APPENDIX B - QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES

Interlaboratory Comparison for Wastewater Effluent Analysis

A comparison study was conducted to determine the amount of variability between laboratories analyzing the same constituents of POTW effluent. Two effluent samples (from City of San Diego and Orange County Sanitation District) and one reference standard were distributed to all of the labs for analysis.

The individual agencies followed their respective normal protocols for sample analysis and 48-hour holding times. A total of three samples were distributed among laboratories for analysis, two effluent samples (City of San Diego and Orange County Sanitation District) and one reference sample of known concentration. The reference sample was provided in two separate containers (one for nitrate, one for ammonia). Samples were collected at the POTW agencies, brought to SCCWRP, homogenized, and split for distribution to each laboratory. Split samples were sent via overnight delivery to each of the laboratories. Each laboratory received 500ml of sample, on ice, without preservative, in a HDPE container. The samples were analyzed within the 48 hour holding times.

Table B-1 List of the constituents that were analyzed by the large POTWs (indicated by an "X") as part of the Bight 2008 Water Quality Study and the comparison study. The empty boxes indicate that B'08 WQ samples were sent to CRG laboratories for analysis.

Constituents to be analyzed for Bight Study	Hyperion	JWPCP	OCSD	PLWTP
Nitrate	X	X		X
Nitrite	X	X		
Ammonia	X	X	X	X
Phosphate				X
Silicate				
Urea				
Particulate Nitrogen				
Total Nitrogen				
Particulate Phosphorus				
Total Phosphorus	X	X		

Methods

Table B-2 The analysis methods and detection limits provided by each lab for the Bight '08 Water Quality interlaboratory calibration study in December 2008.

Parameter	Units	Agency				
		CRG	HTP	JWPCP	OCSD	PLWTP*
Ammonia-N		EPA 350.1	EPA 350.1	SM 4500-NH_3 C	SM 4500-NH_3 G	SM 4500-NH_3 B & E
	mg/L	0.03	0.1	1.0	0.7	0.3
Nitrate-N		EPA 300.0	EPA 300.0	SM 4500-NO_3 E	NA	EPA 300.0
	mg/L	0.05	0.1	0.1	--	0.04
Nitrite-N		EPA 300.0	EPA 300.0	SM 4500-NO_2 B	NA	NA
	mg/L	0.05	0.1	0.01	--	--
Total P		SM 4500-P E	SM 4500-P E	SM 4500-P E	NA	EPA 300.0**
	mg/L	0.05	0.1	0.1	--	0.2**

NA = Not Analyzed

Dash = Not Applicable

*Data from 2007 Point Loma Ocean Outfall Annual Monitoring Report

**PLWTP analyzes ortho-Phosphate

Results

Table B-3 Results of the effluent interlaboratory comparison. Effluent nutrient concentrations, calculated mean and standard deviation.

Parameter	Units	CRG	HTP	JWPCP	OCSD	PLWTP	Mean	Std dev
Ammonia-N								
Sample 1	mg/L	39.9	39.7	37.6	27.1	32.7	35.4	5.5
Sample 2	mg/L	32.6	56.4	37.6	31.7	28.8	37.4	11.1
Sample 3 (reference standard)	g/L	14.2	15.7	12.8	11.2	NA	13.5	1.9
Nitrate-N								
Sample 1	mg/L	<0.05	<0.1	<0.1	NA	0.46	0.15*	
Sample 2	mg/L	1.33	0.82	1.33	NA	4.92	2.1	1.9
Sample 3 (reference standard)	g/L	17.8	16.2	NV	NA	NA	17.0	1.1
Nitrite-N								
Sample 1	mg/L	<0.05	<0.1	<0.01	NA	NA	0.03*	
Sample 2	mg/L	0.29	0.15	0.47	NA	NA	0.30	0.2
Total P								
Sample 1	mg/L	2.98	3.05	2.76	NA	4.77**	3.39	0.2
Sample 2	mg/L	2.86	3.17	2.32	NA	4.75**	3.28	0.4

NA = Not Analyzed
NV = Result Not Valid
<"X" = Not Detected, where "X" is the Detection Limit
*Means were calculated using 1/2 the detection limit for each not detected result
**Analyzed as ortho-Phosphate

Riverine Runoff Quality Assurance and Quality Control Procedures

Standard quality assurance/quality control (QAQC) procedures were used for the collection, analysis, and data management of the wet and dry weather samples. QAQC procedures are detailed below for each applicable component of data collection and management.

All data collection complied with the quality assurance and quality control procedures and data quality objectives compatible with the Surface Water Ambient Monitoring program (SWAMP), which maintains a high standard to meet regulatory requirements for use of these data. QA objectives are the detailed specifications for representativeness, comparability, and completeness (Table B-4). The data quality objectives for field sampling and laboratory analysis are presented in Table B-5. These QA objectives were used as comparison criteria during data quality review by SCCWRP to determine if the minimum requirements were met and the data were used as intended.

Table B-4 Quality assurance objectives for representativeness, comparability, and completeness.

Representativeness	Comparability	Completeness
The selected stations and sampling frequency were chosen for their representativeness of conditions during dry and wet weather. Wet weather sampling is important because this is when water quality in the streams is most frequently compromised. The extent to which the measurements represent actual environmental conditions will be somewhat restricted by the time of year the samples are taken and the overall weather conditions of that year (i.e. wet versus dry year).	To maximize the quality of the data collected, and to collect data that is comparable with other studies, accepted sampling procedures will be used during this study. All samples collected will be sent to laboratories that use Standard Methods.	If the data collected is sufficient to complete the Bight '08 Water Quality Monitoring report, than the data is considered to be complete. Measurement performance criteria help determine the completeness of a data set. Evaluation of collected data will be conducted to insure that data quality objectives, as outlined in the QAPP, were achieved.

Table B-5 Data quality objectives.

Constituent	Method	Units	MDL	RL	Precision / RPD[1]	Accuracy (value/%)	Recovery 1 (%)	Complete-ness (%)
Flow	Field	ft^3/s	na	na	na	±10%	na	90
pH	Field	na	na	na	± 5	± 0.5 units	na	90
Temperature	Field	deg C	na	na	± 5	± 0.5	na	90
Dissolved Oxygen	Field	mg/L	na	na	± 20	± 0.5	na	90
Turbidity	Field	NTU	na	na	± 10	±10%	na	90
Electrical Conductivity	Field	µS/m	na	na	± 5	± 5	na	90
Solids, Total Suspended	SM 2540B	mg/L	0.5	0.5	25	80-120%	80-120%	90
Ammonia-N	SM 4500NH3H	mg/L	0.01	0.05	25	80-120%	80-120%	90
Nitrate	EPA 300.0	mg/L	0.01	0.05	25	80-120%	80-120%	90
Nitrite	EPA 300.0	mg/L	0.01	0.05	25	80-120%	80-120%	90
Phosphate	SM4500PB2	mg/L	0.01	0.05	25	80-120%	80-120%	90
Silicate	SM 4500Si04	mg/L	0.01	0.05	25	80-120%	80-120%	90
Urea	Goeynes et al, 1998	mg/L	0.01	0.05	25	80-120%	80-120%	90
Total Dissolved Nitrogen	USGS I-4650-03	mg/L	0.25	0.5	25	80-120%	80-120%	90
Total Nitrogen	USGS I-4650-03	mg/L	0.25	0.5	25	80-120%	80-120%	90
Total Dissolved Phosphorus	USGS I-2650-03	mg/L	0.25	0.5	25	80-120%	80-120%	90
Total Phosphorus	USGS I-2650-03	mg/L	0.25	0.5	25	80-120%	80-120%	90

[1]RPD Relative Percent Difference

na = not applicable

CTD Data Quality Assurance and Quality Control Procedures

The program performance specifications for temperature, conductivity, dissolved oxygen (DO) pH, transmissivity, and pressure are listed in Table B-6. Maintenance and calibration of the CTD and/or specific sensors, including dates of most recent servicing by each individual agency conducting the ship surveys, were documented. All sensors were calibrated annually by the manufacturer. Preventative maintenance was conducted on the CTD unit periodically.

The temperature and conductivity sensor calibration was conducted by the National Oceanic and Atmospheric Administration/National Regional Calibration Center (NOAA/NRCC) lab and certified and inspected by the manufacturer. Certification was provided when the sensor was returned.

No field QC of any of the parameters was required beyond the cast acceptability check and range checks. DO, pH, pressure offset, and transmissivity performance were carefully monitored and calibrated prior to and immediately following each survey. This evaluation is deemed sufficient to assure performance quality. Conductivity and temperature are evaluated and calibrated on a strict factory maintenance schedule conforming to NOAA/NRCC standards. Their performance and integrity from calibration to calibration are reliable to such a level that field QC is deemed unnecessary. The typical ranges are guidelines only and any value outside of them should be evaluated relative to the entire cast and the entire day's survey; legitimate values may exist outside of these ranges but the vast majority of values will fall within these ranges.

All data were checked to be certain that all data and configuration files were present and properly named. All data files contained proper and complete header information. This check was verified and documented by field personnel. All data were reviewed graphically and statistically for single point outliers (spikes) as well as trends.

Table B-6 The program performance specifications for ship based CTD sampling.

Parameter	Initial Accuracy/Sensitivity	Resolution
Conductivity	0.0003 S/m	0.00004 at 24 Hz
Temperature	±0.001 °C	0.0003 °C at 24 samples/sec
Pressure	0.01%	0.0001%
Dissolved Oxygen	2% of saturation	Not available
pH	0.1 pH	Not available
Light Transmittance	1.25 mV	Not available
Irradiance	$1x10^{17}$quanta/(cm^2·sec)	Not available
Chlorophyll-*a* fluorescence	≥0.03 µg/L	Varies per sensor
CDOM fluorescence	0.100 ppb QSD	Varies per sensor
*Values obtained from manufacturer's specifications (SeaBird Electronics, WETLabs, and Biospherical Instruments.		

Factory Calibration and Maintenance

Glider and/or sensor maintenance and calibration was performed periodically and documented by respective manufacturers/sponsors, with.

Quality Assurance and Quality Control Guidelines for the Discrete Ship Survey Data

QA/QC for the discrete nutrients, domoic acid, chlorophyll and particulate nutrient samples.

1. Field replicates
    a. According to chemistry data quality objectives, acceptance limits should be 80-120% (relative percent difference between field replicates).
    b. Field replicate concentrations should fall within this 80-120% range.
2. Field Blanks
    a. Field blanks consisted of DI water supplied by the POTWs and used during the ship surveys (OCSD collected seawater samples from areas offshore of anthropogenic inputs as blanks).
    b. According to chemistry data quality objectives, concentration values should be less than the method detection limit for constituents.
3. Lab Replicates
    a. According to chemistry data quality objectives, acceptance limits should be 80-120% (relative percent difference between laboratory replicates).
    b. Laboratory replicate concentrations should fall within this 80-120% range.
4. Lab Blanks
    a. According to chemistry data quality objectives, concentration values should be less than the method detection limit for constituents.
5. Lab Standards
    a. According to chemistry data quality objectives, acceptance limits should be 80-120% (relative percent difference between actual concentration and measured concentration).
6. Matrix Spikes
    a. According to chemistry data quality objectives, acceptance limits should be 80-120% (relative percent difference between actual concentration and measured concentration).

Table B-7 Summary of the quality assurance and quality control acceptance limits for the discrete data.

Quality Control	Acceptance Limits
Complete	90%
Field Blanks	<MDL
Lab Replicates	80-120%
Lab Blanks	<MDL
Lab Standards	80-120%
Matrix Spikes	80-120%