

BOYNTON-DELRAY COASTAL WATER QUALITY MONITORING PLAN



(Photo by T. Carsey, 2006)

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INTRODUCTION

The present document provides a water quality monitoring plan for the coastal ocean waters extending from the area of the Seagate Reef to a location north of the Boynton Inlet. The area includes both the South Central District ocean outfall and the Boynton Beach Inlet. The planned monitoring period is for one year, but may be shorter or longer depending on availability of funds. In a separate, but coordinated effort, ambient current data will be gathered both in the area of the Gulfstream Reef and the outfall (ambient current data have been being gathered since April, 2006) throughout the water quality monitoring plan activity. Also in a separate, but coordinated effort, SF₆ and dye tracer studies are planned for both winter and summer seasons. The present document details the goals/objectives and methodologies of the water quality monitoring plan. The plan will be reviewed and amended in response to any changes deemed to improve the plan. Input and recommendations for plan development or change is welcomed from interested parties including the Florida Department of Environmental Protection, the Palm Beach Department of Natural Resources and the US Environmental Protection Agency. Ultimately the present monitoring plan may become incorporated in and extended by the Florida Area Coastal Environment (FACE) program.

BACKGROUND

The coastal ocean area for which this monitoring plan has been designed is subject to the multiple coastal ocean processes and is subject to presence of multiple water mass types. Multiple sources of nutrients to the coastal ocean area are likely to be present including upwelled deep ocean water, inlet outflow, groundwater discharge, ocean wastewater effluent discharge, atmospheric deposition and, possibly, septic discharge. Only a limited database of nutrient and water mass type parameters exists for the coastal ocean area of interest. The group Reef Rescue (Tichenor, 2005) most recently carried out an approximately five month long water quality measurement program extending from August 2005 to December 2005. The present water quality monitoring program will measure many of the same parameters at many of the same (or nearby) sites used in the Reef Rescue effort. Other parameters will also be measured which may be useful in examining water mass types and other regulatory concerns, e.g. ammonia. In addition to the water quality parameters measured routinely in the present monitoring plan, more intense sampling will occur during a coordinated tracer study. High frequency (measurements every 20 minutes), (nearly) full water column, ambient current measurements will be made at two or more sites in the coastal area of interest.

SITE LOCATION

The coral reef system (Gulfstream Reef, Delray Ledge and Seagate Reef) is located approximately one mile offshore of Palm Beach County (Figure 1). This area forms the northern section of reef tract, which runs from the Dry Tortugas, through the Florida Keys and north to Palm Beach County. The reef ranges in depth from 10 to 30 meters and is in close proximity to the Gulf Stream. The Boynton Beach Inlet is located and discharges to the north and west of the reef system, while the South Central Ocean Outfall is located and discharges to the south and east of the reef system with the exception of Seagate Reef which is located to the south of the outfall.

MONITORING GOALS AND OBJECTIVES

The goals and objectives of the monitoring program are provided below.

1. To obtain a database for water quality parameters including the following: (i) the nutrients Ammonia (NH₄⁺), Nitrite (NO₂⁻), Nitrate+Nitrite (NO₂⁻ + NO₃⁻), Orthophosphate (PO₄⁺³), Silica (SiO₄⁻⁴), total dissolved Phosphorus and total dissolved Nitrogen (ii) Chlorophyll a, (iii) Total suspended solids, (iv) pH, (v) Dissolved Organic Carbon
2. To obtain vertical profiles of temperature and salinity essentially concomitantly with water quality samples

WATER QUALITY MONITORING OUTLINE

Sampling Stations and Frequency

Water quality sampling will be conducted on a bi-monthly basis. Sampling events will occur at 18 pre-established monitoring stations. Each station will be sampled at three different depths: surface, mid-depth and near bottom (except for Station BD-13 surface only, and Stations BD-16 thru BD-18 surface and near bottom only). Station locations are identified in Table 1 and shown in Figure 1. Sampling events will be conducted from south to north in an effort to increase the likelihood of obtaining samples from within the same water mass since the predominant current is north. All efforts will be made to sample on Tuesdays of each month in order to allow for a comparison of the waste water treatment plant (WWTP) nutrient data with that collected in this monitoring plan, and to sample on an outgoing tidal cycle in order to get the maximum impact of the Lake Worth Lagoon on the sampling area. This will all be dependent upon timing and weather conditions.

Table 1: Water Quality Sampling Sites

Station #	Latitude	Longitude	Station #	Latitude	Longitude
BD-1A	26.42565	-80.04542	BD-15A	26.55907	-80.03327
BD-1B	26.42565	-80.04542	BD-15B	26.55907	-80.03327
BD-1C	26.42565	-80.04542	BD-15C	26.55907	-80.03327
BD-2A	26.44212	-80.04725	BD-16A	26.54626	-80.04818
BD-2B	26.44212	-80.04725	BD-16B	26.54626	-80.04818
BD-2C	26.44212	-80.04725	BD-17A	26.54266	-80.04793
BD-3A	26.45803	-80.04252	BD-17B	26.54266	-80.04793
BD-3B	26.45803	-80.04252	BD-18A	26.53944	-80.04954
BD-3C	26.45803	-80.04252	BD-18B	26.53944	-80.04954
BD-4A	26.46192	-80.04208			
BD-4B	26.46192	-80.04208			
BD-4C	26.46192	-80.04208			
BD-5A	26.46628	-80.04182			
BD-5B	26.46628	-80.04182			
BD-5C	26.46628	-80.04182			
BD-6A	26.47558	-80.03995			
BD-6B	26.47558	-80.03995			
BD-6C	26.47558	-80.03995			
BD-7A	26.48773	-80.03933			
BD-7B	26.48773	-80.03933			
BD-7C	26.48773	-80.03933			
BD-8A	26.51073	-80.03543			
BD-8B	26.51073	-80.03543			
BD-8C	26.51073	-80.03543			
BD-9A	26.50833	-80.04167			
BD-9B	26.50833	-80.04167			
BD-9C	26.50833	-80.04167			
BD-10A	26.52273	-80.03228			
BD-10B	26.52273	-80.03228			
BD-10C	26.52273	-80.03228			
BD-11A	26.53333	-80.03583			
BD-11B	26.53333	-80.03583			
BD-11C	26.53333	-80.03583			
BD-12A	26.53874	-80.03980			
BD-12B	26.53874	-80.03980			
BD-12C	26.53874	-80.03980			
BD-13A	26.54542	-80.04300			
BD-14A	26.54747	-80.04003			
BD-14B	26.54747	-80.04003			
BD-14C	26.54747	-80.04003			

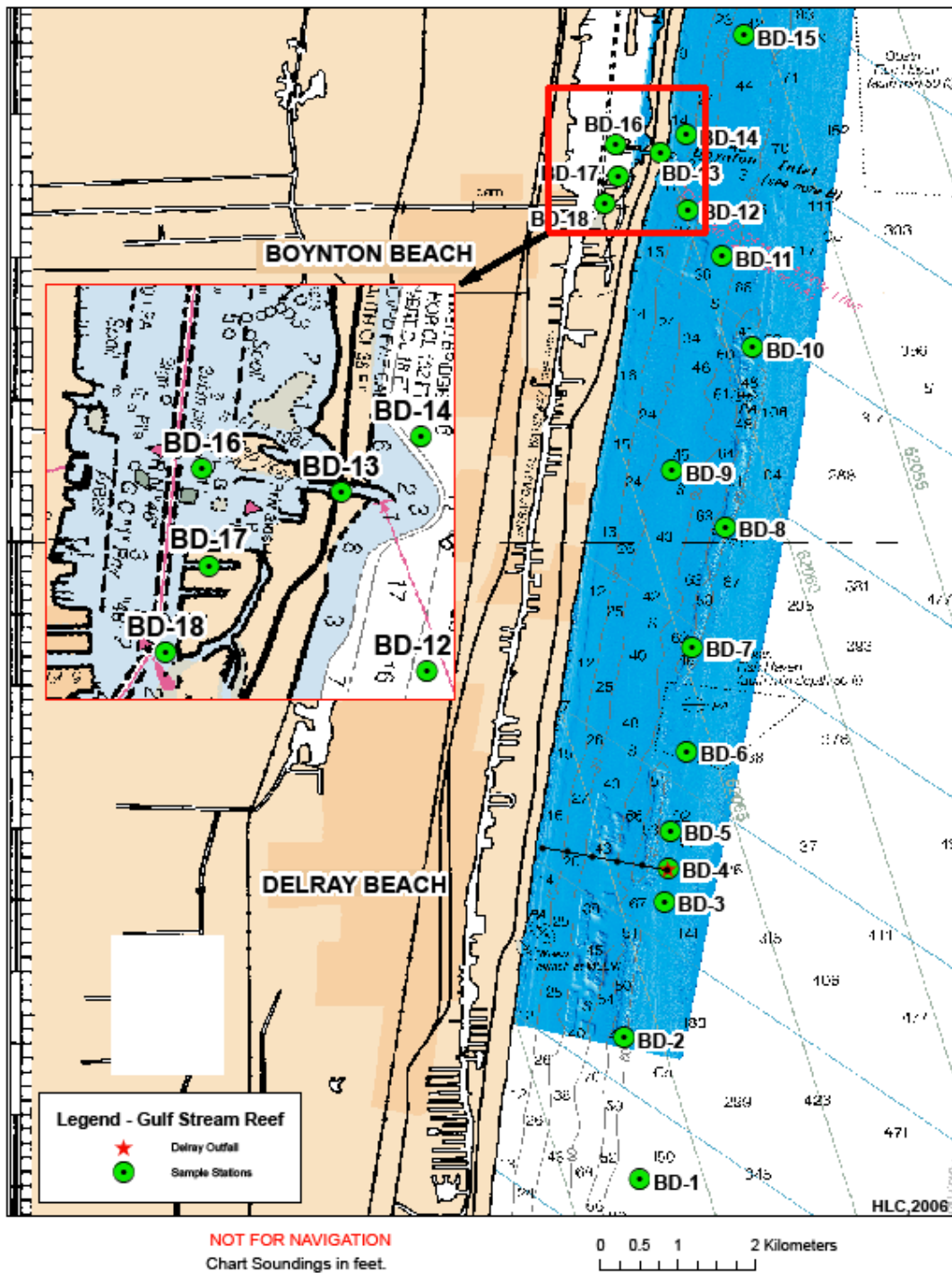


Figure 1: Map of station locations. Red star indicates location of the South Central Ocean Outfall. Numbers indicate sample station.

Field parameters are shown in Table 2 and will be collected according to standard operating procedures.

Table 2: Parameters to be collected for the water quality monitoring program.

<u>WATER COLUMN PROFILES</u>	<u>DISCRETE WATER SAMPLES</u>
Conductivity (mS/cm)	Nutrients (µM)
Temperature (°C)	Chlorophyll a (µg/L)
Depth (m)	pH (units)
Dissolved Oxygen (mg/L)	Total Suspended Solids (mg/L)
pH (units)	Dissolved Organic Carbon (µg/L)
Salinity (ppt)	
Turbidity (NTU)	
Chlorophyll a (µg/L)	

Nutrients to be sampled include Ammonia-N, Nitrite-N, Nitrate+Nitrite-N, Orthophosphate-P, Silica, Total Dissolved Nitrogen and Total Dissolved Phosphorus.

Sampling Vessel

Water quality monitoring will be conducted using the RV Cable, a 21' Parker which is located at AOML. The RV Cable can accommodate the sampling equipment, a boat captain and two technicians. Samples will be collected using a portable winch, which will lower a line with the Sontek/YSI ADV 6600 Sonde and Niskin bottles to the appropriate depths.

Equipment Decontamination

All sample bottles and sampling devices (Niskin bottles) used in this monitoring program must be low in residual nutrients. Pre-field and post-field cleaning will consist of soaking all sample bottles and sampling devices (Niskin bottles) in lab grade detergent for three hours, rinsing with tap water, followed by soaking with 10% HCL (v/v) overnight and thoroughly rinsing with de-ionized water, and letting air dry. Sample coolers will also be washed with lab grade detergent, rinsed with tap water, then with de-ionized water and left to dry. All cleaned equipment will be stored in a clean environment.

In-field cleaning of sampling equipment (Niskin bottles) will consist of rinsing the bottles with de-ionized water and allowing the bottles to sit at their sampling depths for two minutes before closing and collecting the sample. This will give time for the Niskin bottles to be washed with the sample water to avoid contamination from the earlier sites sampled.

Navigation

Sampling sites will be located by use of GPS. The GPS coordinates will be recorded on the Field Data Log Sheet (Appendix A) for each sampling station when the Niskin bottles and sonde enter the water.

Field Notes

Field notes will be taken at each sample site and will include sampling station number, date, time, weather conditions, field parameters, watercolor, field conditions and other observations as necessary. Notes will be kept in a project field notebook. Project data log sheets can be found in Appendix A.

Sample Designation

Sample designations will consist of a series of letters and numbers to indicate the project and sample station identifier. The project prefix will consist of the letters BD for the project name (Boynton-Delray). An example of the sample designation follows:

BD-1A

Field quality control samples will be submitted blind to the laboratory. Field quality control samples will consist of field duplicates taken at random stations. The sample designation for the field duplicates will be the same number and letter designation as the station where the duplicate sample is taken. The quality control sample will be differentiated from the natural sample by adding the following code at the end of the sample designation number:

Field Duplicate “X”

An example of a quality control sample designation follows:

BD-1A-X

FIELD SAMPLE COLLECTION METHODS

Water Column Data Collection

A Sontek/YSI ADV 6600 Sonde cast will be conducted at each monitoring station at the same time the Niskin bottles are lowered. Each time the YSI is turned on, seawater conductivity, temperature, and depth data will be recorded internally every two seconds. For each cast, the station number, cast number and time will be recorded on the Field Data Log Sheet (Appendix A). Additional comments can be written on the log sheets to note any problems that may occur.

The sensors on the YSI unit will be equilibrated with sample water. The YSI unit will be turned on, lowered into the water until the entire unit is submerged, and held stationary for two minutes. The YSI unit is then slowly lowered to the bottom and retrieved. Data will be processed, analyzed and archived back at AOML.

Water Sample Collection

At each station water samples will be collected for nutrients, dissolved organic carbon (DOC), pH, total suspended solids and chlorophyll a. Once on site the depth will be determined from the RV Cable using its depth sounder. The line, which will be holding the niskin bottles and YSI unit will be marked in one foot intervals before leaving AOML. Once the depth is determined three 5-L Niskin bottles will be attached to the line to sample the surface, mid depth and near bottom of that particular station. The Niskin bottles along with the YSI unit will be lowered by the winch and water samples collected by sending a messenger down the line to close the Niskin bottles. This will allow for all three depths to be sampled approximately at the same time and place in the water column. Niskin bottles will be retrieved and sample water withdrawn and placed in pre-labeled sample containers. Sample containers will be placed on ice (4⁰C) in storage coolers aboard the RV Cable and transported back to AOML for processing and analysis.

ANALYTICAL METHODS

Chlorophyll Analysis

Chlorophyll a concentrations will be determined via a standardized filtration-extraction method using a 60:40 mixture of acetone and dimethyl sulfoxide (Shoaf & Lium, 1976; Kelble et al., 2005). The fluorescence of each sample is measured before and after acidification in order to correct for phaeophytin on a Turner Designs model TD-700 fluorometer. The fluorescence values are calibrated using known concentrations of chlorophyll a to yield chlorophyll a concentrations in mg/m^3 .

Total Suspended Solids Analysis

Total suspended solids (TSS) will be determined gravimetrically for each station following Young et al., (1981) and Kelble et al., (2005). As a large a volume of the sample as possible, with a minimum of 200 ml, is filtered onto preweighed filters that are dried and reweighed to calculate TSS via the following equation:

$$\text{TSS} = (W_{\text{post}} - W_{\text{pre}})/V_{\text{filtered}}$$

where W_{pre} is the prefiltration weight, W_{post} is the post filtration weight, and V_{filtered} is the volume filtered.

pH Analysis

pH will be determined spectrophotometrically following the methods of Clayton and Byrne, (1993) and Mosley *et al.*, (2004). A sulfonephthalein dye, *m*-cresol purple, is added to the sample and absorbance readings measured at wavelengths 434 nm, 578 nm and 725 nm. Temperature and salinity are also recorded for each sample. The following equations will be used to calculate the pH of each sample,

$$\text{pK}'a (m\text{CP}) = 8.6353 - 0.3238S^{1/2} + 0.0807S - 0.01157S^{3/2} + 0.000694S^2$$

$$\text{pH} = \text{pK}'a + \log \left(\frac{R - 0.0069}{2.222 - R0.133} \right)$$

where S is the salinity, R is the ratio indicator absorbance at molar absorptivity maxima (i.e. $R = A_{578}/A_{434}$), $\text{pK}'a$ is the acid dissociation constant and *m*CP is the *m*-cresol purple dye.

Nutrient Analysis

Nutrient analyses will be conducted using the following EPA methods.

Method 349.0 will be used to determine the concentration of ammonia for each station (Zhang *et al.*, 1997). This method uses automated gas segmented continuous flow colorimetry for the analysis of ammonia. Ammonia in solution reacts with alkaline phenol and NADTT at 60 °C to form indophenol blue in the presence of sodium nitroferricyanide as a catalyst. The absorbance of indophenol blue at 640 nm is linearly proportional to the concentration of ammonia in the sample.

Method 353.4 will be used to determine the concentration of nitrate and nitrite for each station (Zhang *et al.*, 1997). This method uses automated gas segmented continuous flow colorimetry for the analysis of nitrate and nitrite. In the method, samples are passed through a copper-coated cadmium reduction column. Nitrate is reduced to nitrite in a buffer solution. The nitrite is then determined by diazotizing with sulfanilamide and coupling with N-1-naphthylethylenediamine dihydrochloride to form a color azo dye. The absorbance measured at 450 nm is linearly proportional to the concentration of nitrite + nitrate in the sample. Nitrate concentrations are obtained by subtracting nitrite values, which have been separately determined without the cadmium reduction procedure, from the nitrite + nitrate values.

Method 365.5 will be used to determine the concentration of orthophosphate for each station (Zimmermann and Keefe, 1997; Zhang *et al.*, 2001). This method uses automated calorimetric and continuous flow analysis for the determination of low-level orthophosphate concentrations. Ammonium molybdate and antimony potassium tartrate react in an acidic medium with dilute solutions of phosphate to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by

ascorbic acid. The absorbance measured at 800 nm is proportional to the phosphate concentration in the sample.

Method 366.0 will be used to determine the concentration of silica for each station (Zhang and Berberian, 1997). This method uses automated gas segmented continuous flow colorimetry for the analysis of dissolved silicate concentration. In the method, β -molybdosilicic acid is formed by reaction of the silicate contained in the sample with molybdate in acidic solution. The β -molybdosilicic acid is then reduced by ascorbic acid to form molybdenum blue. The absorbance of the molybdenum blue, measured at 66 nm, is linearly proportional to the concentration of silicate in the sample.

Method 367.0 will be used to determine the total phosphorus concentration for each station (Zhang *et al*, 1998). This method determines total dissolved phosphorus (TDP) concentration by autoclave promoted persulfate oxidation of organically bound phosphorus followed by a gas segmented continuous flow colorimetric analysis of digested samples. In this method, dissolved organic phosphorus (DOP) in the water reacts with persulfate in acidic media at elevated temperature and pressure. An autoclave is used to achieve a temperature of 120 °C and pressure of 2 atmospheres, which promote oxidation. After samples are cooled to room temperature, aliquot of ascorbic acid is added to remove the free chlorine formed in seawater during the digestion. Those autoclaved samples are then analyzed for phosphate concentrations by the molybdenum blue calorimetric method using a gas segmented continuous flow analysis by a Flow Solution Analyzer. In this method phosphate reacts with molybdenum (VI) and antimony (III) in an acidic medium to form an antimonyphosphomolybdate complex. This complex is subsequently reduced by ascorbic acid to form a blue complex and the absorbance measured at 710 nm. Undigested samples are analyzed separately to obtain the concentration of dissolved inorganic phosphate (DIP). Dissolved organic phosphorus is calculated as the difference between total dissolved phosphorus and dissolved inorganic phosphorus ($DOP = TDP - DIP$).

Total dissolved nitrogen is measured using the thermal decomposition/NO detection chemiluminescence method in a Shimadzu total organic carbon analyzer (Schimadzu, 2004). When a sample is introduced into the combustion tube (furnace temperature 720 °C), the TN in the sample decomposes to nitrogen monoxide. Nitrogen gas does not become nitrogen monoxide under these circumstances. The carrier gas, which contains the nitrogen monoxide, is cooled and dehumidified by the electronic dehumidifier. The gas then enters a chemiluminescence gas analyzer, where nitrogen monoxide is detected. The detection signal from the chemiluminescence gas analyzer generates a peak and the TN concentration in the sample can then be measured.

Dissolved Organic Carbon

Dissolved organic carbon is measured by Shimadzu total carbon analyzer (Schimadzu, 2004). This method determines the organic content after the removal of inorganic carbon. The sample is acidified to a pH of 2 to 3 and subsequently degassed. Carbonates are not stable anymore with this pH value and therefore, form carbon dioxide. The inorganic carbon is removed by degassing. The organic carbon contents of the sample are introduced into the combustion tube, which is filled with an oxidation catalyst and heated to 680 °C. The sample is burned in the combustion tube and the contents are converted to carbon dioxide. Carrier gas, which flows at a rate of 150 mL/min to the combustion tube, carries the sample combustion products from the combustion tube to an electronic dehumidifier, where the gas is cooled and dehydrated. The gas then carries the sample combustion products through a halogen scrubber to remove chlorine and other halogens. Finally, the carrier gas delivers the sample combustion products to the cell of a non-dispersive infrared (NDIR) gas analyzer, where the carbon dioxide is detected. The NDIR outputs an analog detection signal that forms a peak. From this the concentration of DOC can be determined.

LABORATORY PROCEDURES FOR SAMPLE ANALYSIS

Chlorophyll Analysis

Water samples are filtered through 25 cm 0.45 um glass fiber filters using a filter apparatus either attached to a hand pump or a vacuum pump. Take 200 ml of sample water and filter. Before filtering the next sample station make sure to clean the filtering apparatus by rinsing with de-ionized water. The filter is then folded in half by forceps, making sure not to touch with hands and placed in a 2 ml polypropylene vial. A duplicate from the same sample is also filtered and placed in the same vial. Sample vials are then placed in a 20 L Dewar of liquid nitrogen until analyzed.

Total Suspended Solids Analysis

Water samples are filtered through pre-weighed 47 mm 0.4 um polycarbonate filters. Each filter is placed in a pre-labeled 47 mm petri dish with lid and placed in a drying oven for 24 hrs. at 60 °C. Petri dishes with filters are taken from the oven and allowed to cool in a dessicator. After cooling, filters are removed from the petri dishes with forceps and weighed on an AD-6 autobalance. Do not touch the filters with your hands or leave out in open air for any period of extended time because they will collect moisture and give erroneous results. All data are recorded on the TSS data log sheet found in Appendix A.

Filters are dried and pre-weighed before each bi-monthly monitoring cruise. Data is recorded on the filter tare log sheet found in Appendix A.

pH Analysis

Approximately 30 ul of *m*-cresol purple dye is added to 10 ml of sample and mixed by capping the sample bottle and gently shaking. A subsample is placed in a quartz cuvette. The cuvette is put inside the sample chamber of the UltraPath system, a photodiode array spectrometer, and absorbances measured. Data is recorded on the pH data log sheet found in Appendix A.

Nutrient Analysis

Water samples are filtered through 0.45 um membrane filters using a 50 ml syringe and collected in two 8ml polystyrene test tubes, one for Ammonia-N analysis and the other for Nitrate + Nitrite-N, Nitrite-N, Orthophosphate-P and Silica analysis. Wash the filter before use by passing 50 ml of reagent water through the filter. Pass at least 10 ml of sample through the filter and discard before taking the final sample. Care must be taken to avoid the contamination of nutrient samples especially at low concentrations. Centrifugation is an alternative technique to remove particulate matter from the sample. 8 ml polystyrene test tubes are used for sample storage and analysis. Sample tubes should be rinsed three times with sample water, shaking with the cap in place after each rinse. Finally, fill the tubes with sample water and preserve. Ammonia samples should be preserved by addition of 0.2% (V/V) of chloroform and cap firmly and place upright in a test tube rack and refrigerated in the dark at 4 °C until analyzed. All other nutrient samples must be frozen until analyzed.

Dissolved Organic Carbon Analysis

Water samples are filtered through GF/F filters to remove any particulate materials from the sample. Before filtering, the filters are baked at 450 °C for 4 hours to remove any organic carbon from the filters. After filtration a subsample is placed in a pre-cleaned 10 ml glass vial and placed in the auto-sampler of the Shimadzu Total Organic Carbon Analyzer V-CPH/CPN and the amount of dissolved organic carbon measured.

QUALITY ASSURANCE AND QUALITY CONTROL

Quality assurance provides a process for ensuring the reliability and value of measured data. Sound QA practices are essential to acquire data of the necessary type and quality for their intended use. Data quality will be measured in terms of accuracy, precision, completeness, representativeness, comparability and bias.

MEASUREMENT QUALITY OBJECTIVES

Measurement quality objectives (MQO's) are defined as acceptance criteria for the quality attributes measured by project quality indicators (EPA, 2002). They are quantitative measures of performance. These are often the accuracy, precision, completeness, and bias guidelines against which laboratory and some field QC results are compared. The acceptable levels listed in Table 4 are to be applied to batch-level data and may be assessed by only a few QC samples. Failing to meet these criteria would trigger corrective action (see that section).

Table 4: Measurement Quality Objectives

ANALYTE	ACCURACY	PRECISION	COMPLETENESS
FIELD CONSTITUENTS			
Conductivity	± 0.5%	NA	90%
Salinity	± 1%	NA	90%
Temperature	± 0.15 °C	NA	90%
pH	± 0.2 units	NA	90%
Dissolved Oxygen	± 2%	NA	90%
ORP	± 20 mV	NA	90%
Turbidity	± 5%	NA	90%
Chlorophyll	N/A	NA	90%
LAB CONSTITUENTS			
Ammonia-N	10%	10%	95%
Nitrate + Nitrite-N	10%	10%	95%
Nitrite-N	10%	10%	95%
Orthophosphate-P	10%	10%	95%
Silica	10%	10%	95%
Total Phosphorus	10%	10%	95%
Dissolved Organic Carbon	10%	10%	95%
Total Nitrogen	10%	10%	95%
pH	10%	10%	95%
Chlorophyll	20%	20%	95%
Total Suspended Solids	10%	10%	95%

ACCURACY

Accuracy is the measure of the agreement between an observed value and an accepted reference value or true value.

Laboratory Accuracy

Laboratory accuracy will be assessed through the analysis of matrix spikes and/or laboratory control samples, as and if required by the analytical methods, to determine percent recoveries (%R). The %R utilizing matrix spikes is calculated as follows:

$$\%R = \frac{(C_s - C_U)}{C_A} \times 100$$

where C_S = measured concentration of spiked sample
 C_U = measured concentration of unspiked sample
 C_A = actual concentration of spike added

The %R utilizing laboratory control samples is calculated as follows:

$$\%R = \frac{(C_M)}{(C_A)} \times 100$$

where C_M = measured concentration of control sample
 C_A = actual concentration of control sample

Dilution blank samples and method blank samples will be generated by the laboratory, as and if required by the analytical method, for use in assessing contamination resulting from laboratory practices.

Field Accuracy

Field accuracy will be assessed through use of field blanks. In order for the accuracy assessment to be relevant, all protocols concerning sample collection, handling, preservation, and holding times must be maintained.

For grab sampling, field blanks will be used to determine if samples collected have been contaminated. Field blanks consisting of reagent grade deionized water will be submitted to the analytical laboratory to assess the quality of the data resulting from the field monitoring program. Field blanks will be analyzed to check for procedural contamination at the laboratory that may cause sample contamination.

PRECISION

Precision is a measure of the variability in the results of replicate measurements due to random error (Lombard, 2001). Random errors are always present due to normal variability in the many factors affecting the measurement results. Precision will be determined by the following:

1. Collection and analysis of field duplicates for nutrients, TSS, chlorophyll a, pH and DOC
2. Calculation of the percent relative percent difference (%RPD)
3. Documentation of ongoing field equipment maintenance, calibration and operation

Laboratory Precision

The precision of the laboratory analysis is assessed by the comparison of matrix spikes (MS) and matrix spike duplicates (MSD), if required by analytical method. The RPD between the analyte levels measured in the MS sample and the MSD sample is calculated as follows:

$$RPD = \frac{|C_{MS} - C_{MSD}|}{0.5(C_{MS} + C_{MSD})} \times 100$$

where C_{MS} = measured concentration of the matrix spike
 C_{MSD} = measured concentration of the matrix spike duplicate

Field Precision

Field precision tests will be conducted for grab samples and physical parameter readings. The precision of grab samples is assessed by the comparison of field duplicates. The relative percent difference (RPD) between the analyte levels measured in the field duplicates is calculated as follows:

$$RPD = \frac{|C_A - C_B|}{C_A} \times 100$$

$$0.5(C_A + C_B)$$

where C_A = measured concentration of sample
 C_B = measured concentration of duplicate sample

The precision of physical parameters readings may be assessed by the comparison of each instrument's calibration readings versus the post check readings. The RPD between the readings is calculated as follows:

$$RPD = \frac{|R_X - R_Y|}{0.5(R_X + R_Y)} \times 100$$

where R_X = calibration reading
 R_Y = post check reading

COMPLETENESS

Completeness is a measure of the amount of valid data obtained from the monitoring program compared to the amount of data that were expected. Events that may contribute to reduction in measurement completeness include sample container breakage, inaccessibility to proposed sampling locations, automatic sampler failure, and laboratory equipment failures.

The percent completeness (%C) is determined as follows:

$$\%C = \frac{(M_V)}{(M_P)} \times 100$$

where M_V = number of valid measurements
 M_P = number of planned measurements

If the completeness objectives are not achieved for any particular category of data, the Project Manager will provide documentation why the objective was not met and how the lower percentage impacted the overall study objectives. If the objectives of the study are compromised, re-sampling or re-measurement may be necessary.

Laboratory Completeness

Laboratory completeness is a measure of the amount of valid measurements obtained from all samples submitted for each sampling activity. The completeness criterion for all measurements is 95 percent.

Field Completeness

Filed completeness is determined by the number of measurements collected versus the number of measurements planned for collection. The details concerning the actual number of field samples to be collected are discussed in the sampling stations and frequency section of this plan. The completeness criterion for all measurements and sample collection is 90 percent, but will be influenced by environmental situations that may alter monitoring schedules.

REPRESENTATIVENESS

Representativeness is the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

For sample collection, representativeness will be assured by following the work plans and applying proper collection techniques including the proper sample sizes and volumes, sampling times, and sampling locations. In the laboratory, representativeness will be ensured by using the appropriate sample preparation techniques, by following appropriate analytical procedures, and by meeting the recommended sample holding time.

The objective for data comparability is to generate data for each parameter that are comparable between sampling locations and comparable over time. Data comparability will be promoted by:

1. Using standard approved methods, where possible;
2. Consistently following the sampling methods;
3. Consistently following the analytical methods;
4. Achieving the required detection limits

All sample collection and analytical methods will be specified, and any deviations from the methods will be documented. All results will be reported in standard units. All field and laboratory calibrations will be performed using standards traceable to National Institute of Science and Technology (NIST) or other U.S. EPA approved sources.

BIAS

Bias is considered the consistent deviation of measured values from the true values, caused by systematic errors in a procedure. Bias within the monitoring program will be reduced to the extent practicable by the following:

1. Strict adherence to sampling procedures
2. Complete data collection and organization
3. Regular and documented field meter calibration and maintenance
4. Periodic reviews and evaluations of field sampling procedures
5. Analyzing data in an appropriate manner based upon essential considerations, such as temporal variations

FIELD QUALITY CONTROL

Field Quality Control will follow DEP-SOP-001/01 (<http://www.dep.state.fl.us/labs/qa/2002sops.htm>) found in Appendix B. Table 5 below lists the type and number of quality control samples to be collected for each parameter during each sampling trip. The field cleaned equipment blanks will be collected after sample collection in the boat since this is the most likely area where contamination may occur if equipment is not properly cleaned. In addition to samples listed below a field sample will be spiked with a known quantity of Ammonia to determine percent loss if any between time of collection and analysis.

Table 5: Field quality control samples

PARAMETER	Pre-cleaned Equipment Blanks	Field Cleaned Equipment Blanks	Field Blanks	Field Duplicates (10% of total)
Chlorophyll a	1	1	1	49
TSS	1	1	1	5
Ammonia-N	1	1	1	5
Nitrite-N	1	1	1	5
Nitrate+Nitrite-N	1	1	1	5
Orthophosphate-P	1	1	1	5
Silica	1	1	1	5
pH	1	1	1	5

Dissolved Organic Carbon	1	1	1	5
Total Dissolved Phosphorus	1	1	1	5
Total Dissolved Nitrogen	1	1	1	5

LABORATORY QUALITY CONTROL

The laboratory quality control should consist of at least the analysis of laboratory reagent blanks, laboratory duplicates and laboratory fortified blanks with each set of samples analyzed.

The laboratory should analyze at least one laboratory reagent blank (LRB) with each set of samples. LRB data are used to assess contamination from the laboratory environment. If an analyte value in the LRB exceed the minimum detection limit (MDL), then laboratory or reagent contamination should be suspected. When the LRB value constitutes 10% or more of the analyte concentration for a sample, duplicates of the sample must be prepared and analyzed again after the source of contamination has been corrected and acceptable LRB values have been obtained.

The laboratory should analyze at least one laboratory fortified blank (LFB) with each set of samples. The LFB must be a concentration that is within the daily calibration range. The LFB data are used to calculate accuracy as percent recovery. If the recovery of the analyte falls outside the required control limits of 90-110%, the source of the problem should be identified and resolved before continuing the analyses.

The laboratory should analyze at least one duplicate with each set of samples.

The MDL's, preservation and holding times are listed in Table 6.

Table 6: Laboratory minimum detection limits, number of samples and preservative.

Analyte	Sample Matrix	Number of Samples/trip	MDL	Preservative
Chlorophyll a	NA	49	0.05 µg/L	Liquid N
TSS	Total	49	0.1 mg/L	4°C; 7 days
Ammonia-N	Dissolved	49	0.3 µg N/L	Chloroform; ASAP
Nitrite-N	Dissolved	49	0.075 µg N/L	Freezing; 2 weeks
Nitrate+Nitrite-N	Dissolved	49	0.075 µg N/L	Freezing; 2 weeks
Orthophosphate-P	Dissolved	49	0.7 µg P/L	Freezing; 2 months
Silica	Dissolved	49	1.2 µg Si/L	Freezing; 2 months
pH	NA	49	0.004 pH units	4°C; ASAP
Dissolved Organic Carbon	Dissolved	49	4 µg C/L	Freezing, 2 months
Total Dissolved Phosphorus	Total Dissolved	49	0.3 µg P/L	Freezing; 2 months
Total Dissolved Nitrogen	Total Dissolved	49	4 µg N/L	Freezing; 2 months

EQUIPMENT CALIBRATIONS

The main piece of field equipment used on the water quality monitoring trips is the Sontek/YSI ADV 6600 Sonde. The sonde is a specialized system that will give accurate and precise results when properly calibrated and maintained. Maintenance and calibration procedures are fully described in the sondes operating manual.

The sonde should be calibrated according to the schedule in Table 7. All calibration check data will be recorded on the YSI calibration data log sheet (Appendix A) and archived at AOML.

Table 7: YSI Sonde calibration and maintenance schedule.

Sensor	Bi-monthly Calibrations	Bi-monthly Checks	Annual Factory Calibrations
Conductivity	X		X
Temperature		X	X
Pressure		X	X
Dissolved Oxygen	X		
pH	X		
Turbidity	X		
Chlorophyll	X		
Salinity	X		X

SAMPLE CUSTODY

The field data log sheet will act as the sample custody. All samples are analyzed at AOML. Below are the personnel who will be analyzing the laboratory samples.

1. Nutrients – Dr. Jia-Zhong Zhang and Charlie Fischer, Ocean Chemistry Division
2. Chlorophyll – Lloyd Moore and Charles Featherstone, Ocean Chemistry Division
3. Total Suspended Solids – Charles Featherstone, Ocean Chemistry Division
4. pH- Charles Featherstone, Ocean Chemistry Division
5. Dissolved Organic Carbon- Dr. Jia-Zhong Zhang and Charlie Fischer, Ocean Chemistry Division

Upon arrival at AOML the water samples will be processed and given to the appropriate personnel for analysis.

CORRECTIVE ACTION

Corrective actions will be implemented as required to rectify problems identified during the course of normal field and laboratory operations. Possible problems requiring corrective action include:

1. equipment malfunctions
2. analytical methodology errors
3. non-compliance with quality control systems

Equipment and analytical problems that require corrective action may occur during sampling and sample handling, sample preparation, and laboratory analysis. For non-compliance problems, steps for corrective action will be developed and implemented at the time the problem is identified. The individual who identifies the problem is responsible for notifying the Project Manager of the problem immediately.

REPORTING

A report will be prepared following completion of all monitoring activities. The report will contain a discussion and summary of monitoring activities, any deviations in either methods or procedures from this water quality monitoring plan, and sufficient text, tables and figures to provide the reader with an understanding of the methods used and the resultant data. Bi-monthly data summary sheets will be prepared and made available upon request.

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- Zhang, Jia-Zhong, Ortner, P.B., Fischer, C.J. and Moore, L.D., 1997. Determination of Ammonia in Estuarine and Coastal Waters by Gas Segmented Continuous Flow Colorimetric Analysis, EPA Method 349.0.
- Zimmermann, C.F. and Keefe, C.W., 1997. Determination of Orthophosphate in Estuarine and Coastal Waters by Automated Colorimetric Analysis, EPA Method 365.5.

APPENDIX A

PROJECT DATA LOGS

**NOAA-Atlantic Oceanographic and Meteorological Laboratory
Ocean Chemistry Division
Coastal Environments Section**

EQUIPMENT CALIBRATION FORM

Equipment Description: _____
Manufacturer: _____
Serial Number: _____
Model Number: _____

Calibration Date:
By:
Next Calibration Due:

Calibration Date:
By:
Next Calibration Due:

Calibration Date:
By:
Next Calibration Due:

Calibration Date:
By:
Next Calibration Due:

Calibration Date:
By:
Next Calibration Due:

Calibration Date:
By:
Next Calibration Due:

Calibration Date:
By:
Next Calibration Due:

Calibration Date:
By:
Next Calibration Due:

Calibration Date:
By:
Next Calibration Due:

**NOAA-Atlantic Oceanographic and Meteorological Laboratory
Ocean Chemistry Division
Coastal Environments Section**

EQUIPMENT MAINTENANCE FORM

Equipment Description: _____
Manufacturer: _____
Serial Number: _____
Model Number: _____

Maintenance Date:
By:
Maintenance Description:

Maintenance Date:
By:
Maintenance Description:

Maintenance Date:
By:
Maintenance Description:

Maintenance Date:
By:
Maintenance Description:

Maintenance Date:
By:
Maintenance Description:

Maintenance Date:
By:
Maintenance Description:

Maintenance Date:
By:
Maintenance Description:

Maintenance Date:
By:
Maintenance Description:

Maintenance Date:
By:
Maintenance Description:

**NOAA-Atlantic Oceanographic and Meteorological Laboratory
Ocean Chemistry Division
Coastal Environments Section**

pH DATA LOG SHEET

Cruise Name: _____ **Date:** _____

Sample #	Vial #	Amt. of Dye Added	Absorbance Units 434 nm	Absorbance Units 578 nm	Absorbance Units 725 nm

**-Atlantic Oceanographic and Meteorological Laboratory
Ocean Chemistry Division
Coastal Environments Section**

YSI CALIBRATION FORM

Date of Calibration:

Technician:

Serial Number:

Project Name:

Record battery voltage: _____

Turbidity wiper changed? Yes No

Chlorophyll wiper changed? Yes No

Wiper parks 180° from optics? Yes No

Wiper parks 180° from optics? Yes No

Note: Change wiper if probe will not park correctly

Note: Change wiper if probe will not park correctly

RECORD CALIBRATION VALUES

Conductivity: _____

pH 4: _____

pH 7: _____

pH 10: _____

ORP: _____

Turbidity (0 NTU): _____

Turbidity (10 NTU): _____

Turbidity (100 NTU): _____

Chlorophyll (0 µg/L): _____

DO: _____

Record following diagnostic numbers after calibration

Conductivity cell constant: _____ Range 5.0 +/-0.45

pH MV Buffer 4: _____ Range +177MV from 7 Buffer

pH MV Buffer 7: _____ Range 0MV +/-50MV

pH MV Buffer 10: _____ Range -177MV from 7 Buffer

DO Charge: _____ Range 50 +/-25

DO Gain: _____ Range 1.0 0.7 to 1.4

Pressure Offset: _____ Range 0 +/-6

ORP Offset: _____ Range 0 +/-100

Turbidity Offset: _____

Chlorophyll Offset: _____

Dissolved oxygen sensor output test (after DO calibration probe in saturated air). The following test will confirm proper operation of your DO sensor. The DO charge and gain must meet spec before proceeding.

Turn off the sonde, wait 60 seconds. Power up the sonde and go to Run Mode, watch the DO% output; it must display a positive number and decrease with each 4 second sample, eventually stabilizing to the calibration value in approximately 60 to 120 seconds. **Note:** You can disregard the first two samples, they can be affected by electronics warm up.

The ACCEPT/REJECT criteria is as follows:

The DO output in % must start at a positive number and decrease during the warm up. Example: 117, 117, 114, 113, 110, 107, 102, 100. Should the output display a negative number or start at a low number and climb up to the calibration point, the probe is rejected and must not be deployed.

ACCEPT REJECT

Notes: _____

NOAA-Atlantic Oceanographic and Meteorological Laboratory
Ocean Chemistry Division
Coastal Environments Section

FILTER TARE FORM

Filter ID #	Weight (mg)	Filter ID #	Weight (mg)	Filter ID #	Weight (mg)	Filter ID #	Weight (mg)

**NOAA-Atlantic Oceanographic and Meteorological Laboratory
Ocean Chemistry Division
Coastal Environments Section**

TSS DATA LOG SHEET

Filter ID #	Sample Bottle #	Filter & TSS (mg)	Blank Filter (mg)	TSS (mg)	Volume Filtered (L)	Concentration (mg/L)	Comments

**NOAA-Atlantic Oceanographic and Meteorological Laboratory
Ocean Chemistry Division
Coastal Environments Section**

EQUIPMENT DECONTAMINATION FORM

Equipment Description: _____
Cleaned By: _____
Date: _____

Check all that apply:

- Soaked in Lab Grade Detergent
- Rinsed with Tap Water
- Soaked in 10% HCL Overnight
- Rinsed with De-ionized Water
- Air Dry
- Stored in Clean Area

Equipment Description: _____
Cleaned By: _____
Date: _____

Check all that apply:

- Soaked in Lab Grade Detergent
- Rinsed with Tap Water
- Soaked in 10% HCL Overnight
- Rinsed with De-ionized Water
- Air Dry
- Stored in Clean Area

Equipment Description: _____
Cleaned By: _____
Date: _____

Check all that apply:

- Soaked in Lab Grade Detergent
- Rinsed with Tap Water
- Soaked in 10% HCL Overnight
- Rinsed with De-ionized Water
- Air Dry
- Stored in Clean Area

APPENDIX B

FIELD QUALITY CONTROL REQUIREMENTS DEP-SOP-001/01

DEP-SOP-001/01
FQ 1000 Field Quality Control Requirements**FQ 1000. FIELD QUALITY CONTROL
REQUIREMENTS**

Field quality control measures monitor the sampling event to ensure that the collected samples are representative of the sample source and that the field-collected data have stated limits of precision and accuracy.

1. Field-collected blanks must demonstrate that the collected samples have not been contaminated by:
 - The sampling environment
 - The sampling equipment
 - The sample container
 - The sampling preservatives
 - Sample transport
 - Sample storage
2. Field Measurement Quality Controls must demonstrate that
 - The instrument was properly calibrated; and
 - The instrument maintained acceptable calibration during use.

FQ 1100. Sample Containers

Sample containers must be free from contamination by the analytes of interest or any interfering constituents and must be compatible with the sample type.

FQ 1200. Sampling Operations

1. When collected, analyze all quality control samples for the same parameters as the associated samples.
 - 1.1. When collected, collect blanks for the following parameter groups and tests:
 - Volatile Organics
 - Extractable Organics
 - Metals
 - Ultratrace Metals
 - Inorganic Nonmetallics
 - Radionuclides
 - Petroleum Hydrocarbons and Oil & Grease
 - Volatile Inorganics
 - Aggregate Organics except Biochemical Oxygen Demand
 - 1.2. Blanks are not required for:

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FQ 1000 Field Quality Control Requirements

- Microbiological (all types)
 - Toxicity
 - Field parameters such as pH, Specific Conductance, Residual Chlorine, Temperature, Light Penetration, Dissolved Oxygen, ORP and Salinity,
 - Radon
 - Algal Growth Potential
 - Biological Community
 - Physical and Aggregate Properties
 - Biochemical Oxygen Demand
2. Preserve, transport, document and handle all quality control samples as if they were samples. Once collected, they must remain with the sample set until the laboratory has received them.
 3. Prepare equipment blanks by rinsing the sampling equipment set with the appropriate type of analyte-free water and collecting the rinsate in appropriate sample containers (see FQ 1100).
 4. Except for trip blanks, prepare all quality control samples **on-site in the field**.
 - 4.1. Do not prepare precleaned equipment blanks in advance at the base of operations.
 - 4.2. Do not prepare field-cleaned equipment blanks after leaving the sampling site.
 5. Perform and document any field QC measures specified by the analytical method (such as trip blanks for volatile organics).

FQ 1210. QUALITY CONTROL BLANKS

FQ 1211. Precleaned Equipment Blanks

1. USE: Monitors on-site sampling environment, sampling equipment decontamination, sample container cleaning, the suitability of sample preservatives and analyte-free water, and sample transport and storage conditions.
2. Collect these blanks on sampling equipment that has been brought to the site precleaned and ready for use.
3. Collect these blanks before the equipment set has been used.

FQ 1212. Field-Cleaned Equipment Blanks

1. USE: Monitors on-site sampling environment, sampling equipment decontamination, sample container cleaning, the suitability of sample preservatives and analyte-free water, and sample transport and storage conditions.
2. Collect these blanks using sampling equipment that has been cleaned in the field (i.e., between sampling points).

FQ 1213. Trip Blanks

1. USE: Monitors sample container cleaning, the suitability of sample preservatives and analyte-free water, and both contain and sample transport and storage conditions.

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FQ 1000 Field Quality Control Requirements

2. These blanks are applicable if samples are to be analyzed for volatile constituents (volatile organics, methyl mercury, etc.).
3. The organization that is providing the VOC vials must provide the trip blanks by filling one or more VOC vials with analyte-free water.
4. Place a set of trip blanks in each transport container used to ship/store empty VOC vials. They must remain with the VOC vials during the sampling episode and must be transported to the analyzing laboratory in the same shipping or transport container(s) as the VOC samples.
5. Trip blanks must be opened **only** by the laboratory after the blank and associated samples have been received for analysis.

FQ 1214. Field Blanks

1. USE: Monitors on-site sampling environment, sample container cleaning, the suitability of sample preservatives and analyte-free water, and sample transport and storage conditions.
2. Prepare field blanks by pouring analyte-free water into sample containers for each parameter set to be collected.
3. Field blanks are not required if equipment blanks (FQ 1211 or FQ 1212) are collected.

FQ 1220. FIELD DUPLICATES

1. USE: Designed to measure the variability in the sampling process.
2. GENERAL CONSIDERATIONS:
 - 2.1. Collect duplicates by **repeating** (simultaneously or in rapid succession) the entire sample acquisition technique that was used to obtain the first sample.
 - 2.1.1. Collect, preserve, transport and document duplicates in the same manner as the samples. **These samples are not considered laboratory duplicates.**
 - 2.2. If collected, analyze field duplicates for the same parameters as the associated samples.
 - 2.3. When possible, collect duplicate samples from sampling locations where contamination is present.
 - 2.4. Field duplicates must be collected if required by the analytical method.

FQ 1221. Water Duplicates

Collect water duplicates by sampling from successively collected volumes (i.e., samples from the next volume of sample water).

FQ 1222. Soil Duplicates

Collect soil duplicates from the same sample source (i.e., soil from the same soil sampling device).

FQ 1230. MANDATORY FIELD QUALITY CONTROLS

1. The respondent, permittee or contractor and the sampling organization are responsible for ensuring that blanks (excluding trip blanks) are collected at a minimum of 5% of each reported

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FQ 1000 Field Quality Control Requirements

test result/matrix combination for the life of a project. Collect at least one blank for each reported test result/matrix combination each year.

- 1.1. If a party wishes to claim that a positive result is due to external contamination sources during sample collection, transport or analysis, then at least one field collected blank (excludes trip blanks) must have been collected at the same time the samples were collected and analyzed with the same sample set.
2. When collecting a set of blanks, use the following criteria:
 - 2.1. Equipment Blanks:
 - 2.1.1. Collect field-cleaned equipment blanks if any sample equipment decontamination is performed in the field.
 - 2.1.2. If no decontamination is performed in the field collect precleaned equipment blanks if the equipment is not certified clean by the vendor or the laboratory providing the equipment.
 - 2.2. Field Blanks:
 - 2.2.1. Collect field blanks if no equipment except the sample container is used to collect the samples or if the sampling equipment is certified clean by the vendor or the laboratory providing the equipment.
 - 2.3. Trip Blanks:
 - 2.3.1. These blanks are applicable if samples are to be analyzed for volatile organic constituents. See FQ 1213 for frequency, preparation and handling requirements.
3. OPTIONAL QUALITY CONTROL MEASURES
 - 3.1. The method or project may require collection of additional quality control measures as outlined in FQ 1210 (Blanks), FQ 1220 (Duplicates) and FQ 1240 (Split Samples).

FQ 1240. SPLIT SAMPLES

The FDEP or the client may require split samples as a means of determining compliance or as an added measure of quality control. Unlike duplicate samples that measure the variability of both the sample collection and laboratory procedures, split samples measure only the variability **between** laboratories. Therefore, the laboratory samples must be subsamples of the same parent sample and every attempt must be made to ensure sample homogeneity.

Collect, preserve, transport and document split samples using the same protocols as the related samples. In addition, attempt to use the same preservatives (if required).

If split samples are incorporated as an added quality control measure, the FDEP recommends that all involved parties agree on the logistics of collecting the samples, the supplier(s) of the preservatives and containers, the analytical method(s), and the statistics that will be used to evaluate the data.

FQ 1241. Soils, Sediments, Chemical Wastes and Sludges

Collecting split samples for these matrices is not recommended because a true split sample in these matrices is not possible.

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FQ 1000 Field Quality Control Requirements

FQ 1242. Water

Collect split samples for water in one of two ways:

1. Mix the sample in a large, appropriately precleaned, intermediate vessel (a churn splitter is recommended). This method shall not be used if volatile or extractable organics, oil and grease or total petroleum hydrocarbons are of interest. While continuing to thoroughly mix the sample, pour aliquots of the sample into the appropriate sample containers. Alternatively:
2. Fill the sample containers from consecutive sample volumes **from the same sampling device**. If the sampling device does not hold enough sample to fill the sample containers, use the following procedure:
 - 2.1. Fill the first container with half of the sample, and pour the remaining sample into the second container.
 - 2.2. Obtain an additional sample, pour the first half into the **second** container, and pour the remaining portion into the first container.
 - 2.3. Continue with steps described in sections 2.1 and 2.2 above until both containers are filled.

FQ 1250. QUALITY CONTROL DOCUMENTATION

1. Document all field quality control measures in the permanent field records.
2. At a minimum, record the following information:
 - The type, time and date that the quality control sample was collected; and
 - The preservative(s) (premeasured or added amount) and preservation checks performed.
3. If blanks are collected/prepared by the field organization, maintain records of the following:
 - Type of analyte-free water used;
 - Source of analyte-free water (include lot number if commercially purchased);
 - A list of the sampling equipment used to prepare the blank.

If items above are specified in an internal SOP, you may reference the SOP number and revision date in the field notes. Note any deviations to the procedure in the field notes.
4. For duplicates, record the technique that was used to collect the sample.
5. For split samples, identify the method used to collect the samples and the source(s) of the sample containers and preservatives.

FQ 1300. References

1. Florida Department of Environmental Protection, DEP Standard Operating Procedures for Laboratory Operations and Sample Collection Activities, DEP QA-001/92, September 1992.
2. U.S. Environmental Protection Agency, Region 4, Environmental Investigations Standard Operating Procedures and Quality Assurance Manual, May 1996.