QUALITY ASSURANCE PROJECT PLAN

for

The San Juan Bay Estuary
Water Quality Volunteer Monitoring Program

prepared by

The San Juan Bay Estuary Program
PO Box 9509
San Juan, PR 00908-9509

prepared for

The United States Environmental Protection Agency
Region 2

November, 2008

Rev (0)

APPROVALS

Jorge Bauzá-Ortega	QAPP Manager	Date
Jorge Ortiz Zayas	SJBEP Quality Assurances Officer	Date
Adelís Cabán Acevedo	QAPP Coordinator	Date
Javier E Laureano	SJBEP Executive Director	Date
Evelyn Huertas	U.S. EPA Program Manager	Date
U.S. EPA QAPP Program Manager		Date

Table of Contents

Sections **Pages**

Appendices

Appendix 1 Standard Operating Procedures (SOPs)
Appendix 2 Training CD and SOPs Spanish Version
Appendix 3 San Juan Bay Estuary Water Quality Score Cards
Appendix 4 EQLAB SOPs
Appendix 5 Field Data Sheet
Appendix 6 Puerto Rico Water Quality Standards Regulation
Appendix 7 Hydrolab Quanta Water Quality System Operating Manual
Appendix 8 LaMotte Dissolved Oxygen Water Quality Kits Instructions Manual
Appendix 9 Hydrolab Quanta Calibration Sheet
Appendix 10 Change of Custody (COC) record sheet
Appendix 11 Sample Bottle Label

Abbreviations/Acronyms

DNER	Department of Natural and Environmental Resources
EQLAB	Environmental Quality Laboratory, Inc.
QAPP	Quality Assurance Project Plan
NEP	National Estuary Program
PRASA	Puerto Rico Aqueduct and Sewer Authority
PREQB	Puerto Rico Environmental Quality Board
USEPA	United State Environmental Protection Agency
USGS	United State Geological Survey
SOPs	Standard Operating Procedures
SJBE	San Juan Bay Estuary Program

3.0 Distribution List

The followings individuals and organizations will receive a copy of the San Juan Bay Estuary Water Quality Volunteer Monitoring Program approved Quality Assurance Project Plan (QAPP) and any subsequent revisions.

Evelyn Huertas	SJBEP Program Manager, United States Environmental Protection Agency (USEPA)
Pedro Gelabert	Director, San Juan Bay Estuary Program (SJBEP)
Javier E. Laureano	Executive Director, San Juan Bay Estuary Program
Jorge F. Bauzá	Environmental Scientist, San Juan Bay Estuary Program
Adelís Cabán	QAPP Coordinator, San Juan Bay Estuary Program
Ernesto Díaz	President, SJBEP Scientific and Technical Committee and Administrator of the Puerto Rico Department of Natural and Environmental Resources (DNER)
Javier Vélez Arocho	Secretary, Puerto Rico Department of Natural and Environmental Resources
Judy Galib	President, SJBEP Implementation Committee
José R. Fuentes	EQLAB Project Coordinator
Ángel Meléndez	Puerto Rico Environmental Quality Board (PREQB)
Martha Rivera	Puerto Rico Aqueduct and Sewer and Authority (PRASA)
Jorge Ortiz Zayas	Associate Professor, Institute for Tropical Environmental Studies
Luís Soler	United State Geological Survey

4.0 Project/Task Organization

The individuals directly involved in this project with their corresponding task responsibilities and the organizational chart of the program is presented in **Table 1** and **Figure 1**, respectively. The Quality Assurance (QA) Officer, QAPP Program Manager, QAPP Coordinator and Field Sampling Leader are responsible for the implementation of this QAPP.

Table 1. Personnel name and their corresponding responsibilities for the San Juan Bay Estuary Program Water Quality Volunteer Monitoring Program.

NAME	ORGANIZATION	RESPONSIBILITY
Evelyn Huertas	USEPA	Advisory Board
Ernesto Díaz	DRNA	Advisory Board
Luis R. Soler	USGS Caribbean District	Advisory Board
Angel Meléndez	PREQB	Advisory Board
Martha Rivera	PRASA	Advisory Board
Jorge F. Bauzá	SJBEP	QAPP Manager
Jorge Ortiz Zayas	Institute of Tropical Environmental Studies	QA Officer
Adelís Cabán	SJBEP	QAPP Coordinator
Jorge Bauzá or Adelís Cabán	SJBEP	Field Sampling Leader

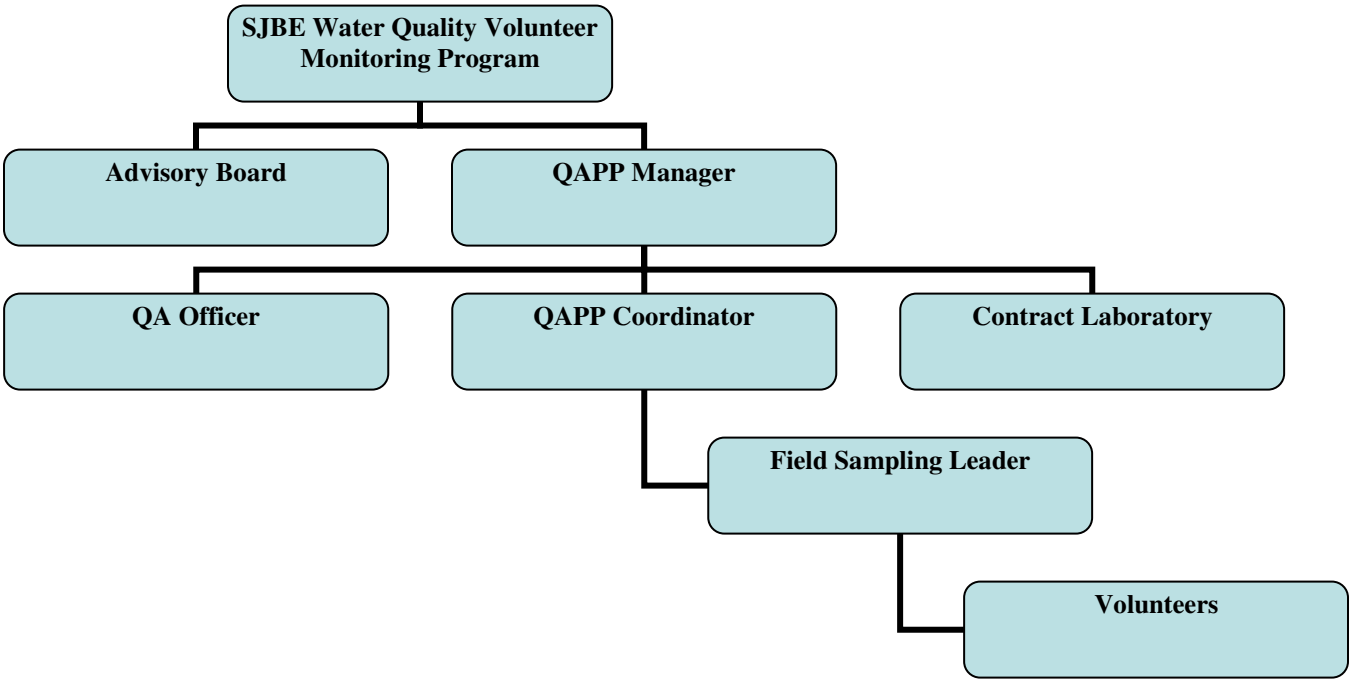
The Advisory Board (**Table 1**) will oversee the development, implementation and subsequent revisions of the SJBEP Water Quality Monitoring Program. The Advisory Board can recommend changes to any component of the sampling program.

The QAPP Manager will be responsible for the overall implementation of the QAPP, assemble the Advisory Board, allocate necessary resources to meet the project objectives, distribute sampling's results, and ensure that technical and schedule objectives are meet. The QAPP Manager is responsible for the correspondence with outside groups, including agencies responsible for approving the QAPP and the users of the collected data. The QAPP Manager will resolve any procedural deficiencies identified during the data audits. The QAPP Coordinator, QA Officer and Field Sampling Leader report to the QAPP Manager.

The QA Officer is responsible for reviewing the data relative to the Data Quality Objectives presented in **Section 8**. The QA Officer will revise the QAPP document and report any data quality problems related to the Data Quality Objectives to the QAPP Coordinator and QAPP Manager. Also, the QA Officer will conduct evaluation of field activities and prepare audits reports, assess whether the laboratory and field sampling protocols are follower as mandated by the QAPP, and monitor laboratory compliance with this QAPP while overseeing verification activities. The QA Officer will also perform in house audit of field operations. The QAPP Coordinator is responsible for managing volunteers, equipment, and laboratory needs related to the water quality monitoring program. The QAPP Coordinator will ensure the QAPP implementation.

The Field Sampling Leader reports to the QAPP Coordinator and manages sampling trip-specific needs including volunteers' availability, training, equipment care, calibrations, and equipment preparation. The Field Sampling Leader can be either the QAPP Coordinator or the QAPP Manager. The primary user of the data collected will be the San Juan Bay Estuary Program as one of the Environmental Indicators Program components. Other users include, but are not limited to, the PREQB, USEPA, PRASA, DNER and stakeholders. Furthermore, the data will be available for students and the general academia for research and publication purposes. The water quality data collected through this program constitute an important component of the Estuarine Environmental Indicators of the SJBE.

Figure 1. SJBEP Water Quality Monitoring Program organizational chart.



5.0 Special Training Needs/Certification

Interested individuals that want to become part of the Volunteer Monitoring Program will participate in two (2) training sessions conducted by the QAPP Coordinator, Field Sampling Leader or the QAPP Manager. The first training section will consist in one lecture about water quality basic concepts, explanation of the goals and objectives of the monitoring program, and field monitoring techniques. Also, monitoring safety precautions and emergencies general procedures will be discussed. During this section, one copy of the Standard Operating Procedures (SOPs) (See **Appendix 1**) will be distributed among the attendees and to be use as a training textbook. The lecture training session will be interactive in order to give the participants opportunity to ask questions and so they may determine if the monitoring program fulfills their expectations and interests. A training evaluation forms will be distributed among the participants in order to measure the success of the training and - if applicable- to correct deficiencies and improve futures training sections. A final test will be given to the participants to test their knowledge acquired and general concepts comprehension. Training will be provided by the Field Sampling Leader, QAPP Coordinator and/or QAPP Manager.

The second training section consists in hands-on field exercise of water sampling techniques, equipment calibration and deployment, field data recording, and safety procedures. This section of the training will be conducted on a dock side and no more than one (1) week after the first training section. The QAPP Coordinator, Field Sampling Leader and/or the QAPP Manager will closely watch the performance of each volunteer during the field practices. A certificate of qualification will be issue to the participants which satisfactory complete both training sections.

The Field Sampling Leader will lead the volunteers during each monitoring events. We will invite one environmental professional from any of the following agencies; (1) PREQB, (2) the USGS, (3) PRASA and/or (4) the academia to participate once a year in any of the monitoring events. This exercise will provide inputs to the Program from of an external expert. A copy of training presentation's CD in PowerPoint®, and the Standard

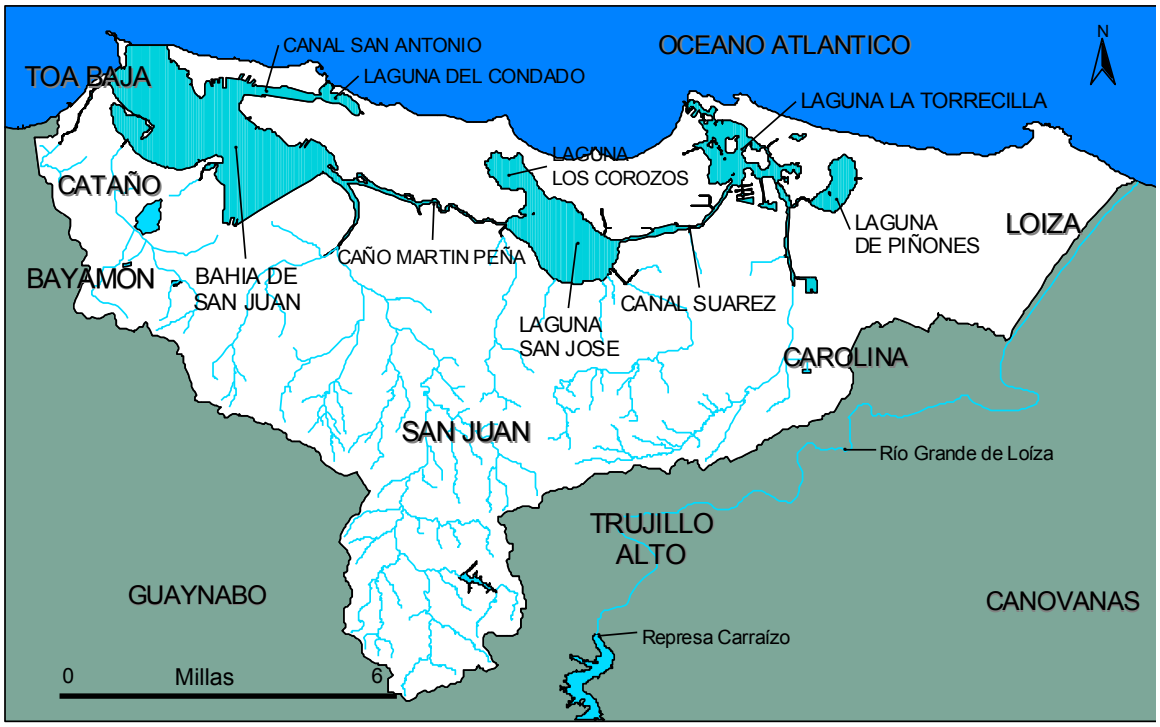
Operating Procedures (training manual) in Spanish are included in **Appendix 2**. These training sections will be offer all year around base on volunteers' demand. The analysis for the water chemical parameters will be performed by Environmental Quality Laboratory (EQLAB), a local environmental private laboratory. Before each sampling event, all volunteers will participate in a brief review of the SOPs.

6.0 Problem Definition/Background

6.1 Problem Definition

For many centuries the San Juan Bay Estuary (SJBE) system (**Figure 2**) has provided valuable resources to the residents of the region. People are attracted to the port, beaches, beautiful parks, and historical and natural areas, and these resources are vital to the regional economy. However, the needs of a growing population have resulted in exploitation of the system's natural resources and degradation and destruction of many of the components of the estuarine system. The main impacts to the SJBE system-development of the land, illegal sewage discharges, and aquatic debris – are all a result of human settlement and human uses. The intrinsic values of the estuary are being destroyed by uncontrolled urban expansion and contamination. In recognition of the continued threats facing the estuary system, the Governor of Puerto Rico nominated the SJBE system for the USEPA National Estuary Program (NEP) on April 16, 1992. The mission of the NEP is to protect and restore the health of estuaries while supporting economic and recreational activities. With inclusion in the NEP, the SJBE system was designated as "an estuary of national significance."

Figure 2. The San Juan Bay Estuary system and watershed.



The SJBE is composed by nine (9) major water bodies namely: San Juan Bay, San Antonio Channel, Condado Lagoon, Martín Peña Channel, San Jose Lagoon, Los Corozos Lagoon (connects directly to San Jose Lagoon), Suarez Canal, La Torrecilla Lagoon, and Piñones Lagoon. Total area in acres and coastal lineal extension (km) for the water bodies of the San Juan Estuary system are presented in **Table 2**.

Table 2. Dimensions of the San Juan Bay Estuary water bodies.

Water body	*Area (acres)*	*Lineal extension*
San Juan Bay	3,280	6.5 miles (10.5 km)
San Antonio Canal	114	1.2 miles (2 km)
Condado Lagoon	102	
Martín Peña Channel	69	3.8 miles (6 km)
San Jose Lagoon	1,129	
Suarez Canal	63	2.4 miles (3.9 km)
Torrecilla Lagoon	608	
Piñones Lagoon	236	

Most water quality monitoring efforts conducted in the SJBE has been largely independent efforts in response to specific assessment goals and in limited areas of the SJBE. Many of these efforts are related to Environmental Evaluations or Environmental Impact Statements related to proposed dredging or other projects or as part of a state compliance monitoring programs. Thus, past environmental studies in the SJBE have not sustained a long-term monitoring approach in order to assess water quality changes trough time.

The Comprehensive Conservation and Management Plan (CCMP) for the San Juan Bay Estuary (SJBE) have identified several goals and approaches to achieve better environmental health within this estuary. Among the proposed activities, cleanup and dredging of the Martín Peña Channel (CCMP Action WS-5), filling of the deep holes in San Jose and Condado Lagoons caused by dredging (CCMP Actions HW-2 and WS-6), and minimization of untreated sewage inputs from point and non-point sources (CCMP Actions WS-1, WS-3, and WS-4) emerge as some of the priorities of the CCMP. It is expected that the combined effects of these measures will enhance the water quality of the

SJBE. Thus, the SJBE Water Quality Volunteer Monitoring Program goal is to establish a long term water quality monitoring program - run by volunteers- to help ascertain the effectiveness of implemented CCMP conservation/restoration efforts. By monitoring the water quality and effectiveness of the implemented actions, the Program can recommend – if necessary- corrective actions.

This monitoring program will established a long- term water quality program for the SJBE by collecting water samples in 23 stations within the estuary system and tributaries (**Table 3** and **Figure 3**). Through this monitoring effort, we may be able to evaluate the effectiveness of implemented CCMP actions and also evaluate natural and human-induced impacts to the system. Annual water quality reports will be provided to the public through the SJBE webpage (www.estuario.org) and every two (2) years the results will be published in the "Estate of the San Juan Bay Estuary" report. Furthermore, the data will be used to provide scientifically-based information to the general public, government, and academia.

Water samples will be collected quarterly for the determination of ammonia, Biological Oxygen Demand (BOD), Chlorophyll *a*, fecal coliform, enterococcus, nitrate + nitrite, total Kjeldahl nitrogen (TKN), oil & grease, total organic carbon, total phosphorus, and turbidity. Also, monthly *in-situ* measurements of surface pH, dissolved oxygen, temperature, specific conductance, turbidity, and water column transparency will be obtained using a Hydrolab QUANTA® Water Quality Monitoring System (Hydrolab Quanta) and 20 cm diameter Secchi disk. We have selected these particular parameters because they are considered indicators of the water quality by different environmental and regulatory agencies such as the USEPA, PREQB, and USGS. Furthermore, these parameters not only are of environmental and public health concern but they concentration levels in natural waters respond to land use and management in the watershed: Thus, providing a synoptic view of the general health of the SJBE system.

Table 3. Monitoring stations along the San Juan Bay Estuary system.

Station's Name	*Latitude (N)*	*Longitude (W)*
PLE	18° 26.912'	-66° 08.127'
BSJ 1	18° 28.046'	-66° 07.676'
BSJ 2	18° 27.091'	-66° 06.743'
BSJ 3	18° 26.419'	-66° 05.828'
CSA	18° 27.570'	-66° 05.633'
LC 1	18° 27.432'	-66° 04.619'
LC 2	18° 27.717'	-66° 05.035'
RPN	18° 25.941'	-66° 04.602'
CMP	18° 25.984'	-66° 03.646'
LSJ 1	18° 25.722'	-66° 02.147'
LSJ 2	18° 25.366'	-66° 00.952'
LLC	18° 26.514'	-66° 02.287'
CS 1	18° 25.561'	-65° 00.024'
CS 2	18° 26.035'	-65° 59.070'
LT 1	18° 27.456'	-65° 59.555'
LT 2	18° 26.676'	-65° 58.905'
LT 3	18° 26.171'	-65° 58.158'
LP	18° 26.912'	-66° 08.127'
CM	18° 26.138'	-66° 08.056'
JM	18° 23.559'	-66° 02.615'
SA	18° 24.939'	-66° 00.629'
BC	18° 25.383'	-66° 58.061'
LS	18° 25.012'	-66° 07.013'

Chart datum = NAD 83

Figure 3. San Juan Bay Water Quality Monitoring Stations.

6.2 Background

Habitat distribution, hydrology, and human activities are the main controls of water and sediment quality in the San Juan Bay Estuary. A synoptic survey of water demonstrated the heterogeneous distribution of a large set of water constituents and contaminants in the SJBE (Webb and Gómez-Gómez, 1998). For example, coliform bacteria (March 95, dry season) at the SJBE are usually lower than 6000 col/100ml but at Martín Peña Channel (MPC) is on the order of 100,000 col/100ml. This indicates that MPC is the most impacted area in the SJBE, an observation that is confirmed by nutrient analysis of water samples (i.e. of ammonium is ca 2.3 mg/L while the levels were maximally 0.36 mg/L at other sites). This is due to direct sewage inputs and limitation of water flow by the encroaching housing communities in MPC. A significant change in coliform contamination has been observed during the wet season (May 1995) where most of the stations surpassed the Environmental Quality Board standards for coliforms in type B and C waters (200 col/100ml), indicating the significance of combined sewer inputs in the SJBE.

The USGS and the PREQB carried out water quality sampling in 23 stations in the SJBE watershed from 2002 to early 2005. These studies were conducted following the monitoring activities that have been done in the past by USEPA, as well as other consultants. The raw data was provided to the SJBEP at no cost. The SJBEP analyzed the results and published a Score Card for the water bodies of the SJBE system (See **Appendix 3**). Other data collecting and water quality monitoring activities that has taken place in the SJBE is presented in **Table 4**. Since 2005, the SJBE water quality has not been monitored systematically.

Table 4. Past and present water quality monitoring programs within the San Juan Bay Estuary.

Monitoring Program	*Descriptions*	*Parameters sampled*
Puerto Rico Environmental Quality Board (PREQB) – U.S. Geological Survey (USGS) Cooperative Program	Measured water and sediment quality (stream flow, nutrients, and total suspended solids) in the San Juan Bay Estuary; 2002 – 2005.	Water and sediment quality parameters, nutrients, and total suspended solids – water quality quarterly.
Puerto Rico Aqueduct and Sewers Administration Agency (PRASA) National Pollutant Discharge Elimination System (NPDES) Bypass Monitoring	As part of the NPDES permit requirements, PRASA must report to U.S. Environmental Protection Agency (EPA) every time there is a bypass and whether permit limits have been surpassed.	Indicator bacteria – storm events with a minimum of quarterly monitoring
Puerto Rico 305(b)/303 (d) Integrated Report	Legislated requirements to define water bodies that are impaired from a water quality perspective	Refer to PREQB's 305(b) Biennial Reports to EPA for sampling parameters and frequency.
PREQB Beach Monitoring and Public Participation Program (Bacterial Monitoring)	Detect and measure coliform bacteria concentration in beach waters	Indicator bacteria – quarterly
U.S. Coast Guard (USCG) Oil Spill Response	The USCG Office of Marine Environmental Response maintains as part of their mission a database on all oil and hazardous material spills in U.S. coastal waters.	Oil and chemicals in spill areas - during spill events

Table 5 exhibit the results of the water quality monitoring program run by the USGS and the PREQB from 2002 to 2005 for dissolved oxygen, ammonium, nitrate + nitrite, phosphorus, turbidity, pH, salinity, temperature, and fecal coliform.

Table 5. Water quality parameters (mean values) obtained from the USGS/PREQB San Juan Bay Estuary Monitoring Program 2002 – 2005.

Parameters	***SJBE Water Bodies***					
	SJB[1]	**MPC[2]**	**SJL[3]**	**SC[4]**	**TL[5]**	**PL[6]**
Dissolved Oxygen (mg/L)	5.79	1.15	4.55	3.51	5.70	5.90
Ammonium (mg/L)	0.33	3.50	0.38	0.49	0.16	0.05
Nitrite + Nitrate (mg/L)	0.02	0.02	0.02	0.03	0.03	0.02
Phosphorus (mg/L)	0.05	0.72	0.25	0.21	0.09	0.07
Turbidity (NTU)	5.00	23.80	5.60	4.10	6.00	8.00
pH	7.82	6.99	7.52	7.37	7.63	7.94
Salinity (ppt)	33.90	15.10	11.90	18.30	26.80	27.50
Temperature (°C)	28.20	28.40	28.40	28.70	28.20	27.80
Fecal Coliforms (No. colonies/100 ml)	181	484,015	1,032	2,363	2,102	7

[1]San Juan Bay, [2]Martín Peña Channel, [3]San José Lagoon, [4]Suárez Canal, [5]Torrecilla Lagoon, and [6]Piñones Lagoon.

7.0 Project/Task Description

A total of twenty three (23) stations (**Table 3**) within the estuary and watershed will be monitor for surface water quality parameters. Water samples will be collected quarterly for the determination of ammonia, nitrate + nitrite, total Kjeldahl nitrogen (TKN), total phosphorus, turbidity, Biological Oxygen Demand (BOD), Chlorophyll, fecal coliform, fecal enterococcus, oil & grease and total organic carbon. Monthly measurements of surface pH, dissolved oxygen, temperature, specific conductance, turbidity, and water column transparency (Secchi depth) will be obtained using a Hydrolab QUANTA® Water Quality Monitoring System (Hydrolab Quanta). Water transparency will be record with Secchi disk (20 cm diameter).

The first group of volunteers will receive the training in July and the monitoring program will start in September. **Table 6** shows the schedule of all tasks that are part of the water quality monitoring program.

Table 6. Schedule of events for the SJBE Water Quality Volunteer Monitoring Program 2008.

TASK	JAN.	FEB.	MAR.	APR.	MAY	JUNE	JULY	AUG.	SEP.	OCT.	NOV.	DEC.
Volunteers training												
SOPs Refresh												
Hydrolab Quanta field measurements												
Water quality parameters collection & analysis												
QA/QC audits												
Annual report												

Water samples will be collected following the procedures presented in the SOPs (See **Appendix 1**). All water quality samples will be analysis by contract with Environmental Quality Laboratory (EQLAB). Samples will be transported to EQLAB following the Change of Custody protocols (See **Appendix 10**) for the analysis of: Ammonia (EPA 350.1), Fecal Coliform (SM9222 D), Fecal Enterococcus (SM 9230 C), Nitrate + Nitrite (EPA 353.2), total Kjeldahl nitrogen (TKN, EPA 351.2), Total Phosphorus (EPA 365.3), Turbidity (SM 2130 B), Total Organic Carbon (EPA 415.1), Oil and Grease (EPA 1664 A), Biological Oxygen Demand (SM 5210 B), and Chlorophyll *a* (SM 10200H). All sampling bottles will be supplied by EQLAB. The EQLAB's SOPs for the aforementioned water quality analysis are provided in **Appendix 4**.

Sampling events will be conducted preferably during the morning hours (8:00 AM to 12:00 PM) and will be completed in five days depending on weather conditions. Station sampling orders will be determined by the Field Sampling Leader based on weather, sea and/or tidal conditions. The sampling team consists of the Field Sampling Leader, boat captain and at least one volunteer.

During each monitoring events, a field data sheet will be filled (See **Appendix 5**). Monitoring results will be compared with the applicable water quality standards included in federal and states regulations for dissolved oxygen, fecal coliform, fecal enterococcus, and turbidity (See **Appendix 6**).

8.0 Quality Objectives and Criteria for Measurements Data

Data quality objectives specify the quality of environmental data required to support decision making processes. The generation and use of quality data is important to the assessment of water quality within the SJBE. **Table 7** shows expected measurements performance criteria described in terms of precision, accuracy and measurements ranges. A short description of the data quality characteristics (precision, accuracy, representativeness, comparability, and completeness) along with the field and laboratory general procedures to ensure high-quality data is follows below.

Table 7. Performance Criteria for the parameters to be measure in the San Juan Bay Estuary Water Quality Monitoring Program.

Parameter	*Analysis Type*	*Units*	*Range*	*Precision RPD*	*Accuracy PR*
Ammonia	Laboratory	mg/L	0.1-20.0	< 20 %	80%-120%
BOD	Laboratory	mg/L	NA	< 20%	80%-120%
Chlorophyll a	Laboratory	mg/L	NA	< 20 %	NA
Fecal coliform	Laboratory	CFU[1] per 100 ml	0 to TNTC[2]	60%	NA
Enterococcus	Laboratory	CFU[1] per 100 ml	0 to TNTC[2]	60%	NA
Nitrate + Nitrite	Laboratory	mg/L	0.01-10.0	< 20%	90%-110%
Total Kjeldahl nitrogen (TKN)	Laboratory	mg/l	0.5 -20.0	< 20 %	90 % - 110%
Oil & Grease	Laboratory	mg/L	5 to 1000	< 20%	80%-120%
Total Organic Carbon	Laboratory	mg/L	0.05-10.0	< 20%	80%-120%
Total Phosphorus	Laboratory	mg/L	0.01-1.20	< 20%	80%-120%
Turbidity (Meter)	Field	NTU	0 - 40	< 20%	90%-110%
Turbidity	Laboratory	NTU	0 - 1000	< 20 %	± 20 %
Specific Conductance	Field	mS/cm	0 - 100	< 20 %	± 20 %
Temperature	Field	°C	-5 - 50	< 20%	± 20 %
Dissolved Oxygen (meter)	Field	mg/L	0 - 50	< 20%	± 20 %
Dissolved oxygen (Winkler)	Field	mg/L	0- 10	NA	NA
Water Transparency	Field	meters	0 - 15	NA	NA
pH	Field	units	2 - 12	NA	± 10 %

8.1 Precision

Precision is a measure of the mutual agreement among individual measurements of the same property, under prescribed similar conditions. The collection of field duplicates measures a combination of field and laboratory precision. Precision of field sampling methods will be evaluated by comparing the duplicate measurements of hydrologic properties. To assess precision in the field, a duplicate sample will be collected at one randomly selected station. The Relative Percent Differences (RPD) will be calculated according to the following formula:

$$RPD = \frac{|Sample(a) - Sample(b)|}{(0.5)(Sample(a) + Sample(b))} * 100$$

Where *Sample (a)* is the sample concentration of the first sample collected and *Sample(b)* is the duplicate sample concentration collected at the same location. If a calculated RPD falls outside the precision criteria range (See **Table 7**) for the specific parameter, the results will be reported and flagged. Personal training will be conducted in all methods to achieve proficiency, minimize errors, and therefore minimize variability. Equipment will be calibrated prior to each sampling activity following the methods presented in the Hydrolab Quanta Operation Manual (See **Appendix 7**).

In the case of laboratory analytical data, precision will described the reproducibility of the analytical data. Precision of laboratory analytical data will be evaluated by EQLAB's SOPs and QA/QC procedures (See **Appendix 4**).

8.2 Accuracy

Accuracy is the degree of agreement of a measurement with an accepted references or true value. Accuracy is usually expressed as the differences between the measured value to the true value or as a percentage (ratio) of the differences between the two values.

Accuracy is a measure of the inherent bias in a system and can be assessed both in the field and in the laboratory.

Accuracy of field measurements will be evaluated by the proper calibration of equipment, along with periodic calibration checks and performing field measurements of blind samples. On the day of each monitoring event before any field data is recorded, the Hydrolab Quanta will be calibrated for dissolved oxygen, specific conductance, pH, and turbidity. These parameters calibration will be performed according to the procedures presented in the Hydrolab Quanta Manual (See **Appendix 7**). If the calibration check indicates that the instrument's calibration has drifted outside the calibration acceptance criteria (See **Table 7**), the data will be flagged and evaluated using the procedures presented in **Section 16**.

The dissolved oxygen instrument's calibration will be validated in randomly collected samples from 10% of the monitoring station during each monitoring events using a field dissolved oxygen kit based on the azide modification of the Winkler titration method. The manual of the field test kit to be use is presented in **Appendix 8**. Details regarding dissolved oxygen sample collection and validation are presented in **Section 11.1** and in the SOPs (See **Appendix 1**). Accuracy of laboratory analytical data will be evaluated by EQLAB according to its Quality Assurance Plan and QA/QC procedures (see **Appendix 4**).

Accuracy of laboratory results will be assessed using the analytical results of surrogate spikes and laboratory control samples. Surrogate spikes will be calculated in terms of percent (%) recovery (*PR*) as follows:

$$PR = \frac{|SSR - SR|}{SA} \text{ X } 100$$

Where *SSR* = Spiked Sample Results
SR = Un-spiked Sample Results and
SA = Spiked Added

8.3 Bias

Bias is the systematic or persistent distortion of a measurement process causing errors in one direction. Bias will be evaluated through validation measurements such as matrix spike sample (expressed as a percent recovery), laboratory blank, and field blank determination.

8.4 Representativeness

Representativeness is the extent to which measurements represent the true system. Samples will be collected from the 23 stations encompassing different aquatic habitats within the SJBE system. In order to monitor inputs to the estuary, some of the samples will be collected on outlets of creeks and known point sources close to possible pollution sources. Others stations will be selected to represent sea and fresh water mixing gradients as well as general environmental conditions. Some samplings sites will be located at the main sea water entrances zones to the estuary in order to monitor what it has been entering and leaving the estuary during tidal cycles. The above scheme is similar to previous studies (i.e. Webb and Gomez-Gomez, 1998) and the water quality monitoring program follow by the PREQB and the USGS from 2002 to 2005. This approach will enable the SJBE program to continue the baseline created by the aforementioned studies and also to evaluate long-term trends within the system.

8.5 Comparability

To insure maximum comparability with other studies, collection of field samples will follow the same standard protocols. All physical and chemical analysis will be referenced to appropriate certified standards and tested according to EPA approved methods used in past investigations (see SOPs presented in **Appendix 1**). We incorporated to this Program all stations occupied during the PREQB and USGS Water Quality Monitoring Program 2002-2005 (see **Table 3**).

8.6 Completeness

All effort will be made to complete all sampling stations. In case of any sampling interruption, all the information will be recorded and finish the sampling on a different day. Even data collected not intended for legal or compliances issues, should account for 90% of the planned amount. The percent completeness (*PC*) for each data set is calculated as follows:

$$PC = \frac{DO}{DP} \text{ X } 100$$

Where *PC* = percent completeness,
DO = data obtained, and
DP = data planned

8.7 Sensitivity

Sensitivity is the lowest detection limit of the method or instrumentations for each of the measurement parameters of interest. Methods with the corresponding detection limits are presented in **Table 8.**

Table 8. Reporting limits and selected methods for the parameters to be measured in this study.

Parameter	*Method*	*Units*	*Detection Limit*	*Reporting Limit*
Ammonia	EPA 350.1	mg/L	0.10	0.10
BOD	SM 5210 B	mg/L	2.00	2.00
Chlorophyll a	SM 10200 H	mg/L	NA	NA
Fecal coliform	SM 9222 D	CFU*per 100 ml	0	0 to TNCT[2]
Enterococcus	SM 9230 C	CFU*per 100 ml	0	0 to TNCT[2]
Nitrate + Nitrite	EPA 353.2	mg/L	0.01	0.01
Total Nitrogen Kjeldahl (TKN)	EPA 351.2	Mg/L	0.20	0.50
Oil & Grease	EPA 1664 A	mg/L	1.4	1.4
Total Organic Carbon	EPA 415.1	mg/L	0.05	0.05
Total Phosphorus	EPA 365.3	mg/L	0.01	0.01
Turbidity	SM 2130 B	NTU	0.05	0.05
Turbidity	Sensor	NTU	0.1	0.1
Specific Conductance	Sensor	mS/cm	0.0	0.0
Temperature	Sensor	Degrees Celsius	-5	-5
Dissolved Oxygen (meter)	Sensor	mg/L	0	0
Dissolved oxygen (Winkler)	Winkler titration (azide modification)	mg/L	0.2	0.2
Water Transparency	Secchi Disk	meters	NA	NA
pH	Sensor	Units	2	2

9.0 Non-Direct Measurements (Secondary Data)

No additional data sources have been identified for report or analysis that could be used by the San Juan Bay Estuary monitoring program. If any other data is identified as useful for the Program objectives, the SJBEP will assess its quality, usability, comparability, and intended use. Any such assessment will be included in this section of the QAPP.

10.0 Field Monitoring Requirements

10.1 Monitoring Process Design

A series of 23 water sampling stations will be visited monthly (See **Figure 3**). The selection was decided considering previous and well-documented sampling efforts. In this way continuity to previous efforts will be archived, providing better opportunities to generate a more complete analysis of environmental trends to meet the SJBEP goals. Also, additional stations were added to broaden the data collection network and to include additional areas in the estuary. A total of 18 water sample stations will be collected in the main water bodies (mixing transition zones) of the SJBE system which include San Juan Bay (BSJ 1, BSJ 2, and BSJ 3), Canal San Antonio (CSA), Condado Lagoon (LC 1 and LC 2), Martín Peña Channel (CMP), Suárez Canal (CS 1 and CS 2), San José Lagoon (LSJ 1, and LSJ 2), Torrecilla Lagoon (LT 1, LT 2, and LT 3), Peninsula La Esperanza (PLE), Los Corozos Lagoon (LLC), Laguna Secreta Lagoon (LS), and Piñones Lagoon (LP). The proposed work will provided data also from five (5) stations that represent the main fresh water sources to the estuary system including La Malaria Canal (CM), San Anton Creek (SA), Juan Méndez Creek (JM), Rio Puerto Nuevo (RPN) and Canal Blasina (CB). All stations will be located using a Global Positioning System (GPS) with an expected location accuracy of three (3) meters (See **Table 3**).

A map of the 23 stations and a table showing the latitude and longitude of each monitoring site is presented in **Table 3**, and **Figure 3,** respectively. EQLAB in Puerto Rico will perform the water analyses including dissolved nutrients (ammonia, nitrate + nitrite, total Kjeldahl nitrogen (TKN), and total phosphorus), BOD, total organic carbon, chlorophyll *a*, fecal coliform, fecal enterococcus, oil and grease, and turbidity. The water quality analyses for these parameters will be performed quarterly. All 23 stations will be occupied monthly for the determination of temperature, specific conductance, dissolved oxygen, turbidity and pH using a Hydrolab Quanta and a Secchi disk for water transparency. Samples preservatives will be added inside the samples bottles provided by EQLAB.

10.2 Monitoring Methods

The San Juan Bay Estuary Volunteer Monitoring Program SOPs (See **Appendix 1**) contain detailed information on all sampling protocols and equipment. A summary of the sampling method requirements for each parameter to be measure are presented in **Table 9.**

Table 9. Specific requirements for the sampling methods implemented in this study.

Parameter	*Method*	*Samples Preservation*	*Sampling Equipment*	*Sampling method*	*Holding Time*
Ammonia	EPA 350.1	Sulfuric acid	250 ml bottle	Grab	28 days
BOD	SM 5210 B	4° C	300 ml BOD	Grab	48 hours
Chlorophyll a	SM 10200 H	4° C	Amber 1L bottle	Grab	24 hours in the dark.
Fecal coliform	SM 9222 D	4° C	250 ml sterile	Grab	6 hours
Enterococcus	SM 9230 C	4° C	250 ml sterile	Grab	6 hours
Nitrate + Nitrite	EPA 353.2	Sulfuric acid	250 ml plastic	Grab	28 days
Total Kjeldahl nitrogen (TKN)	EPA 351.2	Sulfuric acid	250 ml plastic	Grab	28 days
Oil & Grease	EPA 1664 A	Sulfuric + hydrochloric acid	500 ml glass bottle	Grab	28 days
Total Organic Carbon	EPA 415.1	4° C	40 ml amber	Grab	28 days in the dark.
Total Phosphorus	EPA 365.3	Sulfuric acid	250 ml plastic	Grab	28 days
Turbidity	SM 2130 B	4° C	250 ml plastic	Grab	48 hours
Turbidity	Sensor	NA	NA	*In-situ*	Immediate
Specific Conductance	Sensor	NA	Hydrolab Quanta	*In-situ*	Immediate
Temperature	Sensor	NA	Hydrolab Quanta	*In-situ*	Immediate
Dissolved Oxygen (meter)	Sensor	NA	Hydrolab Quanta	*In-situ*	Immediate
Dissolved oxygen (Winkler)	Winkler titration (azide modification)	Manganous Sulfate, Alkaline Potassium Iodide, Sulfuric acid.	LaMotte Kit	Grab	8 hours
pH	Sensor	NA	Hydrolab Quanta	*In-situ*	Immediate
Water Transparency	Secchi Disk	In-water	20 cm Secchi Disk	*In-situ*	Immediate

10.3 Field Quality Control (QC)

Instrumentation will be checked through calibration prior to the sampling day under a controlled environment. Also, the calibration will be performed at the end of the sampling day to ensure less than 20 % instrument drift in one sampling day. If the calibration check indicates that the instrument's calibration has drifted outside the calibration acceptance criteria, the data will be flagged and evaluated following the procedures in **Section 16** of this QAPP. When not in use the Hydrolab Quanta will be

stored in the field laboratory station. The instruments will be secured, padded and protected during transportation. The Hydrolab Quanta Operating Manual presented in **Appendix 7** described the instruments calibration procedures that will be follow for this particular instrument. The Hydrolab Quanta will be calibrated before each monitoring day for specific conductance, pH, dissolved oxygen, and turbidity. Dissolved oxygen observations will be checked and calibrated using the LaMotte Field DO kit (EPA 360.2 modified Winkler titration method). The specific conductance calibration will be checked before and after the monitoring events following the procedures presented in the Quanta manual (**Appendix 7**). Fresh standards will be used daily for instruments calibration.

A maintenance schedule will be prepared and followed for all instrumentation and recorded in the water-resistances field sheets (See **Appendix 9**). No entries will be erased from all data sheet (Field Data and Quanta Calibration Sheets) instead the incorrect information will be crossed out with a single line and correct information will be entered and initiated. The Hydrolab Quanta will be sent to the manufacturer once a year for a certified manufacturer calibration and inspection. Sampling equipment will be checked daily for visual material and mechanical integrity. Other calibration procedures are detailed in the attached SOPs (See **Appendix 1**).

A field dissolved oxygen kit based on the azide modification of the Winkler titration method will be used to validate the instrument's DO calibration on randomly-collected samples from 10 % of the monitoring locations. A manual for the test kit to be used is presented in **Appendix 8**. If the Winkler titration and the Hydrolab Quanta results deviate by more than 1.0 mg/L, the Hydrolab Quanta results will be flagged and the procedures presented in **Section 16** of this QAPP will be implemented.

All field samples collected will be identify with a specific site identifier label. Weather conditions and visual observations of each station will be recorded in the Field Data Sheet. A temperature control water sample (Cooler Temperature Control) will be checked to make sure the samples are maintained within the required 2 – 10^{o}C. If the Cooler Temperature Control is out of this temperature range, the results will be label

"Results Questionable Temperature Control Exceeded 10°C". **Section 16** presents the procedures the SJBE Monitoring Program will follow when the temperature control sample exceeds the acceptable limits. All samples will be sent to EQLAB at the end of the sampling date (before the established holding times).

A duplicate sample for bacteria (Fecal Coliform and Fecal Enterococcus), nutrients (phosphorus, nitrite + nitrate, ammonium, and total Kjeldahl nitrogen), BOD, Chlorophyll *a*, oil & grease, total organic carbon, and turbidity will be collected at one sampling station. The locations where the duplicate samples are to be collected will be selected randomly.

The Field Sampling Leader and/or QAPP Coordinator will be present during each monitoring event. They will check the field and laboratory QA/QC data for any deviation from the Data Quality presented in **Section 8** of the QAPP. Also they will calculated the Relative Percent Deviation Difference of any field duplicates and their corresponding samples using the formula presented in **Section 8.1** of the QAPP if these calculations are not performed by EQLAB. The Field Sampling Leader and/or QAPP Coordinator will ensure that all field equipment is appropriately maintained and/or calibrated, and inspect data for any measurements indicating equipment or method malfunction.

11.0 Analytical Requirements

11.1 Analytical Methods

The San Juan Bay Estuary Volunteer Monitoring Program will measure temperature, specific conductance, turbidity, pH, and dissolved oxygen using a Hydrolab Hidrolab Quanta. Water transparency will be quantified using a Secchi Disk. Both measurement methods are detailed in the SOPs (See **Appendix 1**). All bacteria samples will be analyzed by EQLAB under a contract with the SJBEP. A copy of the EQLAB methods and analysis protocols are presented in **Appendix 4**.

11.2 Analytical Quality Control

The Cooler Temperature Control blank will be checked to be sure the samples are maintained within the required 2 – 10^{o}C in the coolers. If the temperature control sample is out of this temperature range, the results will be label "Results Questionable Temperature Control Exceeded 10^{o}C". **Section 16** presents the procedures the SJBE Monitoring Program will follow when the temperature control sample exceeds the acceptable limits. EQLAB will include all laboratory analytical control samples for each monitoring event. The SJBEP will request the QA/QC data sheets from EQLAB which after examination by the QAPP Coordinator or QAPP Manager will be included in the SJBE Monitoring Program records. Laboratory control elements are described in the EQLAB SOPs (See **Appendix 4).**

12.0 Sample Handling and Custody Requirements

The purpose of the sample custody records is to document, maintain the integrity, and record the routing of all samples during transportation and laboratory login operations. A record of all transactions concerning each sample will be maintained. The Field Sampling Leader is responsible for the care and custody of the samples until they are properly transferred to EQLAB for analysis. The QAPP Manager determines whether proper custody procedures were followed during field operation.

The Chain of Custody (COC) documents that will be completed during each monitoring event is presented in **Appendix 10.** The COC will remain in the field samples coolers to document sample transfer. The laboratory (EQLAB) will return a completed copy of the form after the samples are delivered.

A field data sheet will be completed on-site at the time of sampling (**see Appendix 5**). Each sample container will be clearly labeled at the time of water sample collection using adhesive bickered labels and waterproof ink's pens.

The sample label includes the following information (See **Appendix 11**):

- Sample station identification (ID) number
- Sample station identification name
- No. of Bottles
- Folder No.
- Date Collected
- Time Collected
- Collected By
- Matrix sources
- QC Type
- Preservative
- Sample No.
- Container
- Type
- Color
- Volume needed
- Lot No.
- Serial No.
- Test parameters

Sample volumes, sample preservatives, and holding times are presented in **Table 9**. Small sample containers will be sealed in plastic "zip-lock" bags in order to protect the labels from water damage and to ensure that the containers are not in direct contact with the chilling medium. Water samples will be placed in a sturdy ice chest and chilled from 2 to 10^{o} C. The Cooler Temperature Control vial will be checked to assure the samples were maintained within the required range, if the temperature control sample is out of range, the results are stamped with the qualifying statement "Results Questionable Temperature Control Exceeded 10^{o}C." The associated COC document will be sealed in a plastic bag and accompany the samples in the ice chest. The shipping container will be labeled clearly with the origin and destination of the shipment if applicable. The samples will be transported to EQLAB the same day of the monitoring event. The samples will be logged by the laboratory upon receipt.

13.0 Testing, Inspection, Maintenance and Calibration Requirements

13.1 Instrument/Equipment Testing, Inspection and Maintenance

The Hydrolab Quanta will be calibrate and maintain by the SJBEP. All field equipment including the Secchi disk will be maintained according to the manufacturer instructions and will arrive at each day in proper working conditions. After each monitoring event the Hydrolab Quanta probes will be inspected for damage. Particular attention will be given to the dissolved oxygen probe membrane for the observation of wrinkling or other physical damage. This membrane will be change according to the manufacturer maintenance schedule (See **Appendix 7**). Sampling equipment will be checked for visual material and mechanical integrity daily. When not in use the Hydrolab Quanta will be stored in the field laboratory station. The instruments will be secured, padded, and protected during transportation.

13.2 Instrument Calibration and Frequency

A maintenance schedule will be prepared and followed for all instrumentation and recorded in the Hydrolab Quanta Calibration sheets (See **Appendix 9**). The Hydrolab Quanta will be sent to the manufacturer once a year for a certified manufacturer calibration and inspection. Other calibration procedures are detailed in the attached SOPs (See **Appendix 1**). Instrumentation will be checked through calibration prior to the sampling day under a controlled environment. Also, the calibration will be performed at the end of each sampling day to ensure less than 20 % instrument drift in one sampling day. If the calibration check indicates that the instrument's calibration has drifted outside the calibration acceptance criteria, the data will be flagged and evaluated following the procedures in **Section 16** of this QAPP.

The Hydrolab Quanta Operating Manual presented in **Appendix 7** describes the instruments calibration procedures that will be follow for this particular instrument. Overall, The Hydrolab Quanta will be calibrated before each monitoring day (monthly) for specific conductance, pH, dissolved oxygen, and turbidity. The specific conductance calibration will be checked before and after the monitoring events following the procedures presented in the Hydrolab Quanta manual (See **Appendix 7**) using the corresponding

calibration standard. Temperature calibration is factory set and no calibration is required by the operator. Dissolved oxygen will be calibrated following the Hydrolab Quanta Operation Manual (**Appendix 7**) and validated as described in **Section 10.3** of this QAPP. Water transparency will be measure with a 20 cm Secchi disk (black and white bands) attached to a 20 meters Keson® Surveyor's fiberglass rope. Monitors will ensure that the disk is free of material and that the black/white stripes are completely visible and scratch-free. Fresh standards will be used to calibrate the instruments.

13.3 Inspection and Acceptance Requirements for Supplies

No special requirements are needed. The Field Sampling Leader and/or QAPP Coordinator will be responsible for the appropriate inspection and maintenance of all field equipment including the safety equipment described in the SOPs (See **Appendix 1**). All equipment will be washed in the laboratory prior to sampling according to the SOPs (See **Appendix 1**).

14.0 Data Management

The name of all the volunteers who participates the sampling event will be documented in the field data sheet (See **Appendix 5**). SJBE volunteers' monitors will record the station name (station unique identification number), date, and time of sample collection. No entries will be erased, instead the incorrect information will be crossed out with a single line and the correct information will be entered and initiated. The field data sheet will be reviewed by the QAPP Coordinator or Field Sampling Leader before leaving to each sampling site and then reviewed again at the end of the sampling event to ensure that the sheet is properly completed. The data sheet will be returned to the QAPP Manager after the monitoring events. The QAPP Coordinator will enter the data into a Microsoft Excel spreadsheet developed by the SJBEP following the monitoring event. This will help to evaluate and validate any unclear information and inconsistencies that may have occur during the process. The QA Officer will review the QAPP Coordinator's data entry into the spreadsheet in order to verify the data was transferred correctly and will implement necessary corrective actions. Original data sheet will be scanned into electronic files before its storage under the custody of the SJBEP for a period of five years.

15.0 Assessment/Oversight and Response Actions

The Field Sampling Leader may be the QAPP Coordinator and/or the QAPP Manager depending on personnel availability. Volunteers will be under constant supervision by one the aforementioned coordinator/officers. After each sampling activity, the Field Sampling Leader will meet with the participant volunteers to: (1) discuss problems encountered; (2) solutions proposed or implemented on site; and (3) to insure that the Program quality objectives are achieved. Any deficiencies and/or corrective actions taken will be documented by the Field Sampling Leader. The reasons for any out of control events experienced if the field, will be identified and informed to the QAPP Coordinator and/or QAPP Manager along with any changes performed in the sampling procedures. The Field Sampling Leader should provide to the QAPP Manager a narrative supporting any decisions regarding this point.

Data quality audits will be conducted once a year by the QA Officer. Audits will consist of inspecting the Field Data Sheets, Laboratory QA/QC data, field duplicate RPD calculation, percent recovery of surrogate spikes, and data completeness. Also a field QA/QC audits will be performed once a year to evaluate the effectiveness of the sample collection techniques and that SOPs protocols has been followed. Any deficiencies will be reported to the QAPP Manager, who will oversee the resolution of deficiencies.

16.0 Data Review, Validation Verification and Usability

The volunteer monitor collecting the data will provide the first data review and validation. Also, the results will be reviewed by the QAPP Coordinator at the time of sample collection. Careful attention will be given to any substantial variations in site measurements and that all notes are properly recorder and legible. Volunteers performing the scheduled calibrations of the Hydrolab Quanta, and the DO data validation as described in **Section 10.3** of this QAPP will be under the QAPP Coordinator and/or QAPP Manager supervision. A volunteers monitoring training will be scheduled according to demand and if needed, a SOPs protocols refreshing every other months. Periodically water quality

experts from environmental agencies (PREQB, USEPA, etc.) and the academia will be invited to evaluate the data collection protocols and to provide inputs.

16.1 Data review, Verification and Validation

Quality validation will consist in checking the performance of the data collection procedures where applicable. Data will be compared with historic data sets. Also, any data observed that seems to be inconsistent with previously recorded data will be brought to the attention of the QAPP Manager. The data will be reviewed for transcriptional and typographical errors. Sampling protocols will be reviewed to determine if they were properly followed. The specific routine procedures that will be implemented to access data precision, accuracy and completeness are detailed in **Section 8.0** of the QAPP. The results will be reviewed by the QAPP Coordinator and/or QAPP Manager to see if there is any QC limits been exceeded. EQLAB will perform a QA/QC check of all data analysis by their lab staff according to the established guidelines sets (See **Appendix 4**). The QAPP Coordinator and/or QAPP Manager will check that this review was followed and properly documented in the data report submitted to the SJBEP office.

16.2 Reconciliation with User Requirements

Once the data results are received and compiled, the QAPP Coordinator and/or QAPP Manager will review the data set results to verify if holding times have been met, calibration checks are adequate, qualitative and quantitative results are correct, documentation is complete, and QC results are complete and adequate. If data quality indicators do not comply with the project's requirements as outlined in this QAPP, the data will be flagged with an appropriate explanation noted in the data management Excel software spreadsheet. The QAPP Manager will evaluate the cause and severity of the failure and suggest corrective actions. According to the results of this evaluation, the data will be accepted, rejected or marked as provisional. Calibration or maintenance methods will be reviewed and improved if equipment failure seems to be the cause for the problem. Volunteer monitors will go through a retraining and reevaluation process if the problem was due to a human error. Any major revision or changes regarding the monitoring project specification will be made after approval by the USEPA quality assurance officers.

17.0 Reporting, Documents, and Record

The QAPP Coordinator will enter the data into a Microsoft Excel spreadsheet developed by the SJBEP following the monitoring event. Original data sheet will be scanned and put into electronic files before its storage in the SJBEP files for a period of five years. At the end of the monitoring year, the results will be presented into an annual water quality monitoring report. The report will include an executive summary, introduction, material, methods, sampling collection and handling records, QC sample records, equipment calibration records, assessment reports, tables, graph, discussion of the results and conclusions. The report will be distributed to all the SJBEP Committees, SJBEP Board of Directors, QAPP signatories, QAPP Advisory Board, and others stakeholders. All Field Data and Hydrolab Quanta Calibration sheets will have document control information on each page including: (1) Project Name, (2) Revision Number, (3) Date of Last Revision, and (4) Page Number.

18.0 References

Web, R.M.T., F. Gómez-Gómez, 1998. *Synoptic Survey of Water Quality and Bottom Sediments, San Juan Bay Estuary System, Puerto Rico, December 1994-July 1995. U.S.* Geological Survey, Water Resources Investigations Report 97-4144, San Juan, PR.

SJBEP, 2000.*Comprehensive Conservation and Management Plan for the San Juan Bay Estuary*. San Juan Bay Estuary Program, San Juan, Puerto Rico.