysis of particulate and dissolved organic contaminants.
- Collect water samples from 26 sites for analysis of salinity, total suspended solids, chlorophyll a, nutrients (ammonium, nitrate, nitrite, orthophosphate, silicate), and dissolved organic carbon.
- Collect water samples for analysis of total hardness at 13 sites and any other sites where salinity is less than 5.0 parts per thousand.
- Collect profiles of water-column temperature, conductivity, salinity, dissolved oxygen, and optical backscatterance at 26 sites.
- Collect samples for toxicity analysis from five stations during the wet season cruise and six stations during the dry season cruise.

A minimum of six crew members (excluding vessel captain) are required to conduct a water cruise, although seven crew members are recommended. Cruise member responsibilities are presented in Table 7.

Cruise Members/Number of Crew (Contractor)	Responsibilities
Applied Marine Sciences/1	Cruise management, collection of toxicity samples, CTD operation,
(AMS)	verification of sample record logs, and shipping samples
University of California Santa Cruz/3-4 (UCSC)	Trace element sampling, cognate sampling
University of Utah/2 (UU)	Trace organics sampling
University of California Santa Cruz/1 (UCSC)	Vessel operation

Table 7. Crew responsibilities for RMP water sampling cruise.

The Prime Contractor (AMS) is responsible for oversight of sampling operations, compliance with cruise plan and quality assurance guidelines, maintenance of the sample field log, preparation of chain-of-custody records, operation of the CTD, and acquiring toxicity samples. UCSC is responsible for all trace

element sampling and collection of cognate samples. UU is responsible for collection of all trace organic samples. In addition, UCSC provides the vessel and skipper.

3.1.2 Water Sampling Vessel Safety

The cruise manager develops the cruise plan in coordination with the vessel captain to ensure vessel availability and that tides are appropriate to the work to be conducted. The actual cruise schedule may vary, primarily due to inclement weather. Other factors such as personnel availability and vessel malfunction occasionally require changes to the cruise schedule. Once underway, the skipper and cruise manager consult the cruise plan and incorporate changes induced by weather or other factors to determine which sites are to be sampled on that day.

The vessel skipper is responsible for navigating the vessel to the sample collection sites. Once at a sampling site, a crewmember (usually the cruise manager) will be instructed by the vessel skipper to deploy the anchor. The vessel will swing into the current within a few minutes, at which time the cruise manager will record the vessel position and time of arrival in the cruise logbook. The vessel coordinates are checked against the coordinates listed in the cruise plan.

The vessel captain is responsible for overseeing the safety of the vessel and crew while they are onboard the vessel. It is the responsibility of each crewmember to follow common safety practices while performing their duties. Safety practices include but are not limited to:

- 1. Participants on the rear deck (outside the vessel cabin) may be required to wear a Personal Flotation Device (PFD).
- 2. Participants using hazardous chemicals (i.e. acid or methanol) are required to wear appropriate Personal Protection Equipment (PPE) such as gloves and eye protection, and are required to have MSDS (Material Safety Data Sheets) on board the vessel for all chemicals they bring on board.
- 3. In locations where contact of the skin to the sample water may pose a health risk, participants are required to wear appropriate gloves and thoroughly wash after contact with estuary water.
- 4. Participants are required to store equipment and personal belongings in a safe manner.
- 5. Participants susceptible to motion sickness are advised to take appropriate steps to minimize its effects.
- 6. Tripping hazards are minimized by routing electrical cords and sample lines away from areas of high foot traffic.
- 7. Participants are required to notify the vessel captain and cruise manager of any vessel, operational or personal safety concerns.

3.1.3 Water Sampling Equipment List

It is the responsibility of each participating laboratory to prepare their equipment prior to the sampling cruise. Normally, trace element sampling equipment is prepared by UCSC, trace organics sampling equipment is prepared by UU and miscellaneous support equipment is prepared by AMS. The equipment list for water trace elements sampling is provided in Table 8, water trace organics sampling is provided in Table 9, and the miscellaneous support equipment for water toxicity sampling is provided in Table 10. The equipment list for CTD profiles is provided in table 11.

Quantity	Description		
	General Equipment		
1	15-20 foot sampling pole (2 pieces; 1 hollow, 1 with a telescopic insert)		
1	Solomat TM (for field measurements of salinity, conductivity, pH, dissolved oxygen, and temperature)		
2	Sampling buckets		
2	Chairs		
25	Filter cartridges		
2	Ice chests containing: 20 pounds dry ice/sampling day		
1	Cruise log book and cruise plan		

Table 8. Equipment list for water trace elements sampling.

1	Tape: (2) plastic, (6) labeling		
1	Pens: (6) ballpoint, (6) Sharpies		
1	Razor blades		
1	Trash bags (recycled from lab)		
1	Ziploc TM bags (50 each size; 9 x 12, 12 x 15)		
1	Nylon gloves (4 pair, medium, 2 pair, small)		
1	Polyethylene gloves (6 boxes, medium, 3 boxes, small)		
6	Kimwipes [™] and K-dries [™] , large (3 boxes each)		
1	Sun-protection lotion		
1	Spare batteries		
1	Bucket opener		
1	Foul weather gear		
	6		
1	Water Sampling System		
1	Masterflex TM dual-head peristaltic pump		
2	Pump speed controller boxes		
4	Pump heads		
1	Spare pump head screws		
1	Spare pump fuses (3 amp)		
2-3	Electrical power extension cords, 25 foot		
1	Flexframe TM fittings and clamps (2 small to hold tubing and 2 large for filter cartridges)		
1	1/2 inch aluminum support rod and plastic covered base		
1	Tape: plastic, duct, electrical		
1	Hand tools: screwdriver, pliers, crescent wrench		
3	Stainless steel adjustable (screw-tighten) hose clamps (to hold sample poles together)		
as needed	Straps, bungee cords, nylon rope		
3 sets	Pre-assembled acid-clean tubing, consisting of the following:		
	• Inlet tubing: 25 feet of 5/16 inch ID Teflon [™] tubing		
	 Outlet tubing: 3 feet of 5/16 inch ID TeflonTM tubing 		
	 Pump-head tubing: 2 pieces, 1 foot long of 5/16" ID C-flex tubing 		
	 2 - "Y" polypropylene fittings (to connect 5/16" ID tubing) 		
1	$Z = 1^{-1}$ polypropyrene multigs (to connect 5/10 mb tubing) Ziploc TM tool		
as needed	Cable ties		
1	Gloves: nylon (inner), polyethylene (outer)		
1	Chlorophyll Filtration System		
2 sets	Filtration flask with vacuum tubing		
	6		
2 sets	Filter holder (reservoir, stoppered neck, clamp)		
60	Glass fiber filters (47 mm)		
1	Graduated cylinder (100 ml)		
2	Forceps, filter-type		
1	Rinse bottle		
1	Glass-distilled water $(2 - 2 L)$ (refill)		
2 boxes	Centrifuge tubes, 15 ml screw-cap polycarbonate		
50	Ziploc TM plastic bags (4 x 6), to hold 2 tubes per site		
1	Tube rack		
1	Aluminum foil		
1	Hand-vacuum pump		
	Particulates Sampling Equipment		
1	Bungee cords to support filtration setup		
1 per station	1 L Low Density Polyethylene (LDPE) sample collection bottles		
	Nalgene Polysulfone filtration flasks (trace metal clean), pre-assembled w/filter		
	Vacuum tubing, ¹ / ₄ inch to 5/16 inch I.D.		
	Ultra pure water for rinses		
1	Rinse bottle (for Milli-Q)		
1 per station	Nucleopore Polycarbonate Filters, 47 mm, 0.45 micron, acid-cleaned		
1	Polyethylene gloves		
1	Hand vacuum pump		
	There is a second band		

Table 9. Equipment list for water trace organics sampling.

Quantity	Description		
1	Axys TM organics sampler (custom manufactured for total and particulate fraction sampling)		
1	Cruise log book		
1	Drip pan		
1	Sampler repair kit		
1	Sampler manuals		
1	Cotton tipped swabs		
1	Micro-pump service repair kit		
1	Extra screws, seals, and bushings		
1	Bushing extractor and inserter		
1	Magnet set height tool		
1	Precision forceps		
1	Torque wrench		
1	Silicone lubricant		
1	Sample tubing		
1	Intake/Exit tubing		
1	Spare intake tubing		
1	Spare solvent rinsed tubing		
1	Columns loaded with XAD-2 resin		
1	Glass fiber filters, kilned and rinsed		
2	Coolers with column racks		
2 2	Coolers for dry ice		
1	Pack sample gloves and dry ice gloves Plastic work box		
1	Column assemblies closed with 2 tube to tube Gorilla-Grip [™] unions		
2	Jars each with 4 tube to column Gorilla-Grip [™] unions		
1	Plastic waste beaker		
1	Container of spare Swageloc TM parts		
1	Container of pre-filters, 140m filter cups, and spare Gorilla-Grip [™] unions and ferrules		
1	Safety glasses		
1	Heavy duty aluminum foil		
2	Solvent boxes		
1	Large Kay Dry TM wipers		
1	Plastic bags for filters		
as needed	•		
as needed	Garbage bags		
1	Solvent squirt bottles for methanol		
1	Bag of pens, sharpies, time tape, Teflon tape, and water proof hockey tape		
1	Mobile tool box with tools		
2	Wooden column racks		
2	Empty calibrated carboys with lids and handle		
5	Carboys of distilled or reverse osmosis drinking water		
6	Bottles of methanol (4L)		
2	Towels		
1	Rope		
1	Extension cord		

Table 10. Miscellaneous support equipment list for water toxicity sampling.

Quantity	Description		
3	Igloo TM coolers		
8	Pre-cleaned, 10 L polyethylene carboys; fluoride coated		
1	Extension cord		
1	Extendable aluminum pole		
1	Pack of Nalgene TM tubing, factory cleaned		
20	Lbs. Ice		
1	110 VAC Masterflex [™] peristaltic pump		
1	Duct tape		

Table 11. Equipment for CTD profiles.

Quantity	Description
1	SBE1 19 CTD, calibrated in the laboratory prior to use with attached rope
1	Data terminal and communication cable for CTD
1	CTD Maintenance kit including 8 new "D" size batteries

3.1.4 Sample Containers

The containers required for water sampling are listed in Table 12.

Table 12. Container list for w	water sampling.
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Sample Type	Container		
	Trace Elements Sampling		
Trace metals, other than Hg	2 LDPE (Low Density Polyethylene) containers per station, plus duplicates and		
Hg and MeHg	extra: (64) 1 L (packed in eight 5-gallon buckets)		
	2 Teflon containers per station, plus 2 field blanks, 1 travel blank and extra: (68) 1 L and 500 ml size		
Nutrients	4 per station: (75-100) 125 ml LDPE (packed in one 5-gallon bucket)		
Total suspended solids	(30) 500 ml, 1 L or 2 L LDPE (packed in one plastic box or ice chest)		
Salinity	(30) 500 ml LDPE (packed in one plastic box or ice chest)		
Dissolved organic carbon	2 per station: (60) 30 ml glass vials (packed in ice chest along with small Styrofoam box)		
Chlorophyll	2 per station: (60) 15 ml plastic centrifuge tubes (packed in chlorophyll equipment box)		
Particulates	Acid-cleaned filtration cartridge placed in an acid-cleaned polysulfone filtration assembly, 1 per station		
	Trace Organics Sampling		
Total organics	Pre-cleaned columns (2 per site)		
Particulate organics	Pre-cleaned filters (number used per site depends on turbidity, normally 1 per site)		
Hardness	1 LDPE (500 ml) per site (factory cleaned)		

3.1.5 Trace Elements Sampling Equipment Preparation

The equipment used for water trace elements sampling consists of a peristaltic sample pump, TeflonTM, C-flexTM and polypropylene sample tubing and fittings, trace metals filter (for dissolved trace metals sampling) and assorted sample containers. The following sections outline the preparation for the trace metals sampling system components and sample containers.

The method for collecting the trace elements of particulates is still in a developmental stage. A 0.45 μ m filtration cartridge is used for collecting the filtered samples at each site. The cartridge is acidcleaned and a 0.45 μ m filter (paper disk) is placed in an acid-cleaned polysulfone filtration assembly.

Teflon™ Sample Tubing

The main intake tubing for trace elements sampling is composed of TeflonTM tubing. This tubing is cleaned prior to use at each sample location. A MasterflexTM peristaltic pump is used to fill the TeflonTM sample tubing with reagents and to flush with water between acid cleaning. The TeflonTM tubing ends are joined together with C-flexTM tubing to hold reagents for soaking overnight or between sample sites. Advance preparation of the TeflonTM sample tubing is done in the laboratory 3-4 weeks before the start of a cruise and is also done between each sample site. The following procedures are used for cleaning TeflonTM sample tubing:

- Completely fill tubing with laboratory-prepared Micro solution and let soak 3-7 days at room temperature (60-70 °F).
- Drain Micro solution from the tubing and flush with approximately 10 liters (L) of de-ionized water (DI).
- Completely fill sample tubing with 6 normal (N) reagent-grade hydrochloric acid (HCl) and let soak 7 days at room temperature.
- Drain acid and flush tubing with ultrapure water until pH of the effluent is about 5.0 units to ensure that HCl is completely flushed out.
- Completely fill tubing with 7.5 N reagent grade nitric acid (HNO₃) and let soak 14 days at room temperature.
- Drain acid and flush tubing with ultrapure water until pH is approximately 5.0 units.
- Fill tubing with ultrapure water that has been acidified to pH 1.0 with trace metal grade HNO₃ or HCl. Cap the ends of the tubing with C-flex[™] and store tubing filled with this solution. Keep solution in tubing until used in the field.

Between each sample site and at the end of the sampling day, the Teflon[™] sample tubing is thoroughly cleaned and stored using the following procedures:

- Empty the sample tubing of any residual sample water by pumping with air and flushing with ultrapure water.
- Flush tubing with 1 L of reagent grade methanol. Fill completely with methanol and let sit 15-20 minutes. Drain the methanol from the sample tubing, flush with air then flush with 2 L of ultrapure water.
- Completely fill tubing with 3 N trace metal grade HCl and let sit 1-2 hours (this should be accomplished during the transit between sample sites). Drain acid from the sample tubing and flush with several liters of ultrapure water. For long-term storage (overnight during sample cruise), store tubing filled with weak acid solution.
- Place tubing in two new, large polyethylene bags. The ends of the tubing are covered with two clean polyethylene gloves that are tied closed. Label tubing as "clean". The outside of the new unopened polyethylene bags is wiped clean with ultrapure water and low lint kay dries in a clean work bench area.

C-Flex[™] Pump Tubing

Preparation is done in the laboratory, four weeks before the start of a cruise. The following procedures are used for cleaning C-flexTM pump tubing:

- 1. Cut C-flexTM tubing into 6" and 1' lengths.
- 2. Soak in laboratory-prepared Micro solution for 24 hours.
- 3. Rinse tubing with DI water. Soak tubing in hot 3 N reagent grade HCl for 24 hours.
- 4. Rinse tubing with ultrapure water. Soak in hot 4 N reagent grade HNO₃ for 24 hours.
- 5. Rinse tubing with ultrapure water. Check to ensure that tubing has not lost its integrity.

Polypropylene Sample Tube Fittings

Preparation is done in the laboratory, four weeks before the start of a cruise. The following procedures are used for cleaning sample tube fittings:

1. Soak fittings in laboratory-prepared, hot Micro solution for 24 hours, or at room temperature for seven days.

- 2. Rinse fittings with DI water and soak in 6 N reagent grade HCl for seven days.
- 3. Store fittings in weak trace metal grade HCl for 1-2 weeks or until used.
- 4. Rinse fittings with ultrapure water prior to use.

Trace Metal Filter Cartridges

Filter cartridges are used for collection of dissolved trace metal samples in water. Normally, one filter cartridge is used per sample site, although elevated suspended solids concentrations may require using two or more cartridges per site. Filter cartridges are prepared in the laboratory, brought into the field, exposed to the sample medium, and taken back to the laboratory for sample extraction and analysis. Preparation of filter cartridges is done two weeks before the start of a cruise. The following procedures are used for cleaning filter cartridges:

- 1. Cut at least 50, 4-5" sections of Micro-cleaned C-flex[™] tubing. Two pieces of tubing are required for each filter cartridge used.
- 2. Cut at least 25, 1.5" pieces of acid-cleaned Teflon[™] tubing (5/16" ID). One piece will be needed per cartridge.
- 3. Connect C-flexTM tubing sections to each side of the filter cartridge. Connect TeflonTM tubing to one side of the filter cartridge/C-flexTM tubing assembly. Repeat steps for all filter cartridges.
- 4. Connect several filter cartridge/tubing assemblies together in a chain with the red flow arrows all pointing in the direction of the flow.
- 5. Wet the cartridges with reagent grade methanol. Using a Masterflex[™] peristaltic pump, fill cartridges with reagent grade methanol and let sit for several minutes.
- 6. Pump out methanol by first pumping system with air, then flush thoroughly with 4 L of ultrapure water. Again, flush with air, then 4 L of ultrapure water, then air again. Fill cartridges with ultrapure water and let sit for several minutes, then drain completely. It is necessary that no trace of solvent remains as traces of organic solvent mixed with acid in a closed bottle can become explosive.
- 7. Fill cartridges with 3 N reagent grade HCl and let sit 7 days, at room temperature.
- 8. Pump out acid. Flush with approximately 10 L of ultrapure water, until the pH is about 4.0.
- 9. Fill cartridges with 4 N trace metal grade nitric acid and let sit 7 days.
- 10. Pump out acid. Flush with approximately 10 L of ultrapure water, until pH is about 4.0. Store cartridges filled with this weak acid solution inside until use. Separate cartridges during this step, and continue flushing individually, to ensure that each cartridge is stored with a weak acidic solution.
- 11. Separate cartridges so that there is a piece of C-flex[™] tubing on both the inlet and outlet. By looping the C-flex[™] tubing downward (consider flow direction as indicated by red arrow, and have the vent in an upward position) connect the two pieces with the piece of Teflon[™] tubing between them. Rinse off outside of looped assembly with de-ionized water.
- 12. Bag acid-cleaned cartridges individually in Ziploc[™] polyethylene bags and store in a clean 5 gallon plastic bucket.

Trace Metal Clean Sample Bottles

Preparation is done in the laboratory, 4-8 weeks before the start of a cruise. The following procedures are used for cleaning sample bottles and labware:

- 1. With a diamond-tip stainless steel scribe, etch the cap, side and shoulder of each sample bottle with a unique identification number. One and two liter bottles have separate numbering systems. Record numbers in field log book.
- 2. Place bottles in a bath filled with Micro solution (completely immerse with no air bubbles). Keep immersed for 2-7 days at room temperature.
- 3. Rinse bottles 5-6 times using approximately 10% of bottle volume with tap water, rinsing bottle exterior at same time, including cap and bottle threads. Make sure the final rinses no longer foam when shaken. While rinsing, check seal of cap (toss leaky ones).
- 4. Rinse bottles 2-3 times with DI or ultrapure water and store in large un-pigmented polyethylene bags until next procedure.
- 5. Wipe down fume hood and set inside a large plastic secondary containment tray. The tray should be pre-rinsed with ultrapure water and is stored in a large polyethylene plastic bag when not in use. Set Micro-clean bottles in the tray. Fill bottles to the brim with 6 N reagent grade HCl. Tighten caps excluding any air bubbles. Tilt bottle at approximately a 30 degree angle and squeeze sides while screwing down cap. Rinse outside of capped bottle with ultrapure water. The tray catches any spilled acid and water.

- 6. Place acid-filled bottles into a 2 N HCl bath for at least 2 weeks. The 2 N HCl baths are made with reagent grade HCl and DI water. Acid bath containers are 5 gallon white plastic buckets cleaned with micro and de-ionized water. Three 2 L or six 1 L bottles fit in one 5 gallon acid bath.
- 7. In a clean plastic containment tray set in the fume hood, place a batch of Micro-clean bottles (three 2 liter or six 1 liter). Remove a batch of acid-cleaned bottles from 2 N HCl, rinsing the exterior with ultrapure water over a plastic rinse tray and place in fume hood next to Micro-clean batch. Pour the 6 N HCl from these bottles into the next batch of bottles to be acid-cleaned. Rinse cleaned bottles with ultrapure water to remove most of the acid and store in large polyethylene bags. The 6 N reagent grade HCl can be re-used at most 6-7 times, as long as bottles are pre-rinsed well enough to remove micro residue. If the acid foams at all, discard the acid.
- 8. In a clean lab, rinse exterior of bottles with ultrapure water before opening. Rinse the inside of bottles with ultrapure water 5 times (using about 10% of bottle volume each rinse). Drain each rinse into the cap then pour this over the threads of the bottle.

For sample bottles used at the Golden Gate sampling site or other "low level concentration" oceanic sampling sites:

- 1. In the clean lab, fill bottles with 7.5 N HNO_3 and let sit for one week. Rinse with ultrapure water 5 times.
- 2. Fill each bottle to the base of the neck with ultrapure water and place in a class 100 (HEPA) work area. Add approximately 10 ml of concentrated trace metal grade HNO₃ per each 1 L bottle, then fill to brim with ultrapure water. Tighten cap excluding air bubbles. Make sure cap is secure. Invert to mix.
- 3. Double bag each bottle in polyethylene ZiplocTM bags. Wipe down interior bags with Kay-dryTM to remove any dust particles. Write bottle identification number on interior bag.
- 4. Store four 2L or eight 1L bottles in two large polyethylene bags inside 5 gal polyethylene buckets.
- 5. Prior to use, bottles are filled with weak HNO_3 and are allowed to sit for 2 to 3 weeks.

Recycling Trace-Metal Sample Bottles

Trace metal sample bottles may be recycled after use. The laboratory is responsible for determining when sample bottles may be recycled and when they should be discarded. Preparation of bottles for recycling is done in the laboratory 2-3 weeks before the start of a cruise. Use the following guidelines for recycling trace metal sample bottles:

- 1. Conduct entire cleaning process in class 100 (HEPA) work area and wear polyethylene gloves throughout the procedure.
- 2. Remove old labels with methanol.
- 3. Rinse bottle exterior with ultrapure water before opening. Empty contents from all sample bottles. Rinse one bottle with ultrapure water 3-5 times.
- 4. Fill this sample bottle with freshly made trace metal grade 6 N HCl. (To make a 6 N solution, fill a bottle half-full with ultrapure water, then fill remaining half (to neck) with concentrated trace metal grade 12 N HCl.) Shake and swirl bottle so acid touches all inside surfaces, then set bottle upright.
- 5. While acid is sitting in this bottle, rinse another bottle with ultrapure water 3-5 times.
- 6. Decant the 6 N HCl from the first bottle into the bottle just rinsed with ultrapure water. Cap and re-bag bottle just cleaned with HCl. Shake and swirl HCl in second bottle then set aside while the next bottle is rinsed with ultrapure water.
- 7. Continue to rinse all bottles with same batch of 6 N HCl. Rinse outsides of bottles with ultrapure water before opening.
- 8. Rinse inside of bottles with ultrapure water 3-5 times (using 10% of bottle volume each rinse). Drain each rinse into the cap then pour this over the threads of the bottle. Rinse the bottle exterior also.
- 9. Fill each bottle to the base of the neck with ultrapure water. Add approximately 10 ml of concentrated trace metal grade HNO₃ for each liter bottle.
- 10. Tighten cap, careful to exclude air bubbles. Make sure cap is secure.
- 11. Double bag each bottle in Ziploc[™] bags. Wipe down interior bags with Kay-dry[™] to remove any dust particles. Write bottle identification number on interior bag.
- 12. Store either four 2 L or eight 1 L bottles in two large polyethylene bags. Place the bags in either 5 gal polyethylene buckets or in plastic ice chests. Bottles are allowed to sit for at least 2-3 weeks before being used again.

Teflon[™] Bottles for Hg Samples (provided by UCSC from 2002 on)

Preparation is done in the laboratory 4-8 weeks prior to the start of a cruise. Use the following guidelines for cleaning TeflonTM bottles:

- 1. Number each bottle with a diamond-tip stainless steel scribe. Etch the cap, side and shoulder of each bottle with a unique identification number. One liter and two liter bottles have separate numbering system. Record numbers used in field log book.
- Place bottles in micro bath for at least 2-7 days at room temperature. Rinse inside and outside of bottle 5-6 times using approximately 10% of bottle volume with DI water, including cap and bottle threads. Make sure final rinses no longer foam when shaken. While rinsing, check seal of cap and discard leaky ones.
- 3. Rinse with ultrapure water 3-4 times and store in large, unpigmented polyethylene bags until ready for next step.
- 4. In a fume hood with hood fan on, fill bottles to brim with concentrated reagent grade HNO₃. Tighten caps excluding any air bubbles. Tilt bottle at approximately a 30 degree angle and squeeze sides while screwing down cap, do this over clean rinse tray.
- 5. Place acid-filled bottles into a 7.5 N reagent grade HNO₃ bath and let sit 4 weeks at room temperature or 1 week at hot temperature (60-80 °C). For a hot acid bath, place a 4 L glass beaker on hot plate in fume hood.
- 6. In a fume hood, place a batch of micro-clean bottles. Remove a batch of acid-cleaned bottles from 7.5 N HNO₃, rinsing the exterior with ultrapure water over a plastic rinse tray and place in fume hood next to micro-clean batch. Pour the concentrated HNO₃ from these bottles into the next batch of bottles to be acid-cleaned. Rinse cleaned bottles with ultrapure water to remove most of the acid and store in large polyethylene bags.
- 7. In a clean lab, rinse exterior of bottles with ultrapure water before opening. Rinse the inside of bottles with ultrapure water 5 times (using about 10% of bottle volume each rinse). Drain each rinse into the cap then pour this over the threads of the bottle.
- 8. Fill each bottle to the base of the neck with ultrapure water and place in a class 100 work area. Add approximately 15 ml of concentrated trace metal grade HNO₃ per each 1 L bottle (fill to brim with ultrapure water). Tighten cap excluding air bubbles. Make sure cap is secure.
- Double bag each bottle in polyethylene Ziploc[™] bags. Wipe down interior bags with Kay wipes[™] (moistened with ultrapure water) to remove any dust particles. Write bottle identification number on interior bag.
- 10. Store four 2 L or eight 1 L bottles in two large polyethylene bags placed inside a 5 gallon polyethylene bucket. Bottles will sit 2 to 3 weeks filled with weak HNO₃ prior to use.

In addition to the above sample containers, bottles are used for collection of ancillary samples such as total suspended solids, salinity and chlorophyll. Ancillary sample bottles normally are prepared in the laboratory 4-8 weeks before the start of a cruise. Ancillary sample bottles are rinsed with de-ionized water and air-dried. Ancillary sample bottles may be reused.

3.1.6 Mercury Sampling Equipment Preparation (provided by UMCES in 2000 and 2001)

New Teflon bottles are soaked by completely submerging them in concentrated nitric acid (~12 M; trace metal grade or better) for one week. They are rinsed with de-ionized (DI) water and then soaked in 4 M HCl (trace metal grade or better) for another week. The bottles are then rinsed three times with DI water, double bagged, and filled with 1.5 M HCl and left full until use. Note: Some labs clean their bottles as above but use hot acid. This is recommended for ultra low level samples.

Used bottles are rinsed thoroughly with DI water. If they are relatively clean (no obvious particles stuck to the bottle) and the Hg level in the sample relatively low (<10 ng/L for HgT), then the bottle is filled with 1.5 M HCl and allowed to sit at least one week before being used again. If the bottle is dirty, contained a sample with high Hg, or has obvious stains (especially iron oxides), the bottle is boiled for 2 days in concentrated nitric acid (trace metal grade or better), rinsed in DI, soaked in room temperature HCl for 2 days, double bagged, and filled with 1.5 M HCl until use.

Prior to using the bottles, the 1.5 M HCl is removed. A small amount of new 1.5 M HCl is added to the bottle. (For a 1L bottle, approximately 75ml is added. However, this amount is scaled down for smaller-sized bottles.) The bottle is either shipped or transported to the field. In the field, the remaining 1.5

M HCl is removed. The bottle is first rinsed with the sample, before the bottle is filled three-quarters with sample. Samples are preserved by freezing for MeHg and HgT. If only analyzing for HgT, an alternative method of preservation is to acidify the sample to 1% HCl (trace metal grade or better) and refrigerate.

When using acid, Baker Intra-Analyzed trace metal grade is recommended, since it tends to be the cleanest. Expensive ultra-pure or Ultrex grade acids sometimes contain high concentrations of Hg, since they are repeatedly distilled. Mercury is volatile and, therefore, can carry over in the distillation process. In fact, one of the cleanest acids for Hg is Baker reagent grade. However, the Hg levels vary greatly in reagent grade, so unless a sample of acid is run every time a new case of acid is bought, it is not recommended.

Teflon bottles are kept double bagged at all times. All writing is done on the outer bag. When the bottle is cleaned, the outer bag is discarded. The inner bag then becomes the outer bag, and a new bag is used for the

inner bag. To prevent contamination, only clean plastic bags and gloved hands should be used when handling the bottles.

3.1.7 HDPE Containers for As and Se Samples

The High Density Polyethylene containers that are used for arsenic and selenium sampling are factory pre-cleaned.

3.1.8 Trace Organics Sampling Equipment Preparation

The equipment used for water trace organics sampling consists of an AxysTM organics sampler (custom manufactured to sample both particulate and dissolved fractions at the same time), XAD-2 resin columns (filtered and unfiltered) for organics extraction, and a sample tubing system composed of TeflonTM tubing and SwagelocTM stainless steel fittings. Other than the columns used for sampling total organics and the filters used for sampling particulates, no containers are used for sample collection. Resin for filling TeflonTM columns and filters for sampling particulates are prepared in the laboratory at the University of Utah at least four weeks before the start of a cruise.

Sampler Cleaning

Before the collection of samples, the sampler should be completely cleaned and tested for leaks and other mechanical problems. The bearings and internal gears of the sampler should be replaced at least once a year (normally between the spring and summer sampling trips), or whenever the rpm rate of the sampler is much higher (over 200-300 rpm) than the normal running conditions.

The sampler is cleaned chemically prior to and after every sampling day. Cleaning once a day is plenty when sampling regularly, but if it has been sitting for a while it should be cleaned before and after sampling. To clean the sampler after each day of sampling, remove the filters and resin columns and reassemble the sampler. The glass fiber filter chambers should be drained of all water and rinsed with methanol three times to remove any sediment. The valves on the sampler should be set so that both of the filter chambers are to be cleaned at the same time. The intake line is placed into a four-liter bottle of methanol. The sampler is then primed using the manual suction pump (guzzler). Once the sampler is primed, the outlet is also placed in the methanol bottle. The methanol is allowed to circulate through the sampler for approximately 4 minutes. The intake tube is then lifted to empty the inlet line of methanol. Once air has passed through the filter chambers, turn off the sampler. Drain the methanol in the filter chambers and reseal. With the filter chambers closed, place the inlet of the sampler into the carboy of the distilled or reverse osmosis drinking water. Prime the sampler and run the sampler for approximately 4 minutes or until it has used about half of the water in the carboy (10 liters). Empty the filter chambers and rinse three times with methanol to remove any sediment that might have been dislodged during the cleaning. Replace and seal the filter chambers, close all valves on the sampler. The inlet tube should be rinsed and covered in methanol rinsed foil. If the sampler is to be stored, methanol should be left in the lines to prevent growth of bacteria.

In order to prevent the cross-contamination of samples from different sites, several precautionary procedures are followed. If the filter chamber is going to be used again and has already been used that day for sampling, the filter chamber and O-ring should be rinsed three times with methanol. This rinsing will

remove any sediment from the chamber that might have been collected. At the end of the sampling of a site, the intake tube should be lifted out of the water to allow all of the water to drain from the inlet through the resin columns. Once air has passed through the system, it will prevent the water from back flushing through the filters and resin. The filter and columns can then be removed and packaged for shipment.

After each sampling or during sample collection if the sampler flow rate seems to be slowing and the filters are not particulate laden, remove and clean the pre-filter. Turn the sampler off, remove the inline pre-filter, take apart and rinse the pre-filter cup with GC resolve methanol. If necessary replace the cup if it has holes or looks compromised. Be careful to reassemble in the same order and be sure to seat the cup properly or the pre-filter will leak.

Extraction of Water with XAD-2 Resin

Current sampling protocol requires three batches of resin to be prepared for each cruise. These resin batches remain discrete throughout sampling and extraction. Each batch of resin (1 per giant soxhlet thimble) fills 12-24 sample columns. Normally, one batch of resin is used to sample the "clean" central bay sites, another to sample the "dirtier" north bay sites (not including Petaluma River), and the third for the "dirtiest" south bay (plus Petaluma River) sites. When the sample columns are extracted, each set of columns becomes one extraction set with one set of norms and two extraction blanks, always from the same batch of resin. This minimizes the number of norms, and minimizes variation within the set and between samples and blanks. Extracting the sets in order from cleanest to dirtiest also minimizes potential cross-contamination between sets.

Cleaning XAD-2 resin

Order resin: XAD-2 from Supelco company. Order 20-50 mesh. This means it is >300 microns in size.

Water rinse: Fill one of the glass soxhlet thimbles with resin to about 3 inches from the top. Use a ring stand and a chain clamp to stand the thimble in a sink, and run de-ionized water through the resin for a few minutes. De-ionized water can either be run through at a slow rate (i.e. comparable to how fast it drains), or it can be repeatedly filled and emptied several times.

Load thimble into soxhlet. Have one person hold the extraction reservoir relatively flat while another person slides the thimble in. This will be easier if the thimble does not have resin on the outside. Use tongs with curved tip to slide thimble down to the bottom. Hang the extractor vessel from the top (above the tubes, below the flange lip) using a chain clamp. Set up the rest of the soxhlet.

Methanol rinse: Pour low-grade methanol through the thimble and trip 4 times. Discard the methanol.

Wash with Methanol. Wash the resin with 4 liters B&J Methanol. Burdick and Jackson (B&J) Methanol is used to lower the contamination because this brand has been proven to be the cleanest. Cycle continuously for a minimum of 14 days.

Wash with dichloromethane. Turn the soxhlets off right after they trip. Dump the Methanol. Rinse the resin and trip the soxhlets twice to remove any traces of methanol. Dump the dichloromethane. Rinse the reservoirs thoroughly to be sure there is no water (water in the soxhlets may get into the extractor and clog the frit at the base of the thimble). Fill the reservoirs with 4 liters B&J dichloromethane by pouring through resin. Cycle continuously for a minimum of 14 days.

Unload the resin. Turn the soxhlets off right after they trip. Dump the dichloromethane. Have one person hold the extraction reservoir relatively flat while another person slides the thimble out. Now the resin is clean, so you have to be careful not to touch the thimble or the resin. Use the tongs with curved tip to slide the thimble out until you can grab it with the round pipe tongs. Have a few pieces of rinsed foil on hand, so that you can grab the thimble with your hands. You can put one over the top, and wrap another around the thimble, and then grab the thimble where it is covered by foil. Dump the resin into a large amber resin jars and store in methanol.

Fill the Resin check columns with resin from each batch and check resin prior to filling columns.

Enter the information about how resin was cleaned into the Log Book.

Preparing Teflon for XAD-2 sampling

Empty resin from extracted columns into specified bottle using large funnel. Use Fisher grade methanol. Keep resin from individual cruises together. Try not to mix batches. Check screens for holes or crud. Replace screens if necessary, or take out and scrub with soft sponge to remove crud.

Soak in HOT soapy water for 20 minutes or more. Take the columns apart after each extraction set (don't mix sets, they are easier to clean) and wash them in hot soapy water with a soft sponge.

If any of the screens come loose, wrap the Teflon ring that holds them in with Teflon tape. Be sure screens are secure in columns by banging lightly on counter. If inner ring is loose, wrap with one or two layers of Teflon.

Soxhlet parts in Fisher grade Dichloromethane for 1 day.

Reassemble the columns.

To blank columns: Take the cap off of the end piece and squirt in about 15-30 ml hexane. Close column and shake all around, in every direction, for 15-20 seconds. Make sure you get the solvent into both end pieces. Empty the solvent out and repeat and then collect the second hexane rinse as a blank. Concentrate and run the sample through GC/MS.

Loading XAD-2 resin into columns

Materials:

- blanked Teflon columns, organized sequentially
- clean XAD resin, in a beaker in methanol
- four ring stands with clamps
- four beakers (for waste)
- four 100 ml graduated cylinders, preferably with wide mouth and pour spout
- four small funnels
- methanol squirt bottle
- distilled water squirt bottle

Procedure:

Set up the first four columns. Put clean foil on the counter in front of the ring stands. As you put the columns in the clamps to be loaded, tighten the bottom end piece and loosen the top. Take the cap off the bottom and the entire end piece off the top, and set them on the foil. Put a beaker under each column.

Fill the grad cylinders with resin. Pour the excess methanol off the top of the resin. Using a funnel, pour ~100 ml of the methanol/resin slurry into each graduated cylinder. You may have to use a squirt bottle to keep the resin moving. The resin in the graduated cylinder should settle to between 90 ml and 95 ml.

Pour the resin into the columns. You will need to use the squirt bottle to keep the resin moving. Try not to get resin on the outside of the column! If you do, wait for the solvent to evaporate and clear the threads very thoroughly before you close the column, as resin in the threads will cause a leak. Drain methanol.

Fill the column with organic free water. Put the cap on the bottom and squirt in water to 0.25 inch below the rim. Screw on the top end piece. To do this you will want to loosen the cap, so that air can escape. Fill the column with water by squirting hard and directly on the screen.

Check for leaks. Set the columns out on a Kay-dry and roll them around a bit. Let them sit while you fill the next four columns. Look for wet spots on the paper, indicating methanol leakage.

Repeat steps 1-5 until you have used all of the resin. Label all columns from a batch with the same color 0.5 inch tape. Take the last column from each batch and label with the resin batch number and leave behind as extraction blanks.

Label the columns: If a batch has an even number of columns, plan on leaving 2 unlabeled, one as a field blank and one as an extra. If a batch has an odd number of columns plan on leaving the last column unlabeled as an extra. For the remainder of the columns label the two sets alternately with five different colors of tape. Label in order of extraction.

Preparing water for use in extraction procedure

Materials:

- relatively clean water (de-ionized water, millipore the cleanest available)
- 2L Teflon separatory funnel(s) (clean, but not necessarily blanked)
- ring stand with big rings
- dichloromethane (B&JGC²)
- waste bottle
- empty solvent bottle, for extracted water.

Procedure:

Fill the separatory funnel about halfway with 750 ml to 1000 ml water.

Add ~150 ml dichloromethane.

Shake for 1 minute. Don't forget to vent.

Allow bilayers to separate for a few minutes.

Drain dichloromethane layer, including bilayer.

Repeat steps 1-5 for a total of three rinses.

Drain extracted water into clean solvent bottle.

A note on venting: Before you start to shake, invert the separatory Funnel, open the stopcock, and swirl for 10 seconds. Then close the stopcock and shake vigorously. This will make things much easier.

A note on solvent usage: This procedure uses a lot of solvent. You can recycle this solvent for things like soaking Teflon, cleaning Teflon columns, and other uses where you don't need super-clean dichloromethane. You may have to pour it through a drying column to get the water out, though.

Eluting one set of 8 XAD-2 columns

Spiking Samples and Norms

FIRST: Spike columns and prepare norms. Be sure to spike each column with 100 μ l surrogate (2 columns per sample) totaling 200 μ l per sample, norms and blanks are spiked with 200 μ l surrogate. Keep the columns upright once they are spiked, so the spike doesn't spill, and you elute the columns in the right direction.

COMPOUND	NORM 1 (HIGH)	NORM 2 (LOW)	SAMPLE
	(shot from 400 µl)	(shot from 400 µl)	(shot from 100 µl)
NIST PAH	100 μl (Dilution A)	100 μl (Dilution C)	
NIST PESTICIDE	100 μl (Dilution A)	100 μl (Dilution C)	

NIST PCB	100 μl (Dilution A)	100 μl (Dilution C)	
Norm Surrogate Spike	200 µl	200 µl	NOTHING!
Sample Surrogate Spike	NOTHING!	NOTHING!	200 µl
GCI STD F	PCB NORM ONLY 80 µl	PCB NORM ONLY 80 µl	F1 SAMPLES 20 μl
GCI STD I	· PEST & PAH NORM 80 μl	PEST & PAH NORM 80 μl	F2 & F3 SAMPLES 20 μl

ACTUAL SPIKING DIRECTIONS:

1. Use 6 amber screw caps – label NORMS appropriately

2. Get all appropriate ampoules together: 6 NIST NORM ampoules, one NORM Surrogate Spike (the concentration should be 4 times the sample surrogate spike), and one Sample Surrogate Spike For NIST solutions spike directly from ampoule and discard remainder For Surrogate Solutions you need to transfer contents of ampoule to 4 ml vial prior to spiking

NIST MIXTURES:

3. Spike 100 µl PAH NIST A into PAH NORM 1 using 100 µl drummond

- 4. Change and clean tip
- 5. Spike 100 µl PAH NIST C into PAH NORM 2 using 100 µl drummond
- 6. Change and clean tip
- 7. Spike 100 µl PEST NIST A into PEST NORM 1 using 100 µl drummond
- 8. Change and clean tip
- 9. Spike 100 µl PEST NIST C into PEST NORM 2 using 100 µl drummond
- 10. Change and clean tip
- 11. Spike 100 µl PCB NIST A into PCB NORM 1 using 100 µl drummond
- 12. Change and clean tip
- 13. Spike 100 µl PCB NIST C into PCB NORM 2 using 100 µl drummond
- 14. Change and clean tip

SURROGATE MIXTURES:

15. Using the 250 μl syringe, spike your three number 1 NORMS with 200 μl of NORM Surrogate Spike

Touch tip once inside vial and clean needle (not entire syringe) between spiking

16. Clean entire syringe thoroughly

17. Using the 250 μ l syringe, spike columns with 100 μ l and filters and blanks with 200 μ l of Sample Surrogate Spike

- 18. Cap the vial and clean the needle between each sample spiking
- 18. Clean entire syringe thoroughly

19. Using the 250 μl syringe, spike your three number 2 NORMS with 200 μl of NORM Surrogate Spike

Touch tip once inside vial and clean needle (not entire syringe) between spiking

GCI STANDARD SPIKES:

1. Don't spike any samples or NORMS with GCI until the entire cruise is extracted (filters and columns)

2. Do not begin spiking an entire cruise unless you are absolutely sure you can finish

spiking that day!

3. For all sets the NORM 1 is spiked before the samples and NORM 2 is spiked after Spike the NORMS with 80 μ l (100 μ l drummond), and the samples with 20 μ l (50 μ l drummond)

4. All F1 samples and PCB NORMS are spiked with GCI STD F

5. All F2/F3 and F4 samples and PEST and PAH NORMS are spiked with GCI STD I Spiking F2/F3 and F4 samples/NORMS will require an entire day. Transferring and bringing to volume should occur the next day.

Overall Spiking Scheme: NORMS

PCB NORM:

1. Add 100 μl NIST PCB Dilution A or C with 100 μl drummond

2. Add 200 µl of NORM Surrogate Spike with 250 µl syringe

3. Leave volume as is - you will spike these NORMS with 80 μl GCI STD F prior to shooting on the instrument

You will bring to final volume of these NORMS to 400 µl

You need to spike these NORMS at the same time as all F1 samples.

(*Note: You will be spiking a different volume of GCI STD F into samples and NORMS-see above)

PAH NORM:

1. Add 100 μl NIST PAH Dilution A or C with 100 μl drummond

2. Add 200 µl of NORM Surrogate Spike with 250 µl syringe

3. Leave volume as is - you will spike these NORMS with 80 μ l GCI STD I prior to shooting on the instrument

You will bring to final volume of these NORMS to 400 µl

You need to spike these NORMS at the same time as all F2/F3 and F4 samples.

(*Note: You will be spiking a different volume of GCI STD I into samples and NORMS-see above)

PESTICIDE NORM:

1. Add 100 µl NIST PEST Dilution A or C with 100 µl drummond

2. Add 200 µl of NORM Surrogate Spike with 250 µl syringe

3. Leave volume as is - you will spike these NORMS with 80 μ l GCI STD I prior to shooting on the instrument

You will bring these NORMS to a final volume of 400 µl.

You need to spike these NORMS at the same time as all F2/F3 and F4 samples.

(*Note: You will be spiking a different volume of GCI STD I into samples and NORMS-see above)

Extraction Procedure

Materials:

- 2 wooden column racks (each holds 4 columns)
- 4 elution set-ups:
- reservoir with inlet tubing
- outlet tubing with stopcock
- 4 open-ring clamps, w/ hook clamps
- 4 closed ring clamps
- 8 small 3-prong clamps, w/ hook clamps
- 8 Teflon 1L separatory funnels
- 2 x 250 ml graduated cylinders
- 1600 ml methanol (B&J)
- 2000 ml dichloromethane (B&J)

Procedure:

Set up first 4 columns. These should include one column from each site in the set, as the second column from each site will be eluted through the same elution assembly without the assembly being cleaned.

Hang the reservoirs from the open ring clamps and attach the first column to the reservoir invert column, and attach outlet tube with stopcock. Use 3-prong clamps to fix the column and the stopcock into desired positions and rinse tip of stopcock. Position separatory funnel under stopcock – make sure separatory funnel stopcock is closed!! Adjust the set-up for maximum height between reservoir and stopcock, check column attachments to make sure they are secure. Repeat for columns 2-4.

Separatory funnels should be arranged in linear sequence.

Record site codes on the window of the hood (for future reference).

Record which columns are being eluted into which separatory funnels.

Add 200 ml methanol to each reservoir. Check for leaks. Open stopcocks all the way until flow is established, then close down to 5-10 ml/minute (fast drips, but no flow). Check for leaks again. Let methanol drain through.

Add 250 ml dichloromethane to each reservoir. Let this drain through. As the solvent in the elution system changes from methanol to methanol + dichloromethane to dichloromethane, you will have to adjust the flow rate (i.e., you can't leave this step and come back when it's done).

As the dichloromethane reaches the bottom of the reservoir, adjust the position of the column so that the dichloromethane keeps draining through. Eventually, the column will be inverted, directly above the second column, with the empty reservoir dangling free.

Open the stopcock completely so that all of the dichloromethane runs out of the column.

Close and remove the separatory funnels.

Switch the columns, one at a time, with the second column from each sampling site. Follow the procedures in step 1.

Extracting one set of 8 XAD column eluates

Materials:

- 8 ring clamps
- 16 x 500 ml Erlenmeyer flasks
- 8 large powder funnels
- 1 x 250 ml graduated cylinder
- 100 ml graduated cylinder (for solvent)
- 100 ml graduated cylinder (for salt solution)
- 100 ml graduated cylinder (for extracted water)
- 8 drying columns with glass wool plugs
- 8 x 3-prong clamps, w/ hook clamps
- kilned sodium sulfate
- 800 ml dichloromethane (B&J)
- 1200 ml extracted water (Section 3.0)
- 1200 ml 3% sodium chloride solution (kilned, in extracted water)

Procedure:

Set up 8 samples, in order. Place Erlenmeyer flasks under all the samples, labeled 1-8 Set up a ring clamp over an empty solvent bottle, labeled AQUEOUS ORGANIC WASTE.

Add 150 ml extracted water and 50 ml sodium chloride solution to each separatory funnel to separate the methanol and the dichloromethane.

Shake the separatory funnels for 1 minute each (don't forget to vent).

Drain organic (bottom) layers into flasks, leaving bilayers in the separatory funnels.

Add 50 ml dichloromethane to each separatory funnel to rinse the aqueous methanol layer.

Shake the separatory funnels for 1 minute each. And drain dichloromethane into flasks, leaving bilayers in the separatory funnels.

Repeat steps 7.1.5-7.1.6. This time, drain the bilayer into the flask. Swirl each separatory funnel to get any dichloromethane that sticks to the walls or floats on top of the aqueous layer.

Drain aqueous methanol from separatory funnels into waste containers.

Return dichloromethane phase to separatory funnels. Transfer with 2 rinses. Put the same Erlenmeyer flask back under the separatory funnel. Add 50 ml sodium chloride solution to each separatory funnel (this removes residual methanol).

Shake the separatory funnels for 1 minute each.

Drain the dichloromethane back into the flasks, leaving the bilayers in the separatory funnels. Then, go back and swirl all the separatory funnels, and drain off any leftover dichloromethane, including the bilayers.

Drain aqueous methanol from separatory funnels into waste containers.

Return dichloromethane phase to separatory funnels again. This time, transfer with 3 rinses.

Repeat steps 7.1.9 and 7.1.10.

Set up a flask under a drying column with a ring above to hold each separatory funnel. Put 6 in of sodium sulfate into each drying column. Label the flasks 1-8, and write the sample # (plus "A" or "B" if it is a two column sample).

Drain the dichloromethane layers, including the bilayers, through a 6 inch sodium sulfate column.

Drain aqueous methanol from separatory funnels into waste containers.

Flush each drying column with 2 x 15 ml rinses of dichloromethane.

Rinse the inside of each sodium sulfate column with dichloromethane.

Rinse the ground glass of every flask with hexane.

Rinsing Filters for Sampling

Materials:

- Glass fiber filters (from Filterite in Baltimore (410) 252-0800)
- Soxhlets
- 4 L dichloromethane (B&J)
- 4 L methanol (B&J)

Procedure:

Wrap all filters in one big piece of foil and kiln on standard program.

Soxhlet filter for 2 days in B&J dichloromethane.

Then soxhlet filters for 2 days in B&J methanol.

Put all filters on clean foil and cover, allow to dry.

Wrap each filter individually and place a small piece of tape designating the set on the outside to indicate that the filter is rinsed and clean. Put filter information into the Log Book.

Extracting one set of 8 glass fiber filters

Materials:

- 8 large barrel columns with large glass wool plugs
- 8 ring clamps
- 16 x 500 ml Erlenmeyer flasks
- 1 x 250 ml graduated cylinder
- 8 100 ml graduated cylinder (for dichloromethane)
- 8 100 ml graduated cylinder (for extracted sodium chloride solution)
- 8 drying columns
- 8 x 3-prong clamps, w/ hook clamps
- kilned Na₂SO₄
- dichloromethane (B&J)
- 1200 ml extracted water
- 1200 ml 3% sodium chloride solution (kilned, in extracted water)

Procedure:

Set up the columns with a ring and separatory funnel under each one.

Spike the filters and NORMS according to the protocol described in section 6.0.

Spike directly onto the top of the filter while holding it in the column with large forceps.

Place the filter at the bottom of the column. Add 200 ml of methanol, cover the top with a piece of rinsed foil. After 24 hours, drain into separatory funnel. Repeat with 200 ml of methanol and leave for another 24 hours.

Drain and add 200 ml of dichloromethane, replace foil, and let sit for another 24 hours. Repeat with another 200 ml of dichloromethane.

Once all rinses are collected in the separatory funnel, proceed following the liquid/liquid extraction protocol from Section 7.0.

3.1.9 CTD Preparation

Pre-cruise preparation and calibration of the CTD takes place at least three days prior to the start of a cruise. Refer to the SeaBirdTM SBE-19 CTD operators manual for a full description of calibration and maintenance procedures.

Equipment:

- (1) SBE19 CTD Profiler
- (1) CTD Field Kit containing CTD operators manual, spare batteries, wrench, screwdriver, deionized water and squeeze bottle, syringe and Triton-X DO membrane cleaning solution
- (1) IBM-PC laptop computer with Seasoft CTD software
- (1) floppy disk for saving files

SBE 19 Conductivity, Temperature and Depth (CTD) Profiler Preparation:

The Sea-Bird SBE 19 CTD Profiler is factory calibrated and inspected by Sea-Bird Electronics in Bellevue, Washington, annually before the first winter water cruise of the year. During normal conditions, the CTD will maintain nominal calibration drift for all sensors except for the oxygen sensor, which must be checked and calibrated prior to each water cruise. CTD preparation also takes place three days prior to the winter and spring water cruise. Refer to the Sea-Bird SBE19 Operating Manual for a full description of sensor configuration and calibration procedures.

Guidelines for inspecting and calibrating the SBE19 CTD Profiler:

- 1. Visually inspect the CTD for abnormal wear or corrosion. Check to ensure that the deployment line is secure and that there are no abrasions. Make sure all fittings are secure and all fasteners are firmly in place. Check the integrity of the top o-ring seal and make sure that there are no signs of fouling.
- 2. Verify that the communication connector is secure, waterproof and lubricated with silicone grease.
- 3. Remove the top-fastening nut of the CTD and remove the end-cap. Remove the battery plate from inside the CTD housing and replace the six "D" cell batteries, making sure to replace the batteries in the proper orientation. Reinstall the battery plate. Wipe a small amount of clean silicone grease around the edge threads of the end-cap and reinstall end cap, making sure that the threads are properly aligned. Reinstall the top fastening nut, making sure that the nut is firmly held to the CTD housing.
- 4. Remove the communication connector and attach the communication line to the CTD and to the portable computer running the terminal emulation program (TERM19.EXE).
- 5. Verify that the CTD communicates correctly with the data terminal by running TERM19.EXE.
- 6. Verify that the battery status indicates at least 7.5 volts (new battery) and that the lithium battery status indicates at least 5.0 volts. The lithium battery is located on the CTD main processor board and should be replaced by qualified personnel at Sea-Bird Electronics. Should the lithium battery status indicate voltage less than 5.0 volts, contact Sea-Bird electronics for internal battery service recommendations.
- 7. Calibrate the dissolved oxygen (DO) sensor using the provided guidelines.

Guidelines for Calibration of the SBE19 CTD DO Sensor:

- Calibration of the DO sensor requires measuring the oxygen current output in a zero oxygen environment (sensor environment purged with nitrogen gas) and in an air-saturated environment (sensor environment in a 100% oxygen saturated water bath). The DO meter can be factory calibrated independently of the CTD unit.
- Fill a calibration bath (55-gallon plastic trashcan) with tap water and aerate the bath with an
 airstone placed no greater than 10 cm from the surface. Aerate the bath for at least 24 hours prior
 to calibrating the CTD. Moderate aeration is maintained to avoid air supersaturation. The water
 temperature of the calibration bath is kept between 19-21 °C.
- 3. Measure the zero point oxygen voltage by flushing the sensor with a continuous stream of nitrogen gas. Insure that power has been applied to the sensor for several minutes before the gas is placed in the sensor. Connect the CTD to the data terminal and run the SEASAVE software program to display real-time oxygen current data. Watch the output of the sensor decrease rapidly towards zero volts. Record the voltage output after three minutes. This will be the zero value to use in the calibration. The original calibration sheet that accompanied the oxygen sensor will contain the zero oxygen current that was obtained during the factory calibration. You may compare the results of the recent calibration to those obtained at the last factory calibration.
- 4. Measure the air-saturated oxygen voltage by immersing the CTD into the calibration bath. Leave the CTD in the calibration bath for at least one hour and do not turn the power on to the CTD. After one hour, turn on the CTD power for at least 12 minutes and record the oxygen current output using the SEASAVE program. It is important to make sure that the CTD pump is working and water is being pumped across the DO sensor membrane. Make sure the CTD remains fully immersed during the calibration procedure. Turn off the CTD when the oxygen current is recorded.
- 5. OXFIT.EXE is the software program used to compute new oxygen sensor calibration coefficients. Run the OXFIT.EXE program and fill in the following information:
 - i. Local barometric pressure obtained from the Livermore Airport (or nearest facility), not corrected to sea level.
 - ii. Water temperature of the calibration bath.
 - iii. Oxygen current in the air saturated water (calibration bath).
 - iv. Oxygen current at the zero point oxygen level.
- 6. The OXFIT.EXE program will calculate a new oxygen current bias (Boc) and oxygen current slope (Soc) that are used to compute the actual oxygen concentration. Refer to the Sea-Bird SBE19 owners manual for details on the algorithm used to compute actual oxygen concentrations.

The new Soc and Boc coefficients are compared to the original factory calibration or the last calibration that was performed. Typically, Soc values will slowly increase with time as the sensor is used. The new Soc and Boc values are entered into the SEASOFT.CON file using the SEACON.EXE program.

7. During normal sampling on the Estuary, care must be taken to avoid fouling the CTD oxygen membrane with organic residue. The oxygen sensor may be rinsed with a 1 % solution of Triton-X (kept in the CTD field kit) and flushed with de-ionized water at the end of each cruise day. Store the CTD overnight by filling a plastic syringe with de-ionized water and injecting the water into the CTD intake port. Make sure that the DO sensor is immersed in de-ionized water for overnight storage. For routine cleaning, soak the oxygen sensor in a 1% solution of Triton X(tm) that has been warmed to a temperature of 50 °C. After soaking, drain and flush the CTD with warm fresh water for one minute. The CTD is always stored with the dissolved oxygen sensor fully immersed in de-ionized water.

3.1.10 Water Toxicity Sampling Equipment Preparation

Glassware & Plasticware Washing Procedure (For Both the inside and outside of Containers!)

- 1. Rinse thoroughly with tap water.
- 2. Wash with Liquinox (that's soap!). This requires just a little bit, as it is very concentrated. To prepare the soap in the squeeze bottle requires only 5 ml of the concentrated Liquinox (the big bottle of soap) in a full container of water.

During this step use a brush or scrub pad to get any residue off the glassware. Scrub thoroughly!

- 3. Rinse well w/tap water 3-5 times All of the soap residue must be completely rinsed off; if it isn't, continue rinsing.
- 4. Organic Solvent Rinse:

Rinse with methanol (use squirt bottle). Rinse methanol residue off with de-ionized (DI) water.

If Project Manager indicates, the organic solvent rinse may require the use of acetone. If acetone is used, all solvent rinsing must be performed under the fume hood!

5. Acid (Nitric 10%) rinse:

Prepare 10% nitric acid by mixing ACS reagent concentrated nitric acid with DI water at a ratio of 9 parts water to one part concentrated nitric acid – be sure to prepare the water first and then add the acid to the water (this must be done under the fume hood)!

Preferably, soak the glassware/plasticware item in the acid bath for at least one hour (do not place metal or rubber items in the acid bath).

If item is too large for the acid bath, use squirt bottle containing 10% nitric acid to thoroughly rinse all surfaces of the item.

- 6. Rinse well w/ DI water at least six times. This is an extremely important step. Be thorough and use excess amounts of the DI water!
- 7. The previous steps should have cleaned the glassware. Look to make sure!
- 8. Put on the drying rack and allow it to air dry!
- 9. Inspect glassware and plasticware to ensure completeness of the cleaning.
- 10. Place cleaned glassware/plasticware on the shelves within the appropriate cabinet.

These procedures are set up by the EPA. Guidelines have to be strictly followed when washing the glassware.

3.1.11 Water Sampling Procedures

3.1.11.1 Water Trace Metals Sampling

Water trace metals sampling is conducted after the vessel anchors in the correct position for the sample site and the captain switches off the engines. Sampling requires set-up of a FlexframeTM support rod and base which is assembled and secured onto the starboard rail. The FlexframeTM assembly is installed prior to sampling at the first site of the day and left in place for the day. All trace metals sampling equipment is brought inside the vessel cabin for overnight storage. A dual-head MasterflexTM peristaltic pump is used to pump sample water from the Estuary into the sample bottles. The pump is assembled with the C-flexTM tubing portions of sample tubing passing through the pump heads. The pump and a pump speed controller are secured just below the FlexframeTM assembly and are connected to the vessels power source with an extension cord.

An aluminum sampling pole is assembled and the sample tubing inlet is secured to one end, with the tubing tip hanging loose approximately two feet off the pole end. The sample tubing outlet is secured to the FlexframeTM. During sampling, a plastic cover is removed from the inlet end of the TeflonTM sample tubing and the sampling pole is extended over the starboard side of the vessel. The pole is oriented upcurrent from the vessel and upwind from all equipment and personnel. The sample tubing inlet is submerged approximately 1-2 feet into the water column. Surface water is pumped through the sample tubing and the entire tubing system is flushed continuously for approximately 5 minutes before any samples are collected. Both filtered and unfiltered water is collected at each site.

Two persons are needed to conduct the sampling. The "dirty hands" person assists the primary "clean-hands" sampler by controlling the flow controller for the peristaltic pump, holding on to or adjusting the sample pole, adjusting the outlet tubing or filter cartridge, and handing sample containers to the "clean hands" person. The "dirty hands" person does not touch the trace-metal clean bottles, but opens the ZiplocTM bags so that the "clean hands" person may remove them from the bags. The "clean hands" person, wearing at least one pair of polyethylene gloves, does not touch anything with her/his hands except the inner ZiplocTM bag, the bottles and the water.

The clean hands/dirty hands system is not critical for the ancillary samples, and these bottles may be rinsed just three times with sample water before collecting the sample. For trace element samples, the "clean hands" person drains the ultrapure water from the pre-cleaned sample bottle onto the bottle cap and pours the remaining ultrapure water over the bottle threads several times. The sample container is rinsed with the sample water five times, then filled up to the "neck" with sample water. The sample collection sequence for total trace metals (unfiltered) sampling is as follows:

- Total suspended solids (TSS)
- Chlorophyll
- Particulates
- Total bulk metals
- Total As, Se
- Total Hg and MeHg

After the above samples are collected, the filter cartridge is attached to the sample tubing outlet and secured to the FlexframeTM. The storage solution inside the filter is drained and the entire sample tubing and filter assembly is flushed with sample water for five minutes. The sample collection sequence for dissolved trace metals (filtered) sampling is as follows:

- Salinity
- Dissolved bulk metals
- Dissolved As, Se
- Dissolved Hg and MeHg
- Dissolved organic carbon

A filtered water sample is collected in duplicate to evaluate precision of the sampling equipment and to assess short-term environmental variability at the sample site. Ten percent of all RMP sample stations are collected in duplicate.

The 0.45 micron filtration cartridge is changed after each sampling site. After the unfiltered water sample is poured into the top reservoir for the filtered fraction, the particulates remain on the filter. The entire assembly is tightly sealed with a top cover, placed in a ZiplocTM-bag, and is returned to the lab in a closed bucket. Once in the clean lab, the filter is removed using acid-cleaned forceps, and placed in a trace metal clean digestion vial where it gets dried, acid-digested, and analyzed.

3.1.11.2 General Water Quality Measurements

General water quality is measured by UCSC using a SolomatTM 520C multi-functional chemistry and water quality monitor. This hand-held monitor has several probes, which are submerged approximately 3 feet into the water column to collect readings. A multi-parameter probe measures water temperature, depth and conductivity. A dissolved oxygen probe measures dissolved oxygen and a pH probe measures pH. The meter is calibrated for conductivity with a KCl standard, dissolved oxygen using a mixture of CoC₁₂ and NaSO₃ and for pH using buffers of pH 7 and 10.

The objective of water CTD profiling (conducted by AMS) is to measure conductivity, temperature, salinity, optical backscatterance, dissolved oxygen and depth at the surface while water chemistry samples are being collected. At the completion of sampling, the CTD is lowered to the bottom to profile the entire water column.

3.1.11.3 Water Organics Sampling

Sampling Set Up

Place the sampler on the counter inside the cabin of the boat and secure with ties. Attach the exit tube and the intake tube to the proper Swagelok opening. The intake tube should have a mesh screen on one end and the inline pre-filter with the directional arrow situated appropriately on the other.

If the boat is at anchor, the cabin doors and windows can be open while assembling the columns and inserting the filters. If the boat's engines are running, the cabin doors and windows must be closed and the boat must be moving (leaving the exhaust behind) before opening any part of the sampler to avoid contamination. If the sampler is clean, then two clean filters should be loaded into the filter cups. Place a piece of tape on each filter housing which contains a clean filter. Two field blanks should be collected, one per week. The technique for collecting field blanks is to unwrap a filter and leave it exposed while loading and unloading the filter cartridges. Label the filter: FLDBK, the date, the collector's initials and the site codes it applies to. Fill out a sample sheet for the blanks, as they need to be logged in upon return to UU.

Line the plastic box with foil. Label each column with the site code, date, and the collector's initials. Drain the water from each column and screw on the 4 female Gorilla $grip^{TM}$ connectors. Place the column endcaps into the jar. Remove the straight unions from the column assembly and place the metal tubes in the end of the female Gorilla grip connectors and tighten first by hand and next with the proper wrenches. Make sure the connections are tight (but not too tight or the Teflon threads will strip) and the columns do not leak. Assemble the columns so that the writing is in the proper orientation with the A column on the right and the B column on the left. Record the column numbers as well as the filter batch color on the sample log sheet for each site.

Using two columns per cruise, one per week, collect a column field blank by opening both ends of a column, draining the water and leaving it open while the columns for that site are loaded and unloaded onto the column assembly. Label the blank with: FLDBK, the date, collectors initials and the sight code. Fill out a sample sheet for these samples as they need to be logged in upon return to UU.

When the sampler is ready for sampling, attach the column assembly. Do not over tighten the Swagelok connectors; use the Swagelok gauge to measure the gap at the joint. Make sure the filter valve is open towards the chamber containing the filter to be used.

Attach the intake line to the pole with zip ties. The pole should be extended to its maximum and placed over the rail and secured with a bungee at the rail and red tie at the end to allow the intake to line remain submerged. The intake line should be placed about 1.5 to 2 feet under the surface of the water. If the wave action is severe enough that the sampler takes in air, the pole should be held by hand to keep the line in the water. If the sampler sucks in air, the sample can be contaminated. The foil screen and about 2 feet of the intake line should be rinsed with GC resolve methanol before and after being in the water. In between sites, wrap the foil screen with a rinsed piece of heavy-duty foil. While motoring, coil up the intake line and bring the pole inside the cabin. If this is not possible, place tubing along the side of the cabin in front of the exhaust tower of the boat.

The sampler can usually prime itself if the intake is higher than the exit tube. Allowing the sampler to prime itself while the pump is dry can wear the gears so it is best to use the Guzzler to pull the water up to the pump before pressing the start button. Once the start button is pressed, quickly remove the exit line and place in the carboy to begin collecting the sample. Adjust the rpm to the appropriate level to maintain a time of 10-12 minutes to fill each carboy. If the time is much more than that, increase rpm until the filling time is correct. Write down the time the sampling begins, and check to make sure the column assembly does not leak. Also look for air bubbles in the lines and if detected try to find the source and stop the leak. If the sampler does have a leak that cannot be stopped, record this in the logbook and the approximate flow rate of the leak. Record the start and stop time for each carboy. Collect five total carboys. If the particulate level is high and the psi gauge gets to 10 psi, the pre-filter needs to be changed. If changing the pre-filter does not improve the flow rate, and the filter looks clean, the glass fiber filter may be clogged and should be replaced.

Once the five carboys have been collected, push the off button. Remove the intake line from the water and allow it to run until air bubbles come through the columns before turning it off. Cover the intake line with foil and coil it onto the pole.

Remove the column assembly from the sampler. Take off each column by loosening the Gorilla grips with tools. Drain out any residual water and replace the methanol rinsed endcaps. Wrap the endcaps with Teflon tape and fill out the sample log sheet with any pertinent information. Place the columns in a cooler with a small amount of dry ice. Do not freeze them but keep them cool.

Remove the filter housing containing the used filter. Rinse a pair of large forceps with methanol and remove the filter. Wrap the filter in a piece of methanol rinsed foil. Wrap again with a second piece of foil. Label with time tape with the date, time, site code and the collector's initials. Place in a polyethylene bag, twist and wrap over filter again. Re-label on the outside with the same information. Place in a cooler containing enough dry ice to keep the samples frozen, until they can be placed in a freezer.

3.1.11.4 Water CTD Profiling

The objective of water CTD profiling is to measure conductivity, temperature, salinity, optical backscatterance, dissolved oxygen and depth in the water column over the duration while water chemistry samples are being collected and as a water column profile at the completion of chemistry sampling. CTD profiles are conducted using the following guidelines:

- 1. Prior to arriving at the sampling site, the CTD memory should be reinitialized and all CTD data from previous casts should be stored on the computer hard drive.
- 2. When arriving at a sample site, wait at least five minutes for the vessel to swing into position before activating the CTD and lowering it into the water. The CTD should be deployed before any chemistry samples are taken. Make sure that the CTD deployment line is firmly secured to the vessel and that the water-filled syringe is removed from the CTD intake port.
- 3. Turn on the CTD and lower the unit until the top of the CTD housing is 0.5 meters below the surface of the water. If surface waves are greater than one foot, lower the unit one meter below the surface. Record the time the CTD was activated on the ship's sample log.
- 4. The oxygen and temperature sensors require at least five minutes to equalize temperature with the water. If the CTD has been exposed to unusually cold or warm temperatures during storage, the time to equalize temperature can be longer. During the time it takes for temperature equalization, erroneous measurements for water column temperature and dissolved oxygen may result.
- 5. Leave the CTD just below the water surface for the duration of the water chemistry sampling operations, making sure that the CTD remains fully immersed.

- 6. Two CTD casts are processed at each station: a time cast for the duration at the station and a depth profile cast taken just before departure. Time casts are averaged over one minute intervals to yield a continuous measurement of conductivity, salinity, temperature, dissolved oxygen, and backscatterance at 1 meter below the water surface. All chemistry samples collected aboard the vessel are logged on a collection form and the collection start time, so chemistry samples can be superimposed onto the time cast data to reveal chemistry results that may be associated with temporal changes in the water column.
- 7. When water chemistry sampling is completed, slowly lower the CTD to the bottom. The descent rate of the CTD should not exceed 1.0 meters per second. The recommended speed to lower the CTD is 0.25-0.50 meters per second. A cast whose average descent rate exceeds 1 m/sec must be re-sampled.
- 8. After the CTD reaches the seafloor, it may be brought back to the surface at any speed. Only timeaveraged surface data and down cast water column profile data are used. Bring the CTD on board the vessel and turn off the power.
- 9. Connect the communications cable from the data terminal to the CTD. Boot up the data terminal, go to the MS/DOS prompt and change the directory to the "C:/SEASOFT" directory within MS/DOS. Run the TERM19.EXE terminal emulation program to communicate with the CTD.
- 10. Display the CTD status by pressing the "status" function key [F3]. Check that the battery voltage is sufficient (above 6.0 volts) and that the number of casts equals one. Check the CTD header by pressing the function key [F4] and determine that the number of samples recorded is approximately twice the duration time of deployment (in seconds).
- 11. Upload the raw data by pressing the "upload" function key [F9]. Each cast receives a unique file name that corresponds to the station code and cruise number. File names can have a maximum of six characters. The program will prompt for header information, which will include the cruise name, station name, station code, vessel name, and operator. Enter this information into the header form.
- 12. After the raw data has been successfully uploaded, exit the TERM19.EXE program and run the DATCNV.EXE data conversion program. DATCNV.EXE will convert the hexadecimal raw data from the CTD to ASCII-formatted data. Within DATCNV.EXE, select the raw data file name from the prompt, making sure to process the CTD data collected for the present sampling station. Make sure that the configuration file prompt indicates the proper configuration file used for the most recent CTD calibration. The configuration file is normally labeled after the year of the most recent CTD calibration (i.e. 2000.CON). Select the DATCNV variables prompt and make sure that the following CTD variables are converted into ASCII format:
 - > Time
 - Pressure
 - Conductivity
 - > Temperature
 - > Oxygen Current
 - > Oxygen Temperature
 - Backscatterance
- 13. After the raw data has been successfully converted into ASCII data, view the data file using MS-Excel or other text viewing software. Confirm that the number of data columns equals the number of data variables, and that the data columns contain properly formatted data.
- 14. Only after the CTD data has been converted to ASCII format and the converted data has been viewed for accuracy is it safe to reinitialize the CTD for the next deployment.
- 15. At the end of each day, copy the converted data files to a floppy disk and store the disk in a safe place.

Troubleshooting the SBE19 CTD Profiler

Under normal circumstances, the CTD will operate trouble-free for the duration of the cruise and require no other maintenance other than battery replacement. When problems with the CTD arise, they are usually associated with either battery failure or problems associated with communicating to the host computer. Use the following guidelines for troubleshooting the CTD:

1. Because the CTD runs for up to six hours per day, replacing the batteries is extremely important. Check the battery voltage from the TERM19.EXE program and if the battery voltage is below 5.0 volt, replace the batteries. It is common that the battery voltage will drop below 5.0 volts during CTD deployment, especially if the water temperature is cold or the CTD is operated for extended periods. You may not notice this drop in voltage when reading the battery voltage prior to deployment.

- 2. When replacing batteries, make sure they are oriented in the proper direction. Incorrect placement of the batteries will result in failure to connect the CTD to the host computer.
- 3. Make sure the batteries you are using are fresh. Always use new batteries and make sure all batteries are the same brand.
- 4. Make sure that there is no water condensation inside the CTD housing. Condensation could indicate failure of the CTD end-cap o-ring and should be inspected thoroughly before redeploying.
- 5. When connecting the CTD to the host computer, make sure the power switch to the CTD is off. The CTD cannot connect to the host when it is operating.
- 6. Check the condition of the communication cable and make sure the four communication pins inside the cable are not bent. Attaching the cable to the CTD should result in a slight popping sound when the two cables are joined. Make sure the communication cable is connected to the serial port of the computer.
- 7. When running the TERM19.EXE terminal emulation program, make sure to press any key on the keyboard after the CTD has been connected. This prompts the program to properly "handshake" the CTD and acquire data.
- 8. Within TERM19.EXE, press the status key [F3] and confirm that the battery voltage is normal and that the number of voltages sampled equals 4. If the number of voltages equals 2, the lithium battery has failed and the CTD must be recalibrated. Contact Sea-Bird Electronics if the number of voltage samples indicated anything other then 4 voltages sampled.

3.1.11.5 Water Toxicity Sampling

Water toxicity samples are collected by using a peristaltic pump with no filter. At the sampling site, factory-cleaned NalgeneTM tubing is fastened to an extendable aluminum pole, allowing 1 foot of tubing to extend beyond the end of the pole. The pole is then placed over the rail of the vessel, allowing the sample tubing to be submerged 1-2 feet below the water. The pole is maintained in a stable position so that the sample tubing remains 1-2 feet below the water column. The outlet end of the sample tubing is placed through the peristaltic pump, leaving enough tubing on the excurrent side to reach the sample container. The sample container for water toxicity consists of a pre-cleaned, 10 liter polyethylene carboy with the inside surface coated with a fluoride polymer. Sample water is pumped through the tubing for several minutes to flush the tubing, and then a single sample carboy is filled. The carboy is labeled with the site code, date, analysis, and the collector's initials. Water toxicity sample carboys are placed into IglooTM coolers and held on wet ice until the end of the cruise. Samples are picked up by Pacific Eco-Risk Laboratories (PERL) personnel at the end of the cruise.

3.1.11.6 Watershed Water Sampling

Watershed water sampling is conducted at two sites located in the southern end of the Estuary. The Standish Dam sampling site is on Coyote Creek, approximately 1.5 miles upstream from it's entrance to the bay. The South Bay site is on the Guadalupe River, about two miles upstream from its entrance to the Estuary. Both sites are accessed by car.

The Standish Dam site has no electrical power nearby. Trace metal samples are collected through use of a peristaltic pump with a built in power supply. The organics sampler is provided with 120 VAC power through use of a 12 volt DC deep cycle marine battery coupled to a power inverter. The South Bay site has electrical power, so the inverter is not used there. There are no significant differences in sampling methodologies between sampling from the vessel-accessed sites and sampling from the car-accessed watershed sites. When sampling from the watershed sites, care is practiced to ensure that all work surfaces are kept as clean as possible and sample containers are not exposed to any airborne contaminants during the sampling process.

Watershed sampling typically takes two hours at each site. The longer time is due to greater mobilization times and higher level of suspended solids encountered, which slow the sample pumping volume and require more particulate filter changes during sampling. Sampling the watershed sites typically occurs the day after sampling the last of the vessel-accessed sites. Sampling normally occurs during outgoing tides, though the need to sample both sites on the same day often requires sampling the Guadalupe River site during the start of an incoming tide.

There are a few differences in the setup of the organics sampler at the watershed sites. At the Standish Dam site, the water level is far below where the sampler is set up in the back of the car. An extension must be added to the intake line with a Swagelok male-to-male union, which should already be attached to the tubing. The extension tube is connected in between the intake line and the pre-filter. For the Guadalupe River site, the extension tube can be removed.

There is usually a lot of suspended sediment at both sites, so it is not appropriate to sample at the same rpm as for the boat sites. The rpm should be increased to 1100 to start and adjusted to keep a good flow rate. The carboys will more likely fill at 15-20 minutes instead of the usual 10-12 minutes. Change the filter and/or clean the pre-filter as necessary to maintain a good flow of water out of the exit tube.

3.1.12 Water Sample Handling and Shipping

Samples for trace metals analysis, nutrients, DOC, Chlorophyll, and TSS are maintained on board the vessel and transferred to the laboratory by UCSC personnel. The nutrient samples are frozen on dry ice on the vessel, and maintained frozen until they are transferred to laboratory freezers. All other trace metal and related samples are stored in sealed buckets at room temperature on board the vessel and transferred to the laboratory at the conclusion of the cruise. The UCSC cruise manager(s) are responsible for maintaining sample integrity throughout the cruise. Sample contamination is avoided by double bagging the sample containers, handling the containers with clean gloves, and transferring the samples into sealed buckets/coolers immediately after sampling.

Samples for organics analysis consist of particulate filters and resin filled columns. After obtaining the samples, the columns and filters are handled in the following manner: The column assembly is removed from the sampler with the following steps: the columns are removed by loosening the Gorilla gripsTM with the proper wrenches. Residual water is drained from the columns, and the methanol rinsed end-caps are attached. The end-caps are wrapped with TeflonTM tape and the sample log sheets are filled out with any pertinent information. The columns are placed in a cooler with enough dry ice to keep them cool (usually 5 pounds put in every morning and every evening, depending on ambient conditions). The filter housing containing the used filter is removed with the following steps: a large pair of forceps is rinsed with methanol and used to remove the filter from the filter housing. The filter is wrapped with a piece of methanol rinsed foil, and is over-wrapped with a second piece of clean foil. The filter is labeled with the collection date, site code and the collector's initials and is then placed in a polyethylene bag which is twisted, wrapped over the filter again, and labeled with the same information on the outside of the bag. The bag is placed in a cooler containing enough dry ice to keep the samples frozen (100 pounds is usually enough to add small amounts to the column coolers and keep the filters frozen for one week of the cruise). On return to UU laboratory, they are placed in a freezer.

Samples for analysis of Arsenic and Selenium are double bagged and held in coolers chilled with water ice on board the vessel. The AMS cruise manager maintains them on the vessel, and ships them overnight to BRL in Seattle, Washington at the mid-point and end of the cruise via a commercial carrier. The As and Se samples are packed in coolers with blue ice, and are accompanied by chain of custody form. Hg samples are shipped to the University of Maryland.

Water toxicity samples are collected into clean fluoride coated polyethylene carboys. After obtaining the sample, each carboy is labeled with the site code, date, analysis, and the collector's initials. The samples are held on wet ice, and then picked up by PERL personnel at the dock, or delivered to their facility. Toxicity sampling information is logged on the site information sheet, and COC's are prepared for handing the samples off to PERL personnel.

The samples that are held on either wet ice or dry ice are checked periodically to ensure that samples are appropriately protected and stored ice is added as required. Additionally, coolers containing wet ice are drained periodically to remove water from melted ice.

In addition to the ship's log, a sample record is maintained for each site. The sample record contains the following information:

- 1. Station name and code
- 2. Cruise number and collection date
- 3. Arrival and departure time at each station

- 4. Station coordinates (latitude and longitude)
- 5. Water depth at time of sampling
- 6. A record of every sample bottle filled, with bottle identification code number and quantity of bottles
- 7. Collecting personnel's names
- 8. Water temperature
- 9. Salinity
- 10. CTD file name
- 11. CTD start time
- 12. Other remarks (i.e. any conditions that could possibly influence sample analysis or data interpretation, including present and past weather conditions)

The sample collection form, coupled with a chain of custody record and a laboratory analysis record, allows tracing of the complete history of a sample from time of collection to final entry of data to a computer database.

At the conclusion of each cruise, UU personnel maintain possession of trace organics samples and UCSC personnel maintain possession of trace elements samples. All other samples are shipped by AMS personnel with COC's to the appropriate laboratories for analysis. As, Se, and Hardness samples are shipped overnight in coolers on enough blue ice to maintain a 4°C environment for two days. Hg samples are shipped frozen with dry ice. The receiving laboratories are requested to notify AMS of receipt of samples and forward completed COC's to SFEI.

3.2 Sediment Sampling

3.2.1 Overview and Objectives

Sediment sampling for the RMP consists of 26 stations within the Estuary, including two watershed stations. Sampling normally takes six working days. Five laboratories perform sediment analyses of trace elements, total organic carbon, grain size and organic compounds. In addition, sediment toxicity bioassays are conducted at 13 stations. Pore water chemistry (pH and ammonia) is processed aboard the vessel at all sites. Two grabs are collected from each station and composited to produce a single sample that is partitioned according to the various analyses.

The objective is to collect the active layer of undisturbed sediments for analyses in order to monitor current conditions. To minimize the disturbance of the surficial sediments, a Young-modified, Van Veen grab is lowered slowly onto the substrate. The grab has a surface area of 0.1 m². The top 5 cm of sediment from two undisturbed sediment grabs are scooped into the bucket and homogenized by stirring prior to filling sample containers for the various analyses. In order to minimize contamination of the sample, the grab is constructed entirely of stainless steel and the jaws and doors are coated with KynarTM to improve chemical inertness. A scoop and bucket used to remove and composite sediments are also constructed of stainless steel and coated with KynarTM.

A minimum of five cruise participants (excluding vessel captain) are required to conduct a sediment cruise, although six participants are recommended. Specific responsibilities and assignments for cruise participants is presented in Table 13.

Cruise Participants (Subcontractors)	Responsibilities
Applied Marine Sciences, Inc. (AMS)	Cruise management, sediment chemistry sample collection, sediment and pore water chemistry, CTD operation and watershed sampling
City and County of San Francisco (CCSF)	Benthic sampling
University of California, Santa Cruz (UCSC)	Vessel operation
San Francisco Estuary Institute (SFEI)	Sample collection

Table 13. Crew responsibilities for RMP sediment cruise.

AMS is responsible for oversight of sampling operations, compliance with cruise plan and quality assurance guidelines, maintenance of the sample field log and chain-of-custody records, and operation of the CTD. CCSF is responsible for benthic sampling and processing of benthic samples. UCSC is responsible for vessel operation and safety. SFEI is responsible for providing one or two technicians to assist in sample collections and processing.

It is the responsibility of AMS to ensure that all field personnel are capable of sampling safely and complying with the quality assurance guidelines. AMS is required to ensure that:

- 1. Field personnel understand and follow the vessel operating safety procedures as described by the vessel captain. Any concern or uncertainty about operational procedures or safety practices must be brought to the attention of the vessel captain or the AMS cruise manager immediately.
- 2. Field personnel will strictly adhere to the quality assurance protocols (see QAPP plan) to insure the collection of representative, uncontaminated sediment chemistry samples.
- 3. Field personnel are thoroughly trained in the proper use of sample collection gear and are able to distinguish acceptable versus unacceptable samples in accordance with pre-established criteria.
- 4. Field personnel are thoroughly trained to recognize and avoid potential sources of sample contamination (e.g., engine exhaust, winch wires, deck surfaces, ice used for cooling samples, etc.).
- 5. Field personnel follow established procedures for sample collection, processing, documentation, and distribution.
- 6. Field personnel make use of appropriate personal safety equipment at the discretion of the cruise manager or vessel skipper.

The objectives of the sediment cruise are:

Collect sediment samples at 26 stations for the analysis of:

- Trace metals and trace organics by the Bay Area Dischargers Authority (BADA)
- As, Se by Brooks-Rand (BRL)
- Hg and MeHg by UCSC
- Grain size, TOC and total nitrogen by the University of California, Santa Cruz (UCSC)
- Intercomparison of six samples for selected trace metals via hydrofluoric acid extraction by Santa Cruz (UCSC) and City and County of San Francisco (CCSF)
- Pore water pH and ammonia by Applied Marine Sciences (AMS)
- Hydrogen sulfides, total sulfides, and ammonia by Marine Pollution Studies Lab (MPSL)
- CTD profiles by Applied Marine Sciences (AMS)
- Collect sediment samples at 13 stations for analysis of toxicity by MPSL
- Collect sediment samples at two stations for analysis of benthic infauna by City and County of San Francisco (CCSF).

It is critical that sample contamination be avoided during collection. All sampling equipment (i.e., Van Veen grab, compositing bucket and scoops) is composed of a non-contaminating material and are thoroughly cleaned before each use. Sampling personnel wear polyethylene gloves whenever taking or processing samples to avoid contact contamination. In addition, airborne contamination is avoided by keeping sample containers, sample scoops, and compositing bucket inside the vessel cabin with door closed or appropriately covered when not in use.

3.2.2 Sediment Sampling Vessel Safety

There are 26 sediment sampling sites currently in use by the RMP. Twenty-four sites are sampled from a survey vessel and two sites (watershed sites) are sampled from land. All sites except for the watershed sites are sampled from the *R/V David Johnston*. Important features that make the *David Johnston* well-suited for sediment cruises include a large deck, large enclosed cabin with work benches, and an A-frame for deploying and retrieving the Van Veen and Ponar grabs. The watershed sites (Guadalupe River and Standish Dam) are sampled by car, as they are inaccessible by boat.

The maximum work day cannot exceed 12 hours per United Sates Coast Guard requirements. The captain reserves the right to cancel or modify the cruise for any safety reason that could endanger customer, crew or captain's safety. Captain reserves the right to modify any procedure that could damage the vessel. Customer and any personnel brought aboard by customer agree to follow all safety procedures and policies

implemented by the captain. Any areas of concern for crew members should be brought to the immediate attention of either the cruise manager or the vessel captain.

General safety procedures used on the sediment cruise involve the following guidelines:

- 1. Boating Safety A safety briefing is given by the skipper of the vessel prior to departure from the dock. This briefing shall include at a minimum the location of flotation devices, location of fire extinguishers, and emergency procedures. Enough information is given to allow the crew to communicate with emergency services, and operate the vessel in the event that the captain is incapacitated.
- 2. Equipment Storage All equipment to be used is properly stowed to minimize the possibility of movement during vessel transit.
- 3. Arrival at Sampling Site Sampling cruise personnel assist the skipper in setting the anchor at each sampling site.
- 4. Winch Operation The vessel captain operates the winch that deploys and retrieves the grab. The vessel captain may decline to use the grab when rough conditions preclude its use.
- 5. Chemicals Buffered formalin and dilute solutions of HCl and methanol are used as part of the sampling operations. Personal protective gear is provided for use by field crew, including eye protection, foul-weather gear, and gloves.

3.2.3 Sediment Sampling Equipment List

Preparation of sediment sampling equipment is the responsibility of AMS and begins at least four days before each cruise. The CTD and pore water sampling equipment requires special advance preparation, calibration and cleaning. An equipment list for sediment sampling (not including pore water analysis equipment and sample containers) is provided in Table 14.

Quantity	Description
1	Van Veen grab, 0.1 square meter capacity, Kynar TM coated, (pre-cleaned in the laboratory)
1	Van Veen grab stand
2	Plastic floats for Van Veen grab
2	Weights for Van Veen grab
1	SBE1 19 CTD, calibrated in the laboratory prior to use
1	Data terminal and communication cable for CTD
1	CTD Maintenance kit including 8 new "D" size batteries
1	Sediment overflow bucket
8	Insulated plastic coolers for sample storage, pre-cleaned
1	Keys to Coyote Creek gate (for watershed sampling)
60-90 (lbs.)	dry ice
1	Insulated plastic cooler for dry ice storage
1 (pr.)	Cotton gloves for dry ice handling
1	Cruise plan
30	Sample collection forms
10	Chain of custody forms
30	Pore water collection forms
	MSDS (Material Safety Data Sheets) for reagents on board
2	Label tape
2	Aluminum foil, 100 square feet
48	Ziploc [™] bags, 1 gallon size
2	Sharpie pens, thin and wide
200	Latex gloves, non-powdered
1	Splash-proof eye protection
2	Plastic brushes
3	Five gallon plastic buckets
3	Hydrochloric acid 1%, 4 L amber bottle, reagent grade
3	Methanol, 4 L amber bottle, reagent grade

Table 14. Equipment list for sediment sampling.

5	De-ionized/reverse osmosis water, 4 L polyethylene bottle
1	Alconox TM detergent in squirt bottle
3	Teflon TM squeeze bottles, (pre-cleaned) in the laboratory (labeled for distilled water, 1% hydrochloric
	acid and methanol)
3	Kynar TM coated scoops, (pre-cleaned) in the laboratory
1	Kynar TM coated bucket, (pre-cleaned) in the laboratory
1	Cellular phone with battery charger
as needed	Formalin gloves
as needed	Preprinted sample labels
as needed	Paper and cloth towels

3.2.4 Sample Containers

The sample containers used for sediment samples and the laboratory responsible for providing them are listed in Table 15. Each container is given a permanent sample label written in waterproof ink. At a minimum, each sample label includes station name and code, sample date, collection time, analysis required, and collector's initials.

Sample containers are cleaned and prepared by the analyzing laboratory, or are factory precleaned, and are delivered to AMS at least one week prior to the start of a cruise. Sample containers are pre-labeled and packed into pre-cleaned ice chests. A container list is prepared before a cruise starts and is used to verify that all samples are properly collected in the field. At least two personnel verify that the proper sample containers for each station have been filled with sediment and that the labels correspond to the proper station name and code.

Sample Type	Container
As, Se	18 ml Teflon [™] jar, pre-cleaned by BRL. Fill with sediments to 0.25" from top.
Trace Organics	New 100 ml Ichem [™] , wide-mouth, glass with Teflon [™] liner, certified trace organics clean
	by I-Chem [™] and provided by BADA. Fill with sediments to 1" from top. Do not overfill.
Trace Elements	New 60 ml Nalgene [™] polyethylene jar, certified trace metal clean by Nalgene [™] and
	provided by BADA. Fill with sediments to top.
Hg and MeHg	New 4oz. Polyethylene cups pre-cleaned and provided by UCSC.
Archive	Same as trace organics container. Fill with sediments to 1" from top.
Pore Water Sulfides	4.5 ml glass scintillation vial, pre-cleaned by MPSL and provided by MPSL. Fill with pore
	water to top, leave no head-space.
Toxicity	1 L glass I-chem [™] wide-mouth jars, certified trace organics clean by I-Chem [™] and
	provided by MPSL. Fill with sediments to top, leave no head-space.
Benthic Infauna	500 ml glass jar, pre-cleaned and provided by CCSF.
pH and Ammonia	On-board measurements only

Table 15. Container list for sediment sampling.

3.2.5 Sediment Sampling Equipment Preparation

Sediment sampling equipment is prepared in the laboratory by AMS a minimum of four days prior to the start of a cruise. The sampling equipment that is pre-cleaned include:

- Van Veen Grab (excluding frame and stand)
- Sample scoops (three)
- Compositing bucket
- Wash bottles
- Glass pore water coring tubes (six)

Use the following procedures for cleaning sediment sampling equipment:

- 1. Soak equipment (fully immersed) for three days in a 0.5 % solution of AlconoxTM detergent and deionized water.
- 2. Rinse equipment three times with de-ionized water and let dry in a clean place.

3. Rinse equipment with 1.0 % solution of hydrochloric acid, followed by a rinse with petroleum ether, followed by another set of three rinses with de-ionized water. All equipment is then allowed dry in a clean place.

The cleaned grab is wrapped in aluminum foil until used in the field. All other equipment is stored in clean ZiplocTM bags until used in the field.

Sediment Container Preparation for Mercury and Methylmercury Samples

New 4oz. Polyethylene sediment cups (available from VWR- cat# 44333-000) are placed into 3M HNO3 for two days. They are rinsed with de-ionized water and placed into 1.5M HCl for two days. They are rinsed with de-ionized water and air-dried. They are bagged in clean ziplock bags until use. Sample cups are not reused.

31 bottles plus two field blanks and one travel blank of both the 500ml and the 11 size are shipped from UCSC to AMS prior to the cruise.

The CTD is checked for proper operation at least 48 hours before use. Refer to the section on CTD maintenance and calibration in the Water Sampling section (3.1.7). The pore water ammonia probe must be assembled and calibrated at least 24 hours before use. Refer to the section on pore water sampling (3.2.6.3) for assembly instructions.

3.2.6 Sediment Sampling Procedures

When the vessel reaches a sampling station and the anchor has been deployed, the captain notifies personnel that the vessel is on site and switches on a raw water pump used for rinsing the sampling equipment. Sampling equipment is cleaned at each station using the following methods:

- 1. Fill the compositing bucket with Estuary water from the raw water pump and add approximately 1/8 cup of AlconoxTM detergent to the bucket.
- 2. Place all sampling scoops and glass coring tubes into the bucket and wash thoroughly with the Alconox[™] solution. Wash all Kynar[™]-coated parts of the Van Veen grab with Alconox[™] solution.
- 3. Completely rinse the grab, bucket, sample scoops and coring tubes with Estuary water.
- 4. Rinse the grab, bucket, sample scoops and coring tubes with 1.0 % HCl followed with a rinse of methanol.
- 5. Completely rinse the grab, bucket, sample scoops, and coring tubes with de-ionized water and let air dry. Cover all cleaned parts with aluminum foil until use.

At stations where benthic sampling is conducted, a Ponar grab is used to collect one acceptable benthic sample prior to using the Van Veen grab for collecting sediment chemistry samples. Personnel from CCSF are responsible for operating the Ponar Grab and determining if grabs taken meet acceptance criteria. After benthic samples have been collected, the Ponar grab is replaced on the winch wire with the Van Veen grab for collection of chemistry samples. Two grabs are taken at each site. If the sediments at a station are considerably fine, plastic floats may be attached to the grab frame and secured so they do not interfere with grab operation. Likewise, if the sediments are considerably coarse, weights are added to the grab frame to assist penetration of the sediments. The quality of grab samples is ensured by requiring each sample to satisfy acceptance criteria concerning the depth of penetration and disturbance of the sediment within the grab.

Samples contain only the top 5-cm of sediment within the area of the grab jaws. Samples are rejected under the following conditions:

- There is a rock or shell fragment wedged between the jaws of the grab allowing the sample to wash out.
- The sample surface is significantly disturbed.
- The sample is uneven from side to side, indicating that the grab was tilted when it penetrated the sediment.
- The surface of the sample is in contact with the doors of the grab, indicating over-penetration of the grab and possible loss of material around the doors.

After determining a grab meets acceptance criteria, overlying water is drained off. Using precleaned glass cores, three 5-cm deep cores are taken from each side of the grab. These cores are used for measurement of pH, ammonia, and total sulfides in pore water.

The remaining top 5-cm of sediment is scooped from each of two replicate grabs and mixed in the compositing bucket to provide a single composite sample from each site. Portions of the composited sample are placed into clean containers provided by each laboratory. A duplicate chemistry sample is collected from the composite for archiving and is labeled as an "archive". Cores collected for analysis of pore water are centrifuged onboard the vessel. Part of the supernatant is then used for analysis of ammonia and pH (performed on-board the vessel by AMS) and part is preserved for analysis of sulfides (analyzed in the laboratory by MPSL)

3.2.6.1 Sediment Chemistry

There is no on-board sediment chemistry except for analysis of pore water pH and ammonia. Fill sample chemistry containers according to instructions given in the container list (Table 14). Refer to section 3.2.6.3 for analysis of pore water pH and ammonia.

3.2.6.2 Benthic Infauna

The objective is to collect one infauna sample at each of two RMP sediment stations. Benthic infauna primarily comprises sedentary, invertebrate organisms that burrow in or live on the surface of sediments. Benthic infauna communities fluctuate in response to natural and human induced environmental perturbations and therefore can be important indicators of environmental health. For this reason they often are an important component of many ecological monitoring programs. Benthic infauna is sampled with a Ponar grab with a surface area of 0.05 square meters. The grab is equipped with hinged stainless steel mesh lids with rubber flaps to allow flow-through of water during descent and thus minimize disturbance of surface sediments. The rubber flaps close upon retrieval and prevent winnowing of the sample. Lead weights are added to or removed from the outside of the grab as appropriate for sediment type to control depth of penetration.

After deployment and retrieval, the grab is placed on a stand for processing. The grab lids are opened and the sample is examined for suitability using the following criteria:

- Complete closure of the grab jaws.
- No evidence of sediment washout through the grab doors.
- An even distribution of the sediment in the grab.
- Minimum disturbance of the sediment surface.
- Minimum overall sediment depth appropriate for the sediment type: 4 cm in coarse sands and gravel, 5 cm in medium sands, 7 cm in fine sands, and 10 cm in silty sands, silts, and clay (coarse sands and gravel: > 2mm in grain size; medium sands: 63µm 2mm in grain size; clay and silt: <4µm 63µm in grain size).

If the sample meets all of the criteria, the grab jaws are opened and the sample is dumped into a five gallon plastic bucket placed beneath the grab stand. Estuary water is used to wash all sediment from the grab and grab stand into the bucket. Care is exercised not to lose sediment by overfilling the bucket. The sample bucket is then moved to a wash table for sample sieving.

When a sample bucket arrives at the sieving station, it is lifted to the sieve table and poured slowly onto the nested sieve screens. The raw water hose with a flow control nozzle is used to slowly wash sediment from the sample bucket onto the sieve screens. The sieving process is aided by keeping sediment in suspension as it reaches the screen. The sample is washed from the sample bucket until the bucket is empty and well rinsed. Sediment is washed through the nested sieve screens by gently running estuary water over the top screen. Use of high water pressure damages organisms impinged on the sieve screen mesh.

When all material smaller than 1.0 mm has passed through the top screen, the process is repeated with the finer screen until all material smaller than 0.5 mm has passed through. The material retained on each screen is gently washed into one corner of the screen and with the aid of a canning funnel, washed into

separate, labeled BallTM canning jars. A wash bottle with estuary water is used to rinse any material on the inside screen frame and canning funnel into the sample jar. Any organisms remaining on the screens are carefully removed with forceps and placed in the appropriate sample jars. The sample jars are then capped with lids and bands, labeled with indelible ink on botanical paper inside the jars and on the lids. The jars are then delivered to the on-board formalin station. Great care is exercised to avoid creating fragments when removing organisms from the sieve screens. The sieve screens are rinsed with high-pressure estuary water and scrubbed clean with a stiff-bristle brush between samples.

If the sample contains many shell fragments and/or worm tubes, the sediment sample is added to the top (1.0 mm) screen in stages so that the screen does not become too full. If the bottom screen (0.5 mm) begins to clog with sediment, the field crew ceases adding sample and gently runs the hose nozzle with low flow along the outside bottom of the 0.5 mm screen being careful not to lose sample by allowing water to escape over the top of the sieve. The material retained on a sieve screen is not allowed to fill the sample jar more than half full. In such a case, the material is divided among two or more jars and each jar is labeled as jar 1 of 2, jar 2 of 2, etc., as required.

At the formalin station, each sample jar lid is replaced with screen lids fitted with 0.25 mm NitexTM mesh and the Estuary water is decanted from the sample jars through the screen lids. Relaxant (isotonic MgCl₂) is added to the sample through the screen lid to a level approximately one third higher than the sample level. A wash bottle of relaxant is used to wash down the screen lid and sides of the sample jar. The sample jar is recapped with the sample jar lid and gently rotated several times in a tilted position to ensure mixing of the relaxant throughout the sample. The sample is allowed to sit in the relaxant for 15-30 minutes. After this period, the sample jar lid is replaced with a screen lid and the MgCl₂ is decanted out of the sample jar in preparation for fixing the sample.

At the formalin station, relaxant is decanted out and fixative (10% buffered formalin in pre-mixed seawater) is added to the sample through the screen lid. Fixative is added to a level approximately one third higher than the sample level. A wash bottle of fixative is used to wash down the screen lid and sides of the sample jar. The screen lid is removed, 2 or 3 drops of stain (rose bengal solution) are added to the sample and the sample jar is recapped with the sample jar lid. The jar is gently rotated several times in a tilted position to ensure mixing of the fixative and stain with the sample. Safety glasses and nitrile gloves are worn when working with fixative.

While onboard the survey vessel, benthic infauna samples are stored in plastic trays with dividers, then transferred to cardboard cartons with dividers for travel to the laboratory for sample sorting. Benthic infauna samples fixed in formalin are washed in tap water and transferred to 70% ethyl alcohol between 24 and 72 hours after fixation. Samples can then be held indefinitely in 70% ethyl alcohol.

A sample collection log, maintained by CCSF, records sample date, station, depth of grab penetration, number of grabs, number of bottles per sample, and any problems encountered.

3.2.6.3 Sediment Pore Water Analysis

Overview

Pore water samples removed from benthic grabs are analyzed for pH, ammonia and sulfides. Ammonia and sulfides are a natural component of marine sediments and common constituent of municipal effluents. Ammonia and sulfides may occur in concentrations that are toxic to marine organisms in toxicity tests and, therefore, must be accurately measured.

Table 16 presents the equipment list for pore water analysis. This equipment is prepared in the laboratory at least four days prior to the start of each cruise.

Quantity	Description
1	Cole-Parmer pH meter and probe
1	Hach DR 850 field colorimeter
1 each	Operator's manuals for pH meter and colorimeter
50	Hach nitrogen as ammonia, LR test reagents
50	Hach nitrogen as ammonia, HR test reagents

Table 16. Equipment list for pore water sampling.

-	
1	IEC [™] "Clinical" centrifuge with fixed angle rotor, 6 x 50 ml capacity, fitted with stainless
	steel sleeves
200	50 ml centrifuge tubes with screw caps
3	Standards for pH, 4.0, 7.0 and 10.0, NIST traceable
4	Standard reference solution of 1 ppm ammonia
1	Compressed nitrogen tank with regulator and hose
4	Glass coring tubes, 3.5 cm diameter,
4	Rubber stoppers for coring tubes
1	Centrifuge tube rack
1	Eppendorf TM pipette, 1000 μ l capacity with spare tips
50	Disposable pipette tips
30	4.5 ml glass scintillation vials, screw-cap with plastic liner, prepared with zinc acetate
	preservative (see pore water sulfides procedures)
1	Liquid hazardous waste storage container
1	Scalpel with blades / scissors
	MSDS (Material Safety Data Sheets) for reagents on board
as needed	Paper towels
as needed	Rags
as needed	Kimwipes [™]

Pore Water Sample Collection

Use the following guidelines for pore water sample collection and analysis:

- 1. Prior to fieldwork, wash coring tubes using the same procedures as outlined for preparation of the Van Veen grab and wrap in clean aluminum foil.
- 2. After retrieving the Van Veen grab and determining the sample suitability, insert a coring tube into the sediment so that there is 5.0 cm of sediment in the tube after it has been withdrawn. Three cores are removed from each side of the grab for a total of six cores taken per sampling site. Coring tubes may be reused at the same station without washing.
- 3. Place the sediment from each core into a separate clean centrifuge tube and transport the tubes into the vessel cabin. Purge the headspace of each tube with nitrogen then cap each tube tightly.
- 4. Place the six centrifuge tubes into the centrifuge and spin at a rate of 400-1,000 RPM. Be aware that the centrifuge may transfer excessive heat to the sample if processed for too long a time.
- 5. Rinse a collection pipette with DI water and flush it dry.
- 6. Pipette or pour off the overlaying pore water from the top of each centrifuge tube into one empty centrifuge tube.
- 7. Pipette out enough pore water from the composited centrifuge tube to fill the sulfides vial with no headspace or bubbles. This requires about 1.5-2.0 ml of pore water. Do not spill the preservative in the sulfide bottle and do not contact the pipette with the sample water in the sulfide vial (it contains acid and could corrupt ammonia measurements). Record the station code and date on the sulfides vial and store it in a cool, dark place (do not freeze the sample).
- 8. Follow instructions in Hach Datalogging Colorimeter Handbook for running either the Nitrogen, Ammonia, Low Range (p. 219) or Nitrogen, Ammonia, High Range (p. 225) tests as needed. Use care with reagent powder packets, as reagents can be hazardous to human health. Clean up all spills immediately and empty liquid wastes into appropriate hazardous materials container.
- 9. Rinse the pH probe with DI water, dry, and place directly into the composite centrifuge tube. Record the pH reading when the meter stabilizes. This normally takes less than a minute.
- 10. Dispose all wastes and materials properly.

Measuring Pore Water Ammonia Using the Hach Colorimeter

Measuring ammonia concentrations in pore water is a standard procedure using the portable Hach DR/820 colorimeter. There are two calorimetric tests available, depending on the predicted pore water ammonia concentration. The low range test (0-2.5 mg/L total ammonia) is applicable for most RMP Central Bay sites and sites where sediment grain size is coarse. The high range test (2-5-10.0 mg/L total ammonia) is applicable at most RMP South Bay and North Bay sites. It is standard to run a low range pore water ammonia test first, switching to a high range test if the colorimeter can not provide an accurate result. Use the following guidelines for measuring pore water ammonia with the Hach colorimeter:

- 1. Use method #10023, Nitrogen Ammonia Salicylate Method for analysis of pore water total ammonia as referenced in the Hach colorimeter owner's manual.
- 2. Turn on the colorimeter and enter the program number for the test being performed, for low range ammonia the program number is "66".
- 3. The colorimeter requires that two standards be prepared, a blank and an ammonia standard of known concentration. The ammonia test kit prepared by Hach includes standardized ampules used for preparation of the standard. Refer to the Hach DR/820 colorimeter owner's manual, page 219 for preparation of the standards.
- 4. After a blank and ammonia standard has been analyzed, the colorimeter will be ready to read the ammonia concentration of the pore water sample. Refer to Hach DR/820 colorimeter owner's manual for preparation of the pore water sample using the reagents provided in the Hach ammonia test kit. Measure the ammonia concentration of the pore water sample and note the measurement in the ship sample logbook. If the pore water ammonia value is over the limit for the low range test, repeat the procedure using the high range test kit.

3.2.6.4 Sediment CTD Profiling

A CTD cast is recorded at each station, except for the two watershed sites. The procedures for operating the CTD on the sediment cruise are the same as those for the water cruise. Refer to section 3.1.11 (Water CTD Profiling) for CTD operating instructions.

3.2.6.5 Watershed Sediment Sampling

All equipment is pre-cleaned according to the procedures as outlined above. The guidelines for obtaining grab samples at the watershed sites are as follows:

- Randomly select an area of unconsolidated fine-grain sediment. Unconsolidated sediments lack a diatom covering (usually visible) and are very easily penetrated. Typical locations are the side slope or surface of recent slump blocks and the surface of actively accreting point bars on the inside of meander bends. For drainage divide stations, randomly select a location at least 10 meters from any channel or ditch, and at least 5 meters from the upland edge of the tidal marsh. Do not select spots in ponds or channel pans.
- 2. Insert a cleaned scoop into the sediments to a depth of 5 centimeters. Remove sediments from an area approximately 0.1 square meter. The total amount of sediment sampled is proportional to the amount of sediments removed when using the Van Veen grab at the Estuary sites.
- 3. Place sediment into a pre-cleaned compositing bucket. Thoroughly stir the combined material into one homogeneous mixture.
- 4. Place the appropriate amounts of the sediment into clean containers with appropriate labels, and place the containers on ice for short-term storage.
- 5. To avoid cross-contamination between stations, all utensils, buckets, and the glass core tubes must be rinsed between stations with Estuary water, then scrubbed thoroughly with AlconoxTM, followed successively by one rinse with de-ionized water, one rinse with 1% HCl, one rinse with methanol, and a final rinse with de-ionized water.

3.2.6.6 Sediment Sample Storage and Handling

Samples are stored aboard the vessel according the type of analysis performed. Normally, samples used for chemistry analysis are stored on dry ice while samples used for toxicity analysis are stored on wet ice. On board the vessel, properly labeled sample containers are segregated by analysis required and stored according to the guidelines listed in Table 17.

Analysis	Method of Storage
Trace Elements	Store on dry ice in ice chest
Organics	Store on dry ice in ice chest

Table 17. Storage methods for sediment samples.

Analysis	Method of Storage
Arsenic, Selenium, Mercury	Store on dry ice in ice chest, keep in separate Ziploc [™] bags
Cognates	Store on dry ice in ice chest
Archives	Store on dry ice in ice chest
Toxicity	Store on wet ice in ice chest, replenish ice each day
Benthic Infauna	Preserved, no chilling required
Sulfides	Stored in a dark location

The samples on both wet ice and dry ice should be checked periodically to ensure that samples are appropriately protected. Ice is added as required. Additionally, coolers containing wet ice should be drained periodically to remove melt water.

In addition to the ship's log, a sample record is maintained for each site. The sample record contains the following information:

- 1. Station name and code
- 2. Collection date
- 3. Arrival and departure time at each station
- 4. Station coordinates (latitude and longitude) from the survey vessel's GPS
- 5. Depth at time of sampling from the ship's depth meter
- 6. A record of every sample bottle filled, with bottle identification code and quantity
- 7. Collecting personnel
- 8. Other remarks (i.e. any conditions that could possibly influence sample analysis or data interpretation or notation of the general performance of equipment involved with the sampling.)

The sample collection form, coupled with a chain of custody record and a laboratory analysis record, allows tracing of the complete history of a sample from time of collection to final entry of data to a computer database. In addition to the sample collection form, some of the laboratories may use a bottle labeling system that catalogs the preparation of bottles prior to their use in the field. This system is particularly important for the TeflonTM bottles used in trace element analysis, where exhaustive cleaning procedures are employed before releasing them for field sampling.

3.3 Bioaccumulation Sampling

3.3.1 Overview and Objectives

The bioaccumulation study of the RMP is conducted to document long-term trends in bioavailable contaminants in the Estuary. Bioaccumulation sites are chosen to incorporate contaminant sources from broad regions of the Estuary and reduce effects from specific point sources.

Bioaccumulation sampling consists of collecting oysters (*Crassostrea gigas*) and mussels (*Mytilus californianus*) from "background sites" of known chemistry and deploying the bivalves at 12 locations in the Estuary. Resident clams (*Corbicula fluminea*) are also collected from one site on the Sacramento and one site on the San Joaquin river. Bivalves are deployed once each year, usually in June. The deployment period represents the "dry season". Deployment duration is approximately 100 days with a "maintenance" cruise occurring approximately 50 days after deployment.

Analysis of contaminant concentrations is conducted on a subset of the transplanted bivalves prior to deployment (time zero) in Estuary locations, and after deployment. The differences between pre- and post-deployment contaminant concentrations allow determination of contaminant uptake during the period of deployment. Transplanted bivalves (time one) are also collected from the time zero collection sites at the end of the deployment period, to obtain information on uptake variables affecting wild populations during the deployment period.

Bivalve condition is also measured as part of the bioaccumulation study. Condition is the ratio of dry tissue weight to shell cavity volume. Bivalves have high condition when there is abundant food and few environmental or physiologic stressors.

3.3.2 Oyster Collection

Crassostrea gigas are purchased from a commercial grower located in Tomales Bay, CA. A total of 1200 "extra small" (grower's designation) oysters are obtained from the grower by AMS personnel and transported in coolers to the Bodega Marine Laboratory (BML) in Bodega Bay, CA.

The oysters are placed into 36"long polypropylene mesh bags containing 36 oysters divided into three sections of twelve each; the three sections are separated by nylon cable ties woven through and around the outside of each bag. Room is left in each section to allow for growth and movement of the oysters within the bag.

The bags of oysters are placed on racks in an outdoor tank supplied with aeration and freely flowing, full strength seawater. The oysters are maintained in this tank for a maximum of two weeks prior to deployment. They are transported from BML to the vessel in coolers which have been scrubbed with AlconoxTM detergent, rinsed with fresh water and chilled with freshwater ice. During transportation, the coolers are allowed to drain, preventing the oysters from being submerged in fresh water from the melting ice.

3.3.3 Mussel Collection

Mytilus californianus are collected from a location that is several hundred yards north of the parking lot at Bodega Head, near Bodega Bay, CA. Collection of mussels is done by 3-4 AMS personnel, all of whom have in possession valid California Department of Fish and Game (CDF&G) scientific collecting permits. The CDF&G is notified of mussel collection efforts 24 hours in advance. Additionally, AMS has a permit from the Sonoma County Division of State Parks, who also require a scientific collecting permit and notification prior to collection. When weather conditions are marginal for safe sampling and as deemed necessary by AMS personnel, individuals employed by BML serve as wave spotters, to warn mussel collectors of potentially dangerous incoming waves.

Timing of collection efforts is determined by occurrence of a suitable low tide during daylight hours within two weeks of the beginning of the deployment cruise. Tide levels below 0 feet mean low water (minus tides) are preferred, however mussel collection may be accomplished on higher tides in calm conditions.

Safety gear used is determined by AMS personnel prior to collecting. Safety gear includes: a PFD for each individual, a life ring for emergency rescue, whistles, a hand-held radio or cellular phone, and personal foul weather gear. All personnel monitor incoming waves while collecting, and call out warnings to the other collectors if danger is perceived.

Collectors wear powder free latex gloves and collect mussels which are between 55 and 65 mm in total length. The mussels are counted as they are collected and placed into clean buckets or coolers. Approximately 1,400 mussels are collected during the yearly collection effort.

Mussels are transported to BML and placed into 40"long mesh bags. Each bag contains 40 mussels, divided into four sections of 10 mussels each and separated by nylon cable ties woven through and around the bag. Room is left in each bag section to allow for growth and movement of the mussels within the bags. The bags of mussels are placed in the same tank as the oysters, and are thereafter handled and transported in the same manner.

3.3.4 Resident Clam Collection

Due to a lack of viable *Corbicula fluminea* populations noted in 1998, resident bivalves are now used as a standard element of the bioaccumulation study. Clams are collected from near the historical transplantation sites in the Sacramento and San Joaquin Rivers. The sample station Grizzly Bay is no longer used in the program due to the lack of transplantable "clean" clams.

Resident clams are collected by use of a clam dredge. The dredge is approximately two feet wide by three feet long and weighs approximately 50 pounds. The dredge is deployed from a boat and is dragged along the bottom. When brought to the surface, the clams are placed into a clean plastic container and packaged for analysis.

3.3.5 Vessel Safety

There are 14 bioaccumulation sites in use by the RMP (refer to Table 6 for a complete list of bioaccumulation sites). Twelve sites are bivalve transplantation sites and two are resident bivalve collection sites. All sites except for Davis Point and the two resident bivalve collection sites are sampled from the *R/V Questuary*. The *R/V Questuary* is 36 feet in length and has a cruising speed of 15 knots. Important features that make it suitable for a bioaccumulation cruise include a large deck, enclosed cabin, and removable swim step. The Davis Point site and resident clam sites are sampled from the vessel *M.E. II*. The *M.E. II* is used because low overhead clearance is problematic at Davis Point and requires a smaller vessel for safe access. The *M.E. II* is also used for resident clam sampling because the *Questuary* is too powerful and can break the dredge when it hangs upon bottom debris. The *ME II* just stops when the dredge hangs up.

Cruise plans are developed between AMS and the vessel skipper to ensure boat availability and that excessive currents would not pose hazards to divers. Cruise schedules may vary due to inclement weather.

It is the responsibility of the vessel captain to navigate the vessel to the bioaccumulation sites. All bioaccumulation sites are associated with fixed markers (channel markers or pilings) for easy navigation. Once at a bioaccumulation site, the vessel captain instructs the crew to fasten the vessel to the marker. At some sites, "live-boating" is conducted and the vessel is not fastened to the marker. Securing the vessel to fixed structures can pose a safety concern, thus it is the responsibility of the vessel captain to assess the safety of each site before mooring the vessel.

The maximum workday cannot exceed 12 hours per United Sates Coast Guard requirements. The maximum number of passengers allowed onboard the *R/V Questuary* is six, excluding captain and crew. The captain reserves the right to cancel or modify the cruise for any safety reason that could endanger customer, crew or captain's safety. Captain reserves the right to modify any procedure that could damage the vessel. Customer and any personnel brought aboard by customer agree to follow all safety procedures and policies implemented by the captain.

3.3.6 Dive Safety

The RMP requires only non-decompression SCUBA diving for bioaccumulation deployment, maintenance and retrieval. This section documents the safety procedures involved, responsibilities of the dive team members, equipment used and maintenance procedures, and emergency procedures associated with each of these types of diving.

AMS performs diving operations in a number of areas that are only accessible by water. The general procedure for accessing a dive site is to tie the vessel off to a fixed structure and attach a life ring directly to the structure prior to beginning dive operations. In all RMP diver operations, two divers and one dive tender are used; the two divers are tethered together. AMS uses underwater communication gear to allow the divers to communicate with each other and with the dive tender during the dive. General safety procedures use the following guidelines:

- 1. Boating Safety. A safety briefing is given by the skipper of the vessel prior to departure from the dock. This briefing shall include at a minimum the location of flotation devices, location of fire extinguishers, and emergency procedures. Enough information is given to allow the crew to communicate with emergency services, and operate the vessel in the event that the captain is incapacitated.
- 2. Equipment Storage. All equipment to be used as part of diving operations is properly stowed to minimize the possibility of movement during vessel transit.
- 3. Arrival at Dive Site. The dive tender assists the skipper in mooring the vessel to the fixed structure at each transplantation site. The tender shall also affix a life ring to the fixed structure, in case the vessel must depart from the structure while divers are in the water.
- 4. Pre-Dive Briefing. A briefing session is given by the lead diver or dive safety officer prior to beginning dive operations. The briefing includes such information as weather, currents, dive plan and emergency procedures.
- 5. Diving Safety. Each diver is responsible for performing a functional check of all dive equipment in the presence of the dive buddy or the tender. Dive operations are initiated given appropriate environmental conditions and appropriate health conditions of the divers. The dive operations can be terminated by

either diver or the dive tender for environmental, diver health, equipment, or any other reasons. All AMS diving operations are conducted in accordance with procedures and requirements of the American Academy of Underwater Scientists (AAUS).

- 6. Underwater radio communications gear allowing communications between the divers and tender are used. This gear allows the divers to communicate even with the (commonly poor) visibility found in the San Francisco Estuary.
- 7. Debriefing. At the conclusion of each dive, the dive tender shall fill out the dive logs and the divers and tender discuss any issues of concern arising from the dive.

3.3.6.1 Dive Team Member Responsibilities

The responsibilities of the dive members are as follows:

- 1. Lead Diver In addition to operations performed as part of the scientific investigations, the lead diver is responsible for planning the dive, discussing the plan with the diver and dive tender, and evaluating environmental conditions at each dive site.
- 2. Diver In addition to tasks performed as part of the scientific investigations, the diver shall assist the lead diver in evaluation of the dive plan and environmental conditions. The diver also assists with mooring the vessel at the dive sites.
- 3. Dive Tender The dive tender assists the vessel skipper with tying the vessel off to the fixed structure. The tender also participates in discussions of the dive plan and environmental conditions, assists the divers in preparing materials and equipment needed for dives, records information for dive logs, monitors dive communications, and assists divers returning to vessel.

3.3.6.2 Dive Equipment Use and Maintenance

Each diver is responsible for the safe functioning of their dive equipment. As such, each diver shall set-up their own gear and perform a functional check of all equipment. Divers will make use of AMS equipment logs to record required inspection and maintenance of all equipment.

- Pre-Dive. Each diver shall be responsible for performing a functional check of all dive equipment in the presence of a buddy.
- Post-Dive. The divers shall follow-up on any equipment concerns that developed during the course of a dive prior to re-entering the water.

3.3.7 Dive Operations

Owing to the relatively shallow dive depths and lengthy surface intervals spent in travel time between sites, the dive teams can complete several dives during the course of one day. Diving operations are developed with the conditions of the Estuary in mind and allow for safe diving in conditions of zero visibility, large waves and subsurface currents up to 1 knot. Dive operations have evolved over the course of the monitoring program to incorporate the highest degree of safety possible. Currently, the average dive operation at each site takes approximately 25 minutes. Table 18 presents a simplified outline of a bivalve bioaccumulation operation.

Table 18. Dive operations task list.

Step	Task	Minutes/Task
1	The vessel approaches piling and determines direction and strength of water current and prevailing wind.	3-4
2	Vessel backs up to piling, and a line is attached around the piling to the vessel's stern. The vessel's engine is turned off. A safety line with a flotation device on its end is attached around the piling and is placed in the water.	3
	Should the vessel need to leave the piling while divers are under water, the safety line will remain attached to the piling.	
3	Two divers enter the water from the vessel's stern and maneuver down the piling to the bottom.	1

4	Divers locate a ground line that is attached to the base of the piling. Occasionally, the ground-line is buried and must be dug out of the sediments by hand.	.5
5	Divers follow the ground line approximately 20-40 feet to where the line is secured to the bottom with a "screw-in type" ground anchor. Connected to the ground anchor is a 16 inch diameter plastic buoy attached to a 3-4 foot buoy line. Four bivalve bags are secured to the buoy line with cable ties.	.5
6	Divers perform their work on the bivalve bags by either installing, cleaning or removing bags. Divers check ground and buoy lines for integrity.	5-25
	Divers follow ground line back to base of piling.	.5
7	Divers maneuver up the piling to water surface where vessel stern is still attached to piling. Divers board the vessel from the stern.	1
8	The vessel's engines are started. The safety line is removed from the piling then the vessel's stern line is removed from the piling, and the vessel departs the site.	1

3.3.7.1 Dive Records

During the cruise, the dive tender is responsible for maintaining dive logs for each dive. These logs record any comments pertaining to the dive, time and date, environmental conditions, and dive depth, time, and air usage.

At the conclusion of each cruise, each diver is responsible for completing an AMS dive log in accordance with AMS Dive Program regulations. These logs track all the dives completed by each diver over the course of a calendar year along with associated information listing the details of each dive.

3.3.7.2 Equipment

Equipment needs will vary depending on the type of cruise operations (deployment, maintenance, retrieval). Table 19 presents an equipment list for bivalve deployment, maintenance and retrieval dives.

Quantity	Description
6	Aluminum SCUBA tanks, 80 c.f.
3	Sets of personal dive gear (dry suit, regulator, gauges, fins, weight belt, gloves, knife, hood,
	buoyancy compensator)
3	AGA masks
3	Underwater OTS communication modules
36	AA batteries
1	Field medical kit
1	Life ring with 100 foot floating line
3	Tank straps for communications modules
1	Dive log book
1	Sample collection log book
5-7	Empty coolers, cleaned
1	Tool kit
3	Wire brushes (retrieval cruise only)
2	Boxes latex surgical gloves (retrieval cruise only)
3	Oyster knives (retrieval cruise only)
2	Rolls of aluminum foil, 100 ft. (retrieval cruise only)
65	Zip Loc bags, lg. (retrieval cruise only)
500	Cable ties, assorted size (retrieval cruise only)
2	Cable tie fastening tools (retrieval cruise only)
4	Plastic scrub brushes (maintenance cruise only)

Table 19. Equipment list for bivalve sampling cruise.

3.3.8 Dive Equipment Preparation

- 1. Ensure that there are an appropriate number of complete AGA sets (including second stages, power supplies, and connectors) for the required dives.
- 2. Ensure power supplies are functioning properly. Replace old batteries.
- 3. Ensure each AGA set is in working order by attaching a working power supply, activating the push-totalk switch, speaking into the microphone, and listening for reception.
- 4. Label each power supply with the date examined and the diver for which it is intended to be used on the cruise.
- 5. Clean and place equipment into Communication Gear Field Kit.
- 6. Each diver is responsible for performing a functional check of personal dive gear prior to each cruise.

3.3.9 Bioaccumulation Sample Handling

In addition to the ship's log, a sample record must be maintained for each site. The sample record contains the following information:

- 1. Station name and code.
- 2. Species type and number deployed.
- 3. Date of deployment / maintenance / retrieval.
- 4. Condition of bivalves, i.e., number of dead bivalves in bags on deployment and retrieval.
- 5. Allocation of bivalves among various analyses.
- 6. Other remarks.

For the deployment cruise, the bivalves are stored in clean coolers on wet ice. Any accumulated water is allowed to drain off, so that they do not sit in freshwater in the collers. For the retrieval cruise, once the bivalves are returned to the surface they are immediately placed into a cooler. The bivalves are processed either on the ship's back deck (if vessel is not underway) or within the ship's cabin or on the front deck (if the vessel is underway) to prevent contamination of samples by hydrocarbons in the vessel exhaust.

The initial processing of the bivalves is completed using clean, powder-free latex gloves. Dead bivalves are counted, recorded, and removed from the sample. Live bivalves are then allocated among analyses for organics, trace metals, and condition index (in descending order of priority). The numbers allocated to each of the analyses is then recorded on the sample logs.

The samples allocated to organics analysis are wrapped in aluminum foil, placed in a pre-labeled ZiplocTM bag, and placed in a cooler on dry ice. The samples allocated to trace metals are placed in two layers of ZiplocTM bags, one of them pre-labeled, and placed in a cooler on dry ice. Each labeled bag is marked with the date, site, and number of bivalves.

The samples allocated for condition index do not require "laboratory clean" standards as there is no chemical analysis required. These bivalves are scraped to remove as many of the fouling organisms as is practical, rinsed, and dried. The bivalves are then secured with cable ties to prevent loss of tissue material, placed in a pre-labeled ZiplocTM bag, and stored on dry ice.

All samples are stored on the vessel for the duration of the cruise. Dry ice is replenished as needed to keep samples frozen.

The sample collection form, coupled with a chain of custody record and a laboratory analysis record, allows tracing of the complete history of a sample from time of collection to final entry of data to a computer database.

3.3.10 Standard Methods for the Determination of Bivalve Condition Index (C. I.)

Physical parameters:

- 1. Total volume (sealed shell volume), V_s
- 2. Shell volume (open shell volume with flesh removed), V

- 3. Cavity Volume, $CV = V_s V_o$
- 4. Dry flesh weight, DFW
- 5. Condition, CI = DFW / CV

Equipment and Tools:

- Sartorius PT-1210 balances (2)
- appropriate-sized beakers with hose barb at bottom (2)
- appropriate clamping mechanisms (2)
- 6 8" long clear, flexible hoses (2)
- aluminum weigh pans
- cooler
- frozen blue ice
- cable ties
- cable tie cutters
- sample log (see attached example)
- minute timer
- forceps
- scalpel and extra blades

Methodology in Field

Specimens are individually scrubbed to remove encrusting organisms and sediment. Their shells are then sealed tightly shut by use of a nylon cable tie applied with a cable tie-tensioning tool. The specimens are dried by blotting on a cloth towel, then placed inside doubled, heavy-duty zip-locTM bags. The bags are labeled with the following information: date, site name and code, species and number of specimens, and sample type (i.e., CI). Finally, the sample bags are frozen on dry ice, and transferred to AMS' freezer at the end of the cruise.

3.3.11 Bivalve Handling and Storage

At the conclusion of the retrieval cruise, the samples are all transferred to AMS and placed in onsite freezers. The samples for trace organics analysis are shipped overnight on dry ice to GERG. The samples for trace metals are transferred by AMS personnel to UCSC for homogenization in preparation for 3339laboratory analysis. The samples for condition index are maintained at AMS until they are processed. All shipped samples are shipped overnight in coolers with enough dry ice to keep samples frozen for at least two days.

Data Collection, Quality Assurance, and Sample Archive

- 1. Data are compiled on paper and then transferred to computer. The original data sets are archived.
- 2. The two Sartorius PT-120 balances used for these analyses are serviced and calibrated as necessary by certified Sartorius personnel. Additionally, the scales are checked and calibrated using NIST certified weights prior to beginning the analyses.
- 3. A minimum of 10% of the hand entered-data are checked against the electronic data set. If no errors are found, the electronic data are considered to be error free. If any errors are found, all of the hand-entered data are checked against the electronic data set.
- 4. The dry flesh and shells are archived in labeled zip-lock bags and any unused bivalves are archived in the freezer as requested.

3.3.12 Bivalve Chain of Custody

Chains of custody (COC's) are completed each time control of samples is transferred from AMS to a receiving laboratory. For bioaccumulation samples, in addition to the standard shipping information, the following information is required:

- 1. Cruise number
- 2. RMP station name and code
- 3. Collection date
- 4. Species type
- 5. Analysis required
- 6. Other remarks

Completed COC's are either faxed to the receiving laboratory one day in advance of the shipment or hand-delivered with the samples. Receiving laboratories are requested to confirm delivery of samples by contacting AMS and by sending completed COC's to SFEI.



BADA / RMP Consortium Organizational Chart

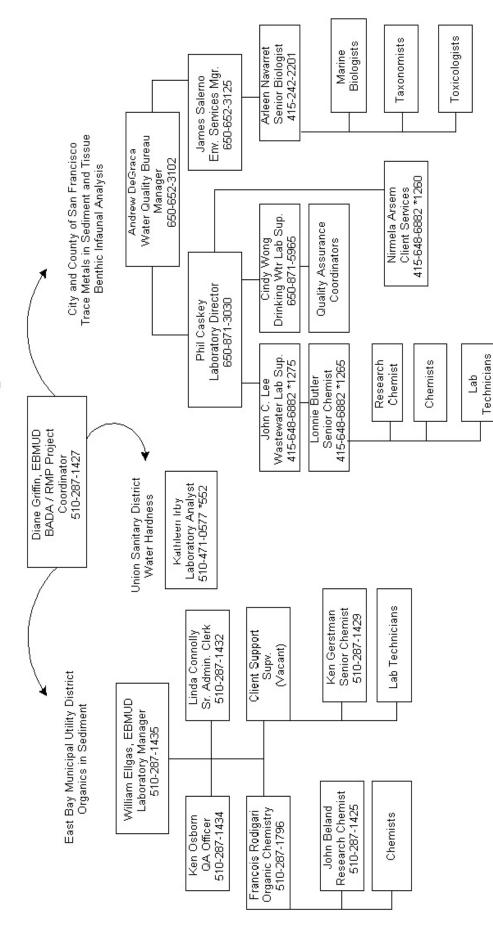


Figure 1. BADA / RMP Consortium Organizational Chart

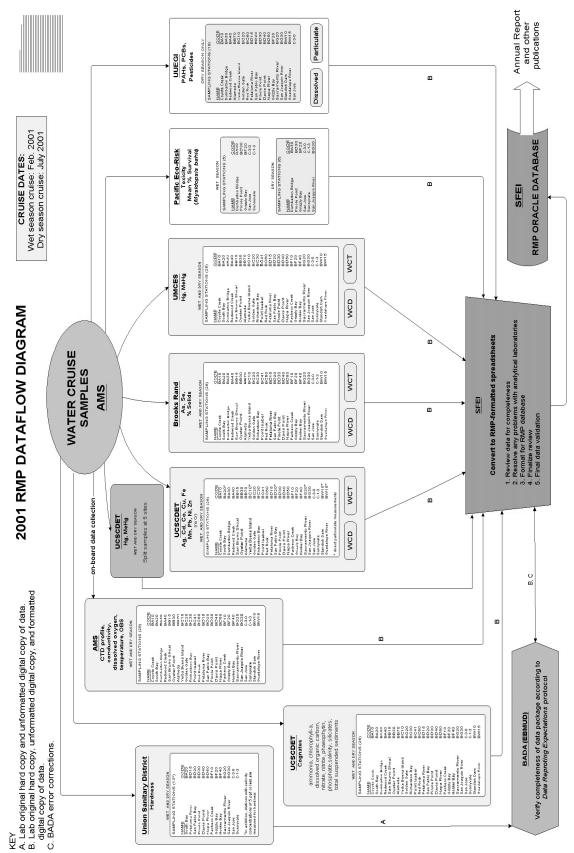


Figure 2. Dataflow Diagram for Water

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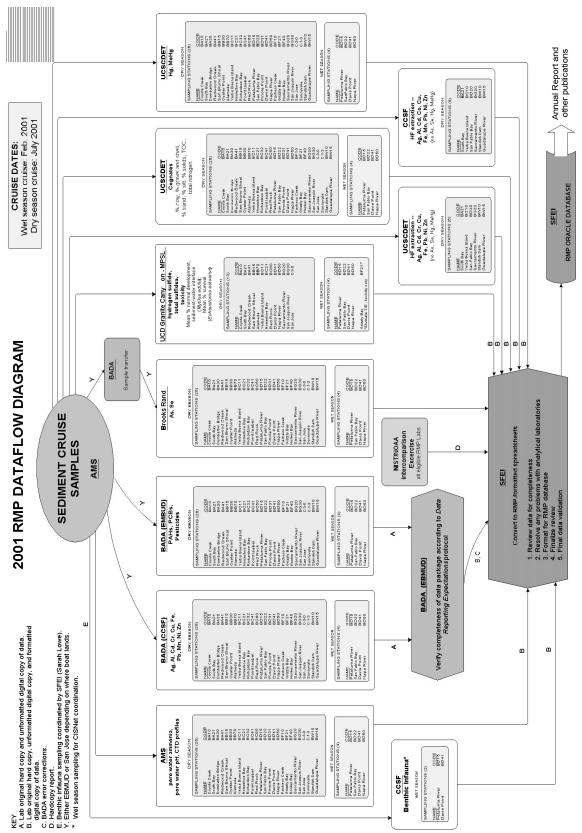


Figure 3. Dataflow Diagram for Sediment

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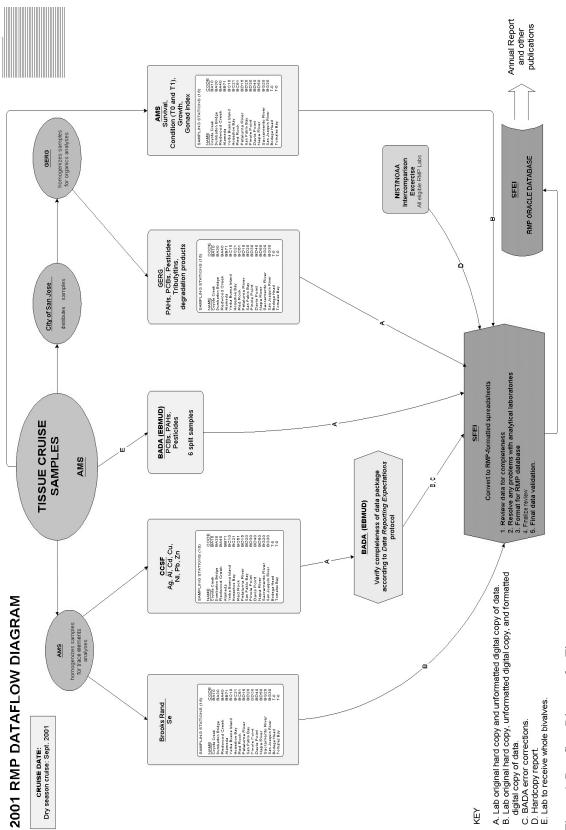


Figure 4. Dataflow Diagram for Tissue.

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