

12 July 2005

Technical Memorandum No. 6

To: Bob Castle, MMWD
Larry Grabow, MMWD

From: Jean Debroux, Kennedy/Jenks

Reviewed: Todd Reynolds, Kennedy/Jenks Consultants
Joe Drago, Kennedy/Jenks Consultants (in review)
Jim Lozier, CH2M HILL (in review)

Subject: Water Quality Sampling and Analysis Program
MMWD Seawater Desalination Pilot Plant Program
K/J 0468029

Introduction

Separate technical memoranda describe the preliminary performance objectives and operations for the different primary components of the MMWD Seawater Desalination Pilot Plant program. The Pilot Plant Program Technical Memoranda (TM) include:

- TM No. 1: Intake and Return Water System Objectives and Operations
- TM No. 2: MF/UF Filtration System Objectives and Operations
- TM No. 3: Conventional Filtration System Objectives and Operations
- TM No. 4: SWRO System Objectives and Operations
- TM No. 5: Solids Handling System Objectives and Operations
- TM No. 6A: Water Quality Sampling and Analysis Program
- TM No. 6B: Corrosion Control, Residuals and Biotoxicity Sampling and Analysis
- TM No. 7: Post Treatment System Objectives and Operations

This memorandum, TM-6A, discusses historical water quality of Central San Francisco Bay and describes the Sampling and Analysis Program designed to comprehensively monitor source water quality as well as assure finished water quality objectives are met by the pilot plant.

Historical Central San Francisco Bay Water Quality Review

The source water for the SWRO pilot plant will be North San Francisco Bay water drawn from an open intake at the end of the pier at the Marin Rod and Gun Club (TM No. 1). The North San Francisco Bay is a complex estuarine water body with influences from the ocean, rivers, and bay discharges that affect water quality on a daily as well as seasonal basis.

The United States Geological Survey (USGS) and the Romberg Tiburon Center (RTC) collect basic water quality data at select locations in San Francisco Bay. The San Francisco Estuary Institute (SFEI) also collects water quality data and its research of the occurrence of select

Technical Memorandum No. 6

12 July 2005

Page 2 of 13

anthropogenic compounds within San Francisco Bay will provide historical data for these compounds.

The purpose of this portion of the technical memorandum is to summarize collected historical source water quality for key parameters that can affect the operation of the pilot plant or the finished water quality. In addition, a hydraulic review is presented to determine if the summarized water quality is representative of water at the SWRO pilot plant intake.

Sampling Locations

The RTC operates two remote analyzers that monitor water quality. These monitoring devices have been in operation for several years and data collected from these devices can be used to observe diurnal as well as seasonal variations. The USGS monitoring sites collect data much less frequently but have been operating for 35 years. The USGS also conducts sampling campaigns where water is collected for a greater suite of analyses. USGS data will be used to review seasonal as well as annual variations. In addition, data from the USGS monitoring sites will be used when water quality parameters of interest are not monitored by the RTC. Table 1 consists of water quality data of interest collected by the RTC and the USGS. Sampling locations and depths summarized in this review can be found on Figure 1, following page 2.

Table 1: Water quality monitoring locations and capabilities (clean up)

Sample Station Name	Sample Depth	Sample Coordinates	Type of Data Collected
USGS 14 "Echo" Buoy	1 ft-13 ft (1 ft increments)	38° 0.4' N 121° 24.3' W	1) Salinity 2) Temperature 3) TSS 4) D.O. 5) Light Penetration 6) Chlorophyll Concentration
USGS 15 Point San Pablo	1 ft-24 ft (1 ft increments)	37° 58.5' N 122° 26.2' W	
USGS 16 "Charlie" Buoy	1 ft-14 ft (1 ft increments)	37° 54.9' N 122° 26.8' W	
RTC South		37° 53.4' N 122° 26.8' W	1) Salinity and Temperature for Surface Water, 5m and near bottom 9-11m 2) Chlorophyll concentration in total and >5um fractions, surface (0m) 3) Light attenuation in surface layer by Secchi disk.
RTC North		38° 0.3' N 122° 22.2' W	
Pilot Plant Intake	Approximately 6 ft	37° 56.8' N 122° 28.5' W	

Technical Memorandum No. 6

12 July 2005

Page 3 of 13

Historical water quality data

Historical water quality from the USGS (Table 2) illustrates the seasonal estuarine characteristics of the area around the pilot intake. Salinity varies greatly from near fresh water to levels found in ocean waters. Table 3 lists the water quality parameters measured at the closest USGS sampling location (i.e., No. 15) by depth. There are minor variations between shallow and deep samples but generally the water appears to be fairly well mixed.

Fresh water sources have the greatest impact in the spring during runoff and the least in the fall. Temperature varies seasonally with highest temperature in late summer and lowest in the winter. Average data for shallow sampling (i.e., ≤2 meters) can be found in Figure 2.

Chlorophyll concentrations, indicative of algae concentration, are highest near the surface and all USGS historical shallow data collected can be found on figure 3. Although there is a consistent low concentration throughout the year the spring and fall are prone to algal blooms.

Table 2: Historical Water Quality Data at USGS Sampling Stations

	Chlorophyll (mg/m³)	Dissolved Oxygen (mg/l)	TSS (SMP) (mg/l)	Exinction Coefficient (per meter)	Salinity (psu)	Temperature (°C)
Station 14						
Min	0.2	6.3	0	0.8	0.13	8
Max	47.4	10.7	604	4.4	31.2	21.66
Average	3.5	8.0	34.4	1.9	23.0	15.3
Standard Dev.	4.8	0.8	51.3	1.2	6.0	3.0
# data points	1,717	1,666	1,775	15	2,011	2,011
Station 15						
Min	0	6.1	0	0.7	0.16	7.7
Max	45.5	10.5	506.0	3.8	33.3	21.2
Average	3.1	8.0	33.6	1.7	24.7	14.9
Standard Dev.	3.4	0.8	50.8	0.9	5.7	2.9
# data points	4,041	2,896	3,149	58	4,311	4,300
Station 16						
Min	0.3	6.1	0	0.4	0.4	8
Max	32.0	10.6	274.0	3.8	32.7	20.9
Average	3.1	7.8	21.4	1.3	25.7	14.7
Standard Dev.	2.9	0.8	24.9	0.9	6.1	2.5
# data points	1,575	1,530	1,623	15	1,805	1,803

Technical Memorandum No. 6

12 July 2005

Page 4 of 13

Table 3: Historical Water Quality Data at USGS Sampling Station
No. 15 – Point San Pablo

	Chlorophyll (mg/m³)	Oxygen (mg/l)	TSS (SMP) (mg/l)	Exinction Coefficient (per meter)	Salinity (psu)	Temperature (°C)
≤ 2 meters						
Min	0	6.4	0	0.7	0.16	7.7
Max	45.5	10.5	191	3.8	33.3	21.19
Average	3.4	8.3	21.4	1.7	21.3	15.3
Standard Dev.	3.8	0.9	22.4	1.0	7.5	3.3
# data points	428	247	355	28	544	539
3-5 meters						
Min	0	6.3	0	0.7	0.26	7.86
Max	44.4	10.4	143.0	3.7	30.9	20.9
Average	3.2	8.2	22.1	1.7	22.4	15.2
Standard Dev.	3.8	0.9	22.4	1.0	7.0	3.1
# data points	545	375	422	13	572	570
≥ 6 meters						
Min	0	6.1	0	0.7	1.74	7.87
Max	34.9	10.4	506.0	3.7	31.4	20.4
Average	3.0	7.9	37.5	1.6	25.7	14.8
Standard Dev.	3.2	0.8	56.6	0.9	4.7	2.8
# data points	3,068	2,274	2,372	17	3,195	3,191

Technical Memorandum No. 6

12 July 2005

Page 5 of 13

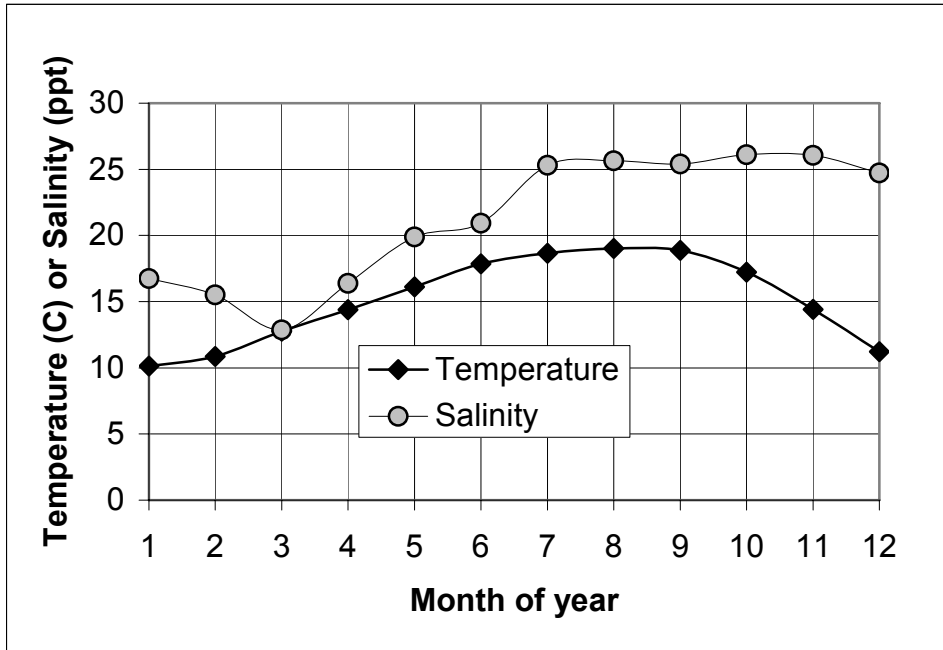


Figure 2: Average Temperature and Salinity for depth ≤ 2 meters at USGS Sampling Station No. 15 (1977-2005)

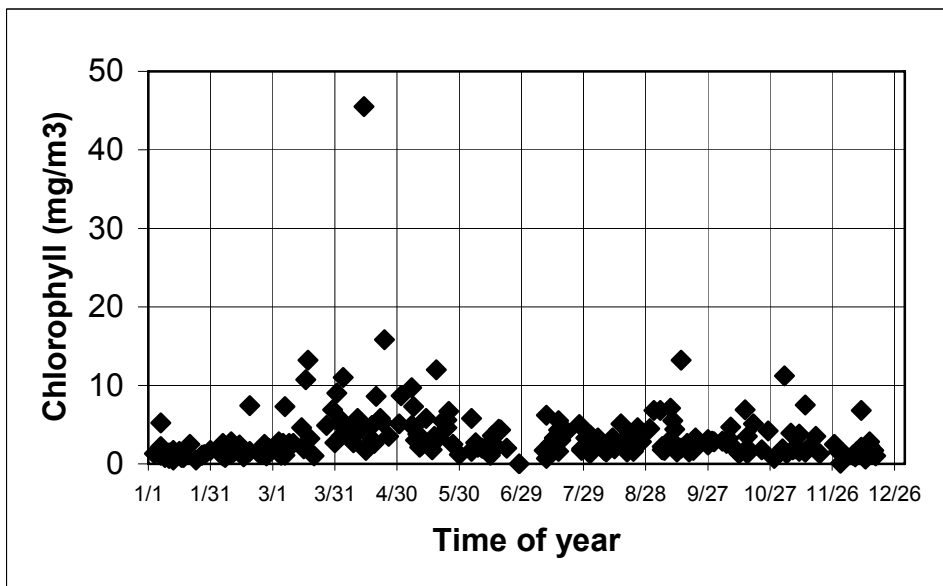


Figure 3 - Chlorophyll concentration at depth ≤ 2 meters at USGS Sampling Station No. 15 (1977-2005)

Technical Memorandum No. 6

12 July 2005

Page 6 of 13

Additional water quality data is pending and will be provided in subsequent water quality reports.

Pilot Plant Sampling and analysis program

The Sampling and Analysis Plan (SAP) presented below contains the water quality analyses to be performed prior to and during the Pilot Plant operation. The primary goals of the SAP will be to:

- 1) Determine the source water quality and variability,
- 2) Verify that the Pilot Plant is operating as designed by monitoring water quality changes through the treatment process,
- 3) Determine if the water quality of the product water (RO permeate) meets the District's stringent water quality goals; and
- 4) Determine if the return water (blended product water, concentrate, etc.) water quality conforms with the necessary discharge requirements of the project.

Other goals include:

- 1) verification of solids quality for land disposal,
- 2) determination of final water quality and its compatibility with District drinking water; and
- 3) Perform biotoxicity studies on return water and concentrate to evaluate potential effects of pilot plant and full-scale discharge on San Francisco Bay biota.

These last three topics are discussed in Technical Memorandum 6B.

The SAP has been designed to obtain the most thorough and accurate water quality characterization within the analytical budget. To this end, the product water SAP is modeled after the extensive MMWD drinking water characterization with additional analyses that are specific to bay source water. In addition, the minimum number of laboratories has been chosen to minimize data transference errors and lowest detection limits were chosen when available.

Process related water quality analyses

Process related water quality parameters (PRWQP) will be monitored to assist in the proper operation of the pilot plant. PRWQP include total organic carbon (TOC), ultraviolet light absorbance at 254 nm (UV₂₅₄), turbidity, total suspended and volatile solids (TSS and TVS), fats, oils and grease (FOGs), total dissolved solids (TDS), conductance, and various inorganic ion analyses. A complete list of PRWQP can be found in Appendix A.

PRWQP will be monitored in the source water and at various sample points in the pilot plant (Appendix C). Sampling at process point will be timed to capture quality at the same relative

Technical Memorandum No. 6

12 July 2005

Page 7 of 13

point in time as the raw water. Flow rates will be monitored and process flow will be calculated to determine appropriate sampling. Sampling will be alternately performed on low and high tide samples to capture representative samples at both locations.

The frequency of sampling and analysis of PRWQP can be found in Appendix B.

Drinking water related analyses

Drinking water related parameters (DWRP) comprise a comprehensive list of water quality constituents that is similar to analyses performed on drinking water produced by MMWD. This list contains federal and state regulated drinking water parameters as well as parameters that require monitoring and non-regulated compounds. Some of these non-regulated parameters that have been added to the DWRP list are specific to the Bay source water.

DWRP analyses will be performed on samples of source water and RO product water as shown in Appendix C.

The complete list of analytes, the laboratory performing the analyses, the analytical method and the minimum reporting limit can be found in Appendix A. This list of parameters is considered the "long list" within the SAP. The "short list" is comprised of drinking water regulated constituents, including federal and state monitoring requirements, only. Monthly samples will be analyzed for the short list of parameters, where as the long list analyses will be performed once every two months.

The frequency of sampling and analysis of the long and short list DWRP can be found in Appendix B.

NPDES permit self-monitoring requirements

NPDES permit no. CA0038814 for the Desalination Pilot Plant requires the District to monitor certain water quality parameters during the operation of the pilot plant. These parameters include source water and pilot effluent:

- Temperature
- Flow Rate
- Conductivity
- TSS
- TDS
- pH
- Total Chlorine Residual
- Acute Toxicity

Technical Memorandum No. 6

12 July 2005

Page 8 of 13

The Temperature, Flow Rate, pH and Total Chlorine Residual will be monitored and recorded by pilot plant operators. MMWD will coordinate sampling and analysis of the Conductivity, TSS and TDS. The protocol for Acute Toxicity Testing is discussed in the memorandum to Joel Faller dated June 10, 2005 and submitted to MMWD. Kennedy/Jenks is coordinating the sampling and review of the acute toxicity analyses. Kennedy/Jenks will provide the results of the acute toxicity analyses to MMWD. The required monthly reporting for the NPDES Permit Self-Monitoring Program will be coordinated and performed by MMWD staff.

SAP Analytical Laboratories

The SAP is designed to allow the resulting water quality of the pilot plant study to be compared with the water quality of other drinking water distributed by MMWD. To this end, the majority of the analyses will be performed by laboratories currently used by MMWD (Table 4).

Analyses of non-regulated constituents have been added based on potential occurrence in the source water. These include anthropogenic compounds analyses performed by the SNWA, PBDE analysis performed by Axys Analytical Services, and Algal Toxins analyses when necessary.

In an effort to obtain the most accurate data, quantifiable values above the minimum reporting limit (MRL) will be reported. Minimum detection limits (MDLs) will be determined by the laboratories in accordance with the requirements of 40 CFR Part 136 Appendix B titled "Guidelines for establishing Test Procedures for the Analysis of Pollutants." The guideline requirements include determination of a standard deviation and calculated 99% confidence level by the analysis of seven replicate reagent water spikes fortified with the analytes of interest.

For EHL, the laboratory performing the majority of the water quality analyses, MRLs are three to five times greater than the MDLs for > 90% of the analytes listed, depending on the analytical method. The remaining 10% achieve a MRL/MDL ratio of two.

Sequoia Analytical strives to maintain MRLs three times greater than MDLs. Depending on analyte, the MRL/MDL ratio can be as low as two. Hexavalent chromium will be the only analyte quantified by Sequoia Analytical that will require a low MRL.

Technical Memorandum No. 6

12 July 2005

Page 9 of 13

Table 4 – SAP Analytical Laboratories

<p>Environmental Health Laboratories Nathan Trowbridge Business Analyst 110 S. Hill Street South Bend, IN 46617 Phone: 1-800-322-4345 ext. 45528 Fax: (574) 233-8207 Nathan.R.Trowbridge@us.ul.com</p>	<p>Sequoia Analytical Leticia Reyes Project Manager 885 Jarvis Drive Morgan Hill, CA 95037 Phone: (408) 782-8154 Fax: (408) 782-6308 www.sequoialabs.com</p>
<p>Southern Nevada Water Authority Shane Snyder R&D Project Manager 1350 Richard Bunker Avenue Henderson, NV 89015 Phone: (702) 856-3688 Fax: (702) 856-3647 Shane.snyder@lvvwd.com</p>	<p>Wisconsin State Laboratory of Hygiene Jocelyn Hemming Miele Barman 2601 Agriculture Drive Madison WI, 53718 Phone: (608) 224-6230 hemminjc@mail.slh.wisc.edu</p>
<p>Axys Analytical Services Laurie Phillips Manager, Client Services PO Box 2219 2045 Mills Road West Sidney, British Columbia Canada V8L 3S8 Phone: (250) 655-5800 analytical@axys.com</p>	<p>MMWD Laboratory Larry Grabow, Laboratory Director Marin Municipal Water District 220 Nellen Avenue Corte Madera, CA 94925-1169 Phone: (415) -945-1551 lgrabow@marinwater.org</p>
<p>BioVir Laboratories Rick Danielson, PhD Lab Director 685 Stone Road, Unit 6 Benicia, CA 94510 Phone: (800) 442-7342 Fax: (707) 747-1751</p>	

Axys Analytical Services performs at least three blanks per sample taken and MRLs are statistically based on blank analysis results. Estimated MRLs, which are five times the estimated MDLs, are listed in Appendix A.

Sampling protocol

All samples will be collected in sample containers provided by the analytical laboratories. Sample containers will be shipped to the pilot plant by the laboratories in coolers that will be used for return shipment. Sample preservatives will be provided by the laboratories and only ice will be provided by the samplers.

Technical Memorandum No. 6

12 July 2005

Page 10 of 13

All efforts will be made to schedule sampling campaigns to assure adequate time for shipping and achieving holding times required by the laboratory. All holding time exceedences will be noted and reported to MMWD.

Sampling for process related water quality analyses will be performed by a single sampler using sampling procedures recommended by the laboratory. Sampling for drinking water related analyses will be performed by two samplers and clean sampling techniques will be employed when necessary. Aspects of clean sampling techniques (EPA Method 1669, Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels) will be employed as needed.

The World Health Organization (WHO) has indicated short-term public health effects risk begins when toxin producing blue-green algae are present at concentrations of 20,000 cells/ml or greater. RTC routinely monitors algae concentrations near the pilot intake but does not speciate them. During the two annual bloom periods (April-May and Sept-Oct), total algae concentrations can rise above 20,000 cell/ml. Algal toxin sampling and analysis will be limited to when RTC monitoring exceeds the WHO guidelines (> 20,000 cells/ml) for total algae levels. In case of an exceedence of the WHO guideline in the Bay, both fresh and saline water algal toxins analyses will be performed.

Analytical Protocol

Six analytical laboratories other than MMWD will be used to quantify approximately 160 regulated and approximately 390 non-regulated water quality constituents. Laboratories will analyze samples, assemble the data, assure QA methods have been performed, and send the results of the analyses to the consultant. All analyses will be performed on a non-rush basis to avoid additional costs associated with rush samples.

The consultant will receive electronic and hard copy data from the laboratories. Electronic data will be processed and inserted into a summary spreadsheet and posted onto the project website. Additional information regarding the electronic transfer of data can be found below. Hard copy data will be reviewed and kept in the consultants project file for the duration of pilot plant operation at which point the data will be given to MMWD.

There will be samples taken at the pilot plant that will possess three different salinity levels. High salinity samples can interfere with certain accurate low-level analyses. Low salinity samples (i.e., water that has passed through the RO process) will not be problematic for the analytical laboratories. Depending on the analytical method, high (source water) and very high salinity (RO concentrate) samples may cause a reduction in instrument sensitivity. A typical solution used to remedy high salinity samples is to dilute the sample to an acceptable salinity level. This is acceptable if the analyte is expected to be present at levels well above the detection limit in the diluted sample (e.g., inorganic ions). Analytical methods that require liquid-liquid extraction prior to quantification, typically add salinity to the sample to enhance extraction efficiency. These methods will not be adversely effected by high and very high salinity samples. Table 5 lists the analytical methods chosen for the SAP, the potential effect of high and very high salinity samples and actions taken to address the salinity levels in the pilot plant samples.

Technical Memorandum No. 6

12 July 2005

Page 11 of 13

Table 5 - Salinity effects on SAP analytical methods

Analytical method	Analyte(s) measured	Salinity effects	Remedy
EPA 120.1	Conductance	Above calibration range	Dilute (10X to 20X)
EPA 140.1	Odor-Threshold	None	
EPA 160.1	TDS	Salinity can affect drying	Dilute appropriately
EPA 180.1	Turbidity	None	
EPA 200.7	Metals	Above calibration range, possible peak interference	Dilute (1X to 40X)
EPA 200.8	Metals	Above calibration range, possible peak interference	Dilute (1X to 20X)
EPA 218.6	Hexavalent Chromium	Probable high TDS interference	Dilute
EPA 245.1	Mercury	None	
EPA 300.0	Inorganic anions	Above calibration range, peak interference	Dilute (100X to 4000X)
EPA 300.1	Bromate	Probable Cl ⁻ peak interference	Dilute
EPA 314	Perchlorate	Possible IC method problem, LC-MS/MS backup method	
EPA 335.4	Cyanide	None	
EPA 353.2	Nitrate, Nitrite	Possible colorimetric interference	Dilute if necessary
EPA 504.1	DBCP	None ^a	
EPA 505	PCBs	None ^a	
EPA 515.3	Organics	None ^a	
EPA 524.2	Organics, DBPs	None ^a	
EPA 525.2	Organics	None ^a	
EPA 526	Organics	None ^a	
EPA 528	Organics	None ^a	
EPA 531.1	Organics	None ^a	
EPA 532	Organics	None ^a	
EPA 547	Organics	None ^a	
EPA 548.1	Organics	None ^a	
EPA 549.2	Organics	None ^a	
EPA 552.2	DBPs	None ^a	
EPA 556	Organics	None ^a	
EPA (or SM?)1613	Dioxin	None	
SM 2120 B	Color	None	
SM 2320 B	Bicarbonate	None	
380-75WE	Fluoride	Possible probe interference with high salinity	Dilute if necessary

Technical Memorandum No. 6

12 July 2005

Page 12 of 13

Analytical method	Analyte(s) measured	Salinity effects	Remedy
EPA 425.2,425.4	MBAS	None	
SM 4500-NH3 D	Ammonia	Possible probe interference with high salinity	Dilute if necessary
SM 5310 C	TOC	Salinity affects instrumentation	Dilute (X3)
SM 5910 C	UV-254	None	
EHL L200	Organics	None ^a	
EHL L211	Organics	None ^a	
EPA 160.2	TSS	None suspected	
EPA 160.4	TVS	None suspected	
EPA 418.1	FOG	None	
EPA 8081	PBDEs (new method needed)	None ^a	
SNWA GC/MS	Organics	None ^a	
SNWA LC/MS	Organics	None	
RAD-A002	Radiological	Possible colorimetric interference	Dilute if necessary
SM 2330B	Corrosivity	None	
SM 4500-P E	Phosphorus	Possible colorimetric interference	Dilute if necessary
SM 7110B	Radiological	Possible colorimetric interference	Dilute if necessary
SM 7500-Sr B	Radiological	Possible colorimetric interference	Dilute if necessary
E-Screen Assay	Organics	None	

a – necessary extraction process includes “salting out” of sample

QA/QC protocol

QA/QC policy and procedure manuals have been collected from the participating laboratories. Review of data will include the adherence to the QA/QC policies stated in the manuals. Attention will be given to MDL definition, MRL-MDL relationships and matrix effects for saline samples.

Electronic transfer of results

A sample template has been generated and its usage has been coordinated with EHL for transfer of data that will easily converted to the project website for team review (Table 6). Although lab data will include numerous data fields, only pertinent data fields will be presented in the summary table. All lab data fields will be kept in the consultant database.

Technical Memorandum No. 6

12 July 2005

Page 13 of 13

Table 6 - Sample Excel data transfer template

EHL ID#	Client ID	Sample Type	Collected	Received	Analyzed	Method	Analyte	CAS Number	Matrix	Result Flag	Result	Units	MRL	Dil Factor
1208738	MMWD Pier High Tide	Field Sample	3/22/2005 9:45	3/24/2005 9:50	3/29/2005 19:16	5310 C	Total Organic Carbon (TOC)	N/A	SW	=	1.72	mg/L	0.5	3
1208739	MMWD Pier High Tide	Field Sample	3/22/2005 9:45	3/24/2005 9:50	3/24/2005 16:20	5910 B	UV absorbance at 254nm	N/A	SW	=	0.062	cm-1	0.009	1
1208740	MMWD Pier High Tide	Field Sample	3/22/2005 9:45	3/24/2005 9:50	3/29/2005 17:12	200.7	Calcium	7440-70-2	SW	=	140	mg/L	0.1	20
1208740	MMWD Pier High Tide	Field Sample	3/22/2005 9:45	3/24/2005 9:50	3/29/2005 16:56	200.7	Iron	7439-89-6	SW	=	0.27	mg/L	0.02	1
1208740	MMWD Pier High Tide	Field Sample	3/22/2005 9:45	3/24/2005 9:50	3/29/2005 17:12	200.7	Magnesium	7439-95-4	SW	=	740	mg/L	0.1	20
1208740	MMWD Pier High Tide	Field Sample	3/22/2005 9:45	3/24/2005 9:50	3/29/2005 17:12	200.7	Potassium	9/7/7440	SW	=	270	mg/L	0.2	20

Appendices

Appendix A – Complete list of analytes

Appendix B – Frequency of sampling and analysis

Appendix C – Sampling Locations on Pilot Process Schematic

TM No. 6A Document Review History:

1. Todd Reynolds draft review (5/11/05)
2. Jim Lozier draft review (5/17/05)
3. Joe Drago draft review (7/1/05)

cc: Joel Faller
File