HOLLYWOOD TRACER AND COASTAL WATER QUALITY MONITORING PLAN

(Photo by C. Featherstone, 2007)

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INTRODUCTION

The present document provides a water quality monitoring (WQM) plan for the coastal ocean waters extending from the area 2.5 km south of the Hollywood ocean outfall to a location just north of the Port Everglades Inlet. The Hollywood coastal area WQM is part of a comprehensive plan that encompasses Miami-Dade, Broward and Palm Beach counties. The northern extent of the Hollywood WQM concludes where the southern most part of the Broward WQM begins. The area includes both the Hollywood ocean outfall and the Port Everglades Inlet. The planned monitoring period is for one year. The present document details the goals/objectives and methodologies of the water quality monitoring plan. Input and recommendations for plan development or change is welcomed from interested parties including the Florida Department of Environmental Protection, the Broward County 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 the 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 septic discharge. Only a limited database of nutrient and water mass type parameters exists for the coastal ocean area of interest. The present water quality monitoring program will measure a suite of parameters monthly at fifteen different sampling stations.

SITE LOCATION AND DESCRIPTION

The Hollywood ocean outfall is located 10,000 feet off of Hollywood Beach in southern Broward County at a depth of approximately 93 feet. The area is also home to a coral reef system which is located offshore of Hollywood Beach and Broward County (Figure 1). This area forms a section of the 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 Port Everglades Inlet is located and discharges to the north and west of the reef system, while the Hollywood Ocean Outfall is located and discharges in the vicinity of the reef system.

MONITORING GOALS AND OBJECTIVES

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

A. Tracer Studies

1. To conduct dye/tracer studies to monitor the far-field path and effluent dilution characteristics of the Hollywood Outfall plume. One dye/tracer study will be conducted during the dry season. A wet season tracer study was conducted June 7-9, 2004 (Wanninkhof et al., 2005).

B. Water Quality Monitoring

1. To obtain a database for water quality parameters including the following: (i) the nutrients Ammonia-N, Nitrite-N, Nitrate+Nitrite-N, Orthophosphate-P, Silicate, Total Phosphorus, Total Nitrogen (ii) Chlorophyll a, (iii) Total Suspended Solids, (iv) pH, (v) Dissolved Organic Carbon and (vi) Microbiological parameters.

2. To obtain vertical profiles of temperature and salinity essentially concomitantly with water quality samples.

TRACER STUDIES

Introduction

As part of the general characterization of the Hollywood outfall and plume a set of tracer studies are planned. The tracers contemplated are those which have been used in recent studies of the South Central outfall, the Hollywood outfall and the Boynton Inlet. These tracers are Rhodamine dye and sulfur hexafluoride. These injected tracers are called "extrinsic" tracers since they are not normally found in outfall plumes. Numerous Rhodamine dye studies were carried out during the Southeast Florida Ocean Outfall Experiment (SEFLOE). There are also" intrinsic" tracers contained within typical oceanic outfall plumes. Examples of intrinsic tracers include salinity deficit, acoustic backscatter, temperature anomalies, turbidity and selected chemical and biological substances. Intrinsic chemical and biological tracers are presently a subject of research and thus in a state of evolution. Each of the above tracers has both advantages and drawbacks.

Tracer Selection

The tracer or tracers selected for use in a single or multiple outfall study depend on the objectives of the study. If determining near-field, e.g. 5 km, dilution of a single outfall plume is of primary interest then a combination of Rhodamine dye, salinity deficit and acoustic backscatter has been shown to be effective.

If the objective of the study centers upon the use of tracers to guide physical, chemical and biological sampling then both intrinsic and extrinsic tracers should be used. Optimally, extrinsic tracer measurements should be made concurrently with the gathering of plume samples. The extrinsic tracer measurements can be made using concurrent approximately co-located with plume samples either via water samples, pumped water samples or both. The presence or absence of tracer material within a water sample serves to determine whether or not the water sample came from within or outside of the effluent plume.

If the objective of the study is to determine far field, e.g. 5km to 20km, or very long range e.g. 20km or more, effluent plume trajectories and dispersion then sulfur hexafluoride is appropriate. At these longer ranges quantities which are subject to regulation are at or below detection limits due to dilution. Generally, in the southeast Florida coastal zone at ranges greater than 10km or so, another plume, e.g. an inlet plume is encountered so that the phenomenon of "interfering plumes" can occur.

If the objective of the study is to examine cumulative effects of multiple outfall plumes then sulfur hexafluoride, or other long-range, tracers should be used, possibly in combination.

Method of Tracer Injection

Two modalities of tracer injection have been used by AOML personnel in outfall plume studies: (a) constant tracer injection and (b) flow proportional tracer injection. In method (a) the flow of tracer injectate into the exiting outfall pipe flow is held constant so that when in-pipe effluent flow variations occur tracer concentrations either increase(effluent flow decreasing) or decrease (effluent flow increasing). In method (b) an effluent flow feedback loop is utilized, employing accurate real-time effluent flow data, so that decreasing in-pipe effluent flow results in decreasing tracer injectate flow and vice-versa. Typically tracers have been injected for a 24 hour time period.

Seasonal Tracer Studies

At a minimum at least two tracer studies should be conducted per outfall. One tracer study to be carried out under winter time conditions and one under summer time conditions. The reason for two studies is to examine the effect of changing water column stratification on the dispersing effluent plume.

Field Methodology

Prior to the commencement of dye injection substantial background information is obtained. Ambient currents are monitored, initial acoustic reconnoiters of plume disposition are made, salinity and temperature depth profiles, and water samples are obtained. All systems are checked for proper functioning and quality control.

Once tracer injection commences a series of transects commences and sampling stations occupied. The effluent plume will be tracked to substantial ranges, likely tens of kilometers, and vertical mixing measurements accomplished with range. In-situ vertical mixing dye sensors may also be deployed within the first five kilometers from the outfall.

The specific details of the tracking plan will be determined in discussions with FDEP personnel and Broward County personnel.

ADCP

An Acoustic Doppler Current Profiler (ADCP) will be placed north of the Hollywood Outfall and will operate for at least 18 months. The data will be compared with other ADCP data recently collected in the area to provide an estimate of the current regime.

WATER QUALITY MONITORING

Sampling Stations and Frequency

Water quality sampling will be conducted on a monthly basis. Sampling events will occur at 15 pre-established monitoring stations (Figure 1, Table 1). Each station will be sampled at three different depths: surface (A), mid-depth (B) and near bottom (C) (except for Stations HW-13 thru 15, surface only). 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. Efforts will be made to sample on an outgoing tidal cycle in order to get the impact of the Port Everglades Inlet on the sampling area. This will all be dependent upon timing and weather conditions.

These fifteen sites were chosen to include sites north, south, and inland of the Hollywood outfall; sites inland as well as along and just east of the reef track, and at locations inside and within the plume of the Port Everglades Inlet. The sites extend nearly 11km north to south. They comprise a segment of an overall FACE monitoring plan that extends from central Miami-Dade to southern Palm Beach Counties.

The list below contains the rationale for the selection of the sample stations for the Hollywood Outfall and surrounding areas. If we come to realize that other past or present monitoring activities have been or are being conducted in the area of concern, then we can modify the planned sampling stations to correspond to those sites.

- Station HW-1: Positioned approximately 2.6 km south of the Hollywood Outfall to determine background water quality up-current of the outfall.

- Station HW-2: Positioned at Harmful Algal Bloom (HAB 2005-2006) study site BR22 and approximately 1.4 km south of the Hollywood Outfall to determine background water quality up-current of the outfall.

- Station HW-3: Positioned approximately 0.5 km south of the Hollywood Outfall to determine near-field water quality up-current of the boil.

- Station HW-4: Positioned at the Hollywood Outfall to determine water quality of the boil.

- Station HW-5: Positioned approximately 0.5 km north of the Hollywood Outfall to determine the near-field water quality down-current of the boil.

- Station HW-6: Positioned approximately 1 km southwest of the Hollywood Outfall to determine the near-field water quality inland and southwest of the boil.

- Station HW-7: Positioned approximately 1 km northwest of the Hollywood Outfall to determine the near-field water quality inland and northwest of the boil.

- Station HW-8: Positioned approximately 3 km north of the Hollywood Outfall to determine the down-current water quality over the reef of the outfall plume.

- Station HW-9: Positioned approximately 5.5 km north of the Hollywood Outfall to determine the down-current water quality over the reef of the outfall plume.

- Station HW-10: Positioned at the OS1 site for Broward County's Pilot water quality monitoring program and located at Harmful Algal Bloom (HAB 2005-2006) study site JLU7. Just south of the Port Everglades entrance.

- Station HW-11: Positioned approximately 2.6 km east of the entrance to Port Everglades to determine water quality of the plume exiting the inlet.

- Station HW-12: Positioned at the OS2 site for Broward County's WQM. Just north of Port Everglades Inlet to determine water quality of the plume exiting the inlet.

- Station HW-13: Positioned at the entrance of Port Everglades to determine Inlet water quality exiting the inlet.

- Station HW-14: Positioned inside the Port Everglades inlet to determine inlet water quality.

- Station HW-15: Positioned inside the Port Everglades inlet to determine inlet water quality.

Table 1: Water Quality Sampling Sites

Station	Latitude	Longitude	Distance to HW o.f. (km)	Distance to Pt.Ev In. (km)
HW-1A	25.99542	-80.08915	-2.65	-11.10
HW-1B	25.99542	-80.08915	-2.65	-11.10
HW-1C	25.99542	-80.08915	-2.65	-11.10
HW-2A	26.00583	-80.08695	-1.43	-9.98
HW-2B	26.00583	-80.08695	-1.43	-9.98
HW-2C	26.00583	-80.08695	-1.43	-9.98
HW-3A	26.01444	-80.08616	-0.52	-9.10
HW-3B	26.01444	-80.08616	-0.52	-9.10
HW-3C	26.01444	-80.08616	-0.52	-9.10
HW-4A	26.01912	-80.08590	0.00	-8.61
HW-4B	26.01912	-80.08590	0.00	-8.61
HW-4C	26.01912	-80.08590	0.00	-8.61
HW-5A	26.02416	-80.08589	-0.56	-8.07
HW-5B	26.02416	-80.08589	-0.56	-8.07
HW-5C	26.02416	-80.08589	-0.56	-8.07
HW-6A	26.01443	-80.09484	-1.03	-8.92
HW-6B	26.01443	-80.09484	-1.03	-8.92
HW-6C	26.01443	-80.09484	-1.03	-8.92
HW-7A	26.02442	-80.09427	-1.02	-7.83
HW-7B	26.02442	-80.09427	-1.02	-7.83
HW-7C	26.02442	-80.09427	-1.02	-7.83
HW-8A	26.04483	-80.09267	-2.94	-5.67
HW-8B	26.04483	-80.09267	-2.94	-5.67
HW-8C	26.04483	-80.09267	-2.94	-5.67
HW-9A	26.06766	-80.08501	-5.40	-3.79
HW-9B	26.06766	-80.08501	-5.40	-3.79
HW-9C	26.06766	-80.08501	-5.40	-3.79
HW-10A	26.08273	-80.09554	-7.12	-1.87
HW-10B	26.08273	-80.09554	-7.12	-1.87
HW-10C	26.08273	-80.09554	-7.12	-1.87
HW-11A	26.09390	-80.08357	-8.32	-2.61
HW-11B	26.09390	-80.08357	-8.32	-2.61
HW-11C	26.09390	-80.08357	-8.32	-2.61
HW-12A	26.10224	-80.09360	-9.27	-1.88
HW-12B	26.10224	-80.09360	-9.27	-1.88
HW-12C	26.10224	-80.09360	-9.27	-1.88
HW-13A	26.09350	-80.10971	-8.61	0.00
HW-14A	26.09424	-80.11556	-8.86	-0.59
HW-15A	26.09011	-80.11448	-8.39	-0.61

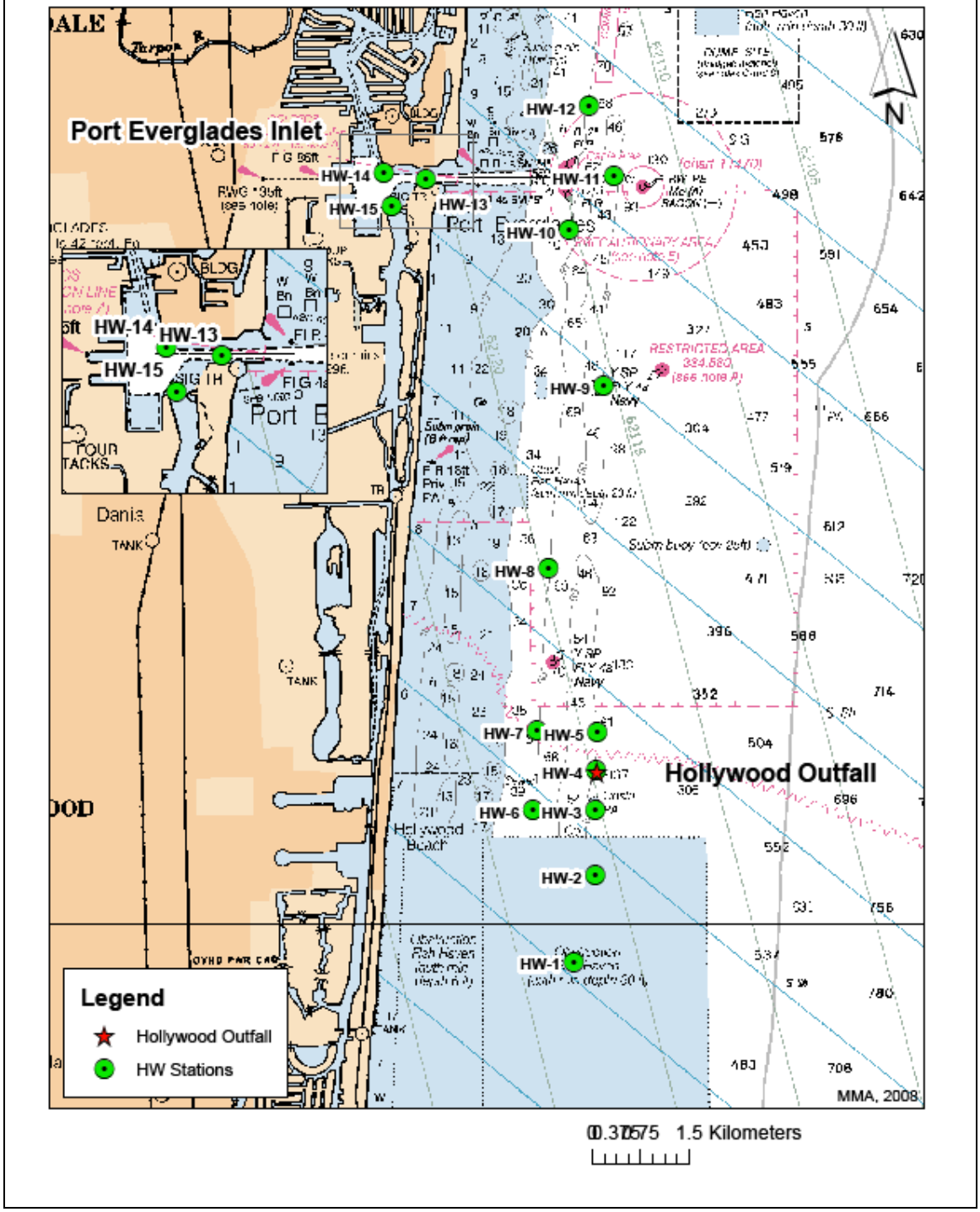

Figure 1: Map of station locations. Red star indicates location of the Hollywood Ocean Outfall. Numbers indicate sample station. Field parameters are shown in Table 2 and will be collected according to standard operating procedures.

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

WATER COLUMN PROFILES
Conductivity (mS/cm)
Temperature (^{0}C)
Depth (m)
Dissolved Oxygen (mg/L)
pH (units)
Salinity (ppt)
Turbidity (NTU)
Chlorophyll a (µg/L)
DISCRETE WATER SAMPLES
Nutrients (µM)
Chlorophyll a (µg/L)
pH (units)
Total Suspended Solids (mg/L)
Dissolved Organic Carbon (mg/L)
Microbiology

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

Sampling Vessel

Water quality monitoring will be conducted using an appropriate sized boat (e.g. 46′ launch) or equivalent that can accommodate the sampling equipment, a boat captain and up to 4 technicians. Samples will be collected using a portable winch, which will lower a SBE 19-plus CTD (conductivity, temperature, and depth recorder) and ECO water sampler with Niskin bottles (Seabird Electronics, Bellevue, WA) to the appropriate sample depths (Figure 2).

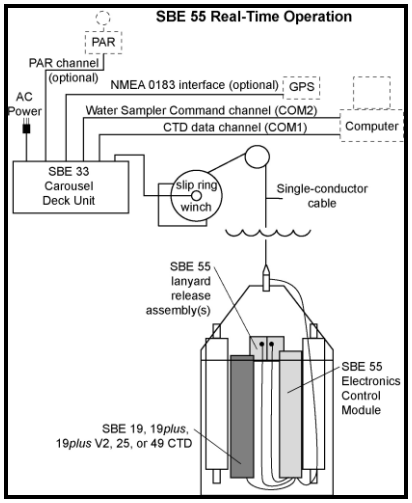

Figure 2: Schematic diagram of the ECO water sampler and CTD system used for water sample collection.

Equipment Decontamination

All sample bottles and sampling devices (Niskin bottles) used in this monitoring program must be free of residual nutrients. Pre-field and post-field cleaning will consist of washing all sample bottles and sampling devices (Niskin bottles) in lab grade phosphate free detergent, rinsing with tap water, followed by soaking with 10% HCL (v/v) (except Niskin, Chlorophyll & TSS bottles) 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 and left to dry.

All sample bottles will have a custody seal placed over the cap before being stored in the appropriate cooler, which will be initialed and dated by the technician responsible for cleaning the equipment. The Niskin bottles will be cleaned and attached to the ECO sampler rosette, after cleaning aluminum foil will be placed at each end of the bottle along with an initialed and dated custody seal before being placed in storage. This will avoid potential contamination of the equipment while being stored and during transport to the sampling stations. All cleaned equipment will be stored in a clean environment. Equipment cleaning will be archived in the Equipment Cleaning log book by filling out the equipment decontamination form in Appendix A.

In-field cleaning of sampling equipment (Niskin bottles) will consist of rinsing the bottles with fresh water and allowing the bottles to sit at their sampling depths for 60 seconds 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 at the time of sample acquisition.

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 log book. 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 HW for the project name (Hollywood). An example of the sample designation follows:

HW-1A

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:

HW-1A-X

FIELD SAMPLE COLLECTION METHODS

Water Column Data Collection

A CTD cast will be conducted at each monitoring station. Each time the CTD is turned on, 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 CTD unit will be equilibrated with sample water. The CTD unit will be turned on, lowered into the water until the entire unit is submerged, and held stationary for 60 seconds. The CTD 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, chlorophyll a and microbiology. Once on site the depth will be determined from the boat using its depth sounder. The CTD rosette will be lowered through the water column and two 4L Niskin bottles will be closed at near bottom, mid depth and surface on the upcast to collect water for sampling. The CTD rosette will be retrieved and sample water withdrawn from the appropriate Niskin bottles for each depth and placed in pre-labeled custody sealed sample containers. All sample bottles should be rinsed three times with sample water before collecting the final sample. Sample containers will be placed on ice (4^0C) in storage their appropriate coolers aboard the boat and transported back to AOML for processing and analysis.

Nutrient samples will be filtered through 0.45 um membrane filters using a 50 ml syringe and collected in 50 ml test tubes. Wash the filter before use by passing 50 ml of sample water through the filter. Care must be taken to avoid the contamination of nutrient samples especially at low concentrations. 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. Samples should be preserved by the addition of one to two drops of chloroform, cap firmly and place upright in a test tube rack in the designated sample cooler on ice (4^0C). TP and TN samples will be collected in 1-L acid cleaned brown bottles, stored on ice and filtered at AOML.

Chlorophyll samples are filtered on board the boat and placed in labeled vials and preserved in Liquid Nitrogen.

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:

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

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

pH Analysis

The pH must be measured as soon as possible following the collection of the water samples. pH will be determined using a hand held Beckman 200 series pH meter. Once water samples are on board and have been transferred from the Niskin bottles into 1-L sample bottles the probe will be inserted into each sample bottle. After insertion the probe will be allowed to stabilize, once the probe has stabilized the pH reading will be recorded on the field data sampling sheet for each designated sampling site.

Nutrient Analysis

Analyses will be conducted using the following EPA methods for dissolved nutrients. The dissolved inorganic form of nitrogen and phosphorus are measured because this form is more readily available for uptake by marine biota (algae). Therefore, it may be the most useful indicator of immediate potential impacts such as algae blooms. Total nitrogen and total phosphorus (non EPA Method) will include the particulate form.

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 ^{0}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 id 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 440.0 will be used to measure the total nitrogen concentration for each station (Zimmermann et al, 1997). An accurately measured amount of particulate matter from a water sample is combusted at 975 ^{0}C using an elemental analyzer. The combustion products are passed over a copper reduction tube to convert

the oxides of N into molecular N. Carbon dioxide, water vapor and N are homogeneously mixed at a known volume, temperature and pressure. The mixture is released to a series of thermal conductivity detectors/traps, measuring in turn by difference, hydrogen (as water vapor), C (as carbon dioxide) and N (as N_2).

The method of Cembella et al (1986) will be used to measure the total phosphorous concentration for each station. This method determines the amount of total phosphorous in seawater by magnesium nitrate oxidation of the organic component concomitant with depolymerization of polyphosphate residues, followed by the standard molybdate colorimetric determination of the liberated orthophosphate. The method will be modified to determine the amount of particulate and dissolved phosphorus.

Dissolved Organic

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 680^0C. 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 $60\ ^0$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 monthly monitoring cruise. Data is recorded on the filter tare log sheet found in Appendix A.

Nutrient Analysis

Nutrient samples must be frozen at the lab until analyzed. Samples are removed from the freezer and thawed. All samples must be at room temperature before analysis. Once at room temperature the samples are loaded into the sample tray and analyzed by the AA3 nutrient analyzer.
TP and TN samples will be filtered thru 47mm GF/F filters and the filters frozen at -20^{0}C until analyzed.

Dissolved Organic

Water samples are filtered through GF/F filters to remove any particulate materials from the sample. Before filtering, the filters are baked at 450 ^{0}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 Schimadzu Total Organic Carbon Analyzer V-CPH/CPN and the amount of dissolved organic carbon measured.

MOLECULAR MICROBIOLOGICAL ANALYSIS

Discrete water samples will be collected at all depths at the boil, 0.5 km north and south of the boil, at a reef station half way between the boil and inlet, and a surface sample from the inlet for the following microbiological parameters: (1) Viable Enterococci (IDEXX ENteroLert™ method), (2) Total Enterococci (qPCR method), (3) Human fecal source Enterococci esp marker (PCR method), (4) Total Bacteroides (qPCR method), (5) Human fecal source Bacteroides HF8 marker (qPCR method), (6) Human fecal source Bacteroides BacHum-UCD marker (qPCR method), (7) Human fecal source Methanobrevibacter smithii marker (qPCR method), (8) Human polymavirus marker = human urine marker (PCR method), (9) Human adenovirus (PCR method), (10) Norovirus group (PCR method) and (11) Enterovirus group (PCR method).

In addition to those parameters list above discrete water samples will be collected for parasite cysts and oocysts at the surface for each outfall boil and 0.5 km downcurrent of each outfall boil. These discrete surface samples will be tested for Cryptosporidium and Giardia by EPA method 1623.

Quantitative PCR:

General Enterococci 23S rRNA gene
Forward primer: 5'-AGAAATTCCAAACGAACTTG-3'
Reverse primer: 5'-CAGTGCTCTACCTCCATCATT-3"
Probe: 5'-6FAM-TGGTTCTCTCCGAAATAGCTTTAGGGCTA-BHQ-3'

Total *Lactococcus lactis* Control 16S rRNA gene
Forward primer: 5'-GCTGAAGGTTGGTACTTGTA-3'
Reverse primer: 5'-TCAGGTCGGCTATGTATCAT-3'
Probe: 5'-6FAM-TGGATGAGCAGCGAACGGGTGA-BHQ-3'

Human-source Bacteroides HF8 gene cluster marker
Forward primer: 5'-ATCATGAGTTCACATGTCCG-3'
Reverse primer: 5'-CAATCGGAGTTCTTCGTG-3'
Probe: 5'-6FAM-TCCGGTAGACGATGGGGATGCGTT-BHQ-3'

Human-source Bacteroides HuBac marker
As per Layton et al., 2005

Norovirus and enterovirus qPCR kits by Cepheid Inc. as per manufacturer's instructions (with some modifications – please contact Dr. Sinigalliano for details)

Non-Quantitative PCR:

Human-source Enterococci esp gene:
As per Scot et al., 2005

Campylobacter jejuni *hipO* gene:
As per LaGier et al., 2004

Salmonella spp. *IpaB* gene:
As per Kong et al., 2005

Pathogenic E. coli strain O157:H7 *rfb* gene:
As per Maurer et al., 1999

Staphylococcus aureus clfA gene:
As per Mason et al., 2001

Human Adenovirus Hexon gene:
As per He and Jiang, 2005

Additional analysis of viruses conducted by Dr. Jill Stewart of the Oceans and Human Health Center at Hollings Marine Lab

Standards and Controls for quantitative PCR:

Quantitation standards for total bacteroides and human source bacteroides use purified genomic DNA from the culture *Bacteroides dorei*, measured by fluorescence with a Qubit Fluorometer using the Molecular Probes Quant-It kit for dsDNA. Quantitation units for these qPCR assays are in genome equivalents (which can then be expressed as relative cell numbers with some assumptions/caveats about average target copy number in the environmental population of target cells). Quantitation standards for total and human-specific *esp*-containing enterococci are based on purified genomic DNA from a culture of *Enterococcus faecium* that contains the *esp* marker (acquired from Dr. Troy Scott at BSC Laboratories). Quantitation units for these qPCR assays are in genome equivalents.

Extraction control: as above each sample is spiked before lysis and extraction with 10^5 cells of an enumerated control culture of *lactococcus lactis*. Variations in CT value of lactococcus indicate variations of extraction efficiency plus any potential inhibition. Variation due to inhibition is removed by comparing extraction controls to inhibition controls.

Inhibition controls: reactions of each sample run in triplicate, one replicate well of each sample gets spiked with known amount of target DNA. Variation in CT of spike corrected for background of unspiked for that sample indicate degree of inhibition.

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 quantative 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 ^{0}C	NA	90%
pH	± 0.2 units	NA	90%
Dissolved Oxygen	± 2%	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%
Silicate-Si	10%	10%	95%
Total Phosphorus	10%	10%	95%
Dissolved Organic Carbon	10%	10%	95%
Total Nitrogen	10%	10%	95%
Chlorophyll	20%	20%	95%
Total Suspended Solids	20%	20%	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 are 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 are 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:

$$RPD = \frac{|C_A - C_B|}{0.5(C_A + C_B)} \times 100$$

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 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 boil since this is the most likely area where contamination may occur if equipment is not properly cleaned. In addition to samples listed below a sample containing de-ionized water will be spiked with a known quantity of Ammonia to determine percent loss if any between time of inoculation in the field and analysis in the lab.

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	39
TSS	1	1	1	4
Ammonia-N	1	1	1	4
Nitrite-N	1	1	1	4
Nitrate+Nitrite-N	1	1	1	4
Orthophosphate-P	1	1	1	4
Silicate-Si	1	1	1	4
pH	0	0	0	4
Dissolved Organic Carbon	0	0	0	4
Total Phosphorus	0	0	0	4
Total Nitrogen	0	0	0	4

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	39	0.05 µg/L	Liquid N
TSS	Total	39	0.1 mg/L	4^0C; 7 days
Ammonia-N	Dissolved	39	0.3 µg N/L	Chloroform; ASAP
Nitrite-N	Dissolved	39	0.075 µg N/L	Freezing; 2 weeks
Nitrate+Nitrite-N	Dissolved	39	0.075 µg N/L	Freezing; 2 weeks
Orthophosphate-P	Dissolved	39	0.7 µg P/L	Freezing; 2 months
Silicate-Si	Dissolved	39	1.2 µg Si/L	Freezing; 2 months
pH	NA	39	0.004 pH units	4^0C; ASAP
Dissolved Organic Carbon	Dissolved	39	4 µg C/L	Freezing, 2 months
Total Phosphorus	Particulate/Dissolved	39	0.05 µg P/L	Freezing; 2 months
Total Nitrogen	Particulate/Dissolved	39	10.5 µg N/L	Freezing; 2 months

EQUIPMENT CALIBRATIONS

The main piece of field equipment used on the water quality monitoring trips is the SBE 19-plus CTD. The CTD 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 CTD's operating manual. The CTD should be calibrated according to the schedule in Table 7. All calibration check data will be recorded on the CTD calibration data log sheet (Appendix A) and archived at AOML.

Table 7: SBE 19-plus CTD calibration and maintenance schedule.

Sensor	Monthly Calibrations	Monthly Checks	Annual Factory Calibrations
Conductivity	X		X
Temperature		X	X
Pressure		X	X
Dissolved Oxygen	X		
pH	X		
Turbidity	X		
Chlorophyll	X		

SAMPLE CUSTODY

Completed chain-of-custody forms will be required for all samples to be analyzed. Chain-of-custody forms will be filled out by the field sampling crew during the sample collection events. The chain-of- custody form (Appendix A) will contain the samples sample ID number, date sampled, time sampled, matrix, bottle type and preservation if any, sample volume and analyte to be measured. The chain-of-custody form will accompany the samples to AOML. All samples are analyzed at AOML.

Upon arrival at AOML the samples will be processed and transferred to the appropriate personnel for analysis. Once the samples are transferred all samples will be recorded in a log book prior to analysis. Chain-of-custodies and log books will be stored at the appropriate work stations.

Sample Receipt

Samples are received in the log-in area where lab personnel are responsible for logging in the samples under the direction of the nutrient lab manager. If samples are brought to the nutrient lab after hours the samples are stored in designated freezers and/or refrigerators and logged-in first thing next business day.

Chain of Custody

Chain-of-Custody (CoC) procedures are followed for all samples submitted to the Nutrient Laboratory. All samples delivered to the lab should be accompanied by CoC records. This is necessary to preserve the traceability and security of samples. Samples are considered secure if they are in one's possession, within view, or in a secured area. The lab is considered secure because access during working hours is monitored and the lab is locked and under video surveillance during non-working hours. The CoC record is, therefore, used to document the change in possession from sampling to delivery to receipt by the laboratory.

Each sample should be clearly identifiable. The condition of the sample and/or container should be noted. Signatures of parties changing custody as well as date and time should be documented on the form. Clients may have forms of their own or use our CoC.

Collectors are required to include field data sheets with the submitted samples. An example of a field data sheet supplied by the Nutrient Lab is shown Appendix A. The following information is required:

1. Unique field ID
2. Date and time collected
3. Collector's name
4. Submitting agency
5. Sample matrix
6. Analysis required

If any of the above information is not present, an effort is made to reach the collector. If the information cannot be obtained in a timely manner the sample will be processed, but the results may be rejected if the proper information has not been obtained.

Sample Log-In

A master job log book is maintained at the log-in area of the Nutrient lab. The following information is entered into the log book to initiate a job:

1. Initials of person receiving and/or logging in the job
2. Date received

3. How samples were delivered to the lab, ie. customer, (designating the samples as having been delivered by an employee of the client) or specific agent (U.S. Mail, UPS, FedEx, etc.)
4. Assigned sequential job number (Laboratory Number)
5. Clients designated sample number or name
6. Project name and/or sampling location
7. Type of analysis (analyte)
8. Sample volume
9. Turnaround time
10. Contact information
11. Date analysis completed
12. Date results reported
13. Comments

At time of receipt, the temperature of the coolers is checked by looking for the presence of ice. If there is no ice present, the temperature of the samples is measured and recorded in the comments section of the log-in sheet. The personnel logging in the samples must verify the field data sheet information against the sample bottles, any discrepancies are resolved.

An assigned job/lab number is given to samples of a similar nature submitted together from one collector from a single event. These lab identification numbers are unique and have the format YY-Letter-xx, where YY is the year (08), Letter is (A, B, C, etc.) and xx is a number (01, 02, etc.) which is reset with each set of samples logged-in. Below is an example of a log-in identification lab number:

Sample 1 09A-01
Sample 2 09A-02
Sample 3 09A-03

The next set of samples submitted would then be,

Sample 1 09B-01
Sample 2 09B-02
Sample 3 09B-03

The letters are reset at the beginning of each year. Example of a log-in sheet is given in Appendix A.

LABORATORY CERTIFICATION

The nutrient laboratory at AOML is currently undergoing the process to obtain certification for the analysis of Ammonia-N, Nitrite-N, Nitrite+Nitrate-N, Orthophospahte-P, Silicate-Si, Total Phosphorus, Total Nitrogen and Dissolved Organic Carbon. Once certification has been obtained the CoC and other forms will be updated to reflect the certification.

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 final 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. In addition monthly data summary reports will be prepared and made available upon request within 45 days of sample collection. These reports will present the data in tabular and graphical form, along with stating and describing any deviations from the sampling plan which may have occurred during sample collection.

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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:
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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:

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

CHLOROPHYLL EXTRACTION DATA SHEET

Criuse Name: ____

Date: _________________

Tube #	Sample #	Volume Filtered	Volume Extract	F_0	F_a	Dilution Factor

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

FIELD DATA FORM

Project Name:

Date:

Field Personnel:

Weather Conditions: Storm (heavy rain), Rain (steady rain), Showers (intermittent rain), Overcast, Clear/Sunny, Windy, Calm, Other:_____

Sea conditions:_____

Station	Date	Time	Latitude	Longitude	CTD Cast #	Nutrient Bottle #	Chl a Bottle #	TSS Bottle #	TP Bottle #	TN Bottle #	DOC Bottle #	Micro Bottle #	pH value	Comments

Station	Date	Time	Latitude	Longitude	CTD Cast #	Nutrient Bottle #	Chl a (ml) filtered	TSS Bottle #	TP Bottle #	TN Bottle #	DOC Bottle #	Micro Bottle #	pH value	Comments

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

CTD CALIBRATION FORM

Date of Calibration:
Technician:
Serial Number:
Project Name:

Record battery voltage:

RECORD CALIBRATION VALUES

Conductivity:_____

pH 4:_____
pH 7:_____
pH 10:_____

Turbidity (0 NTU):_____
Turbidity (10 NTU):_____
Turbidity (100 NTU):_____

Chlorophyll (0 ug/L):_____

DO:_____

Record following diagnostic numbers after calibration

Conductivity cell constant:_____

pH MV Buffer 4:_____
pH MV Buffer 7:_____
pH MV Buffer 10:_____

DO Charge:_____
DO Gain:_____

Pressure Offset:_____

Turbidity Offset:_____

Chlorophyll Offset:_____

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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)

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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
- Custody Seal Attached (Dated and Signed)
- Wrapped in Al foil
- 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
- Custody Seal Attached (Dated and Signed)
- Wrapped in Al foil
- 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
- Custody Seal Attached (Dated and Signed)
- Wrapped in Al foil
- Stored in Clean Area

ATLANTIC OCEANOGRAPHIC & METEOROLOGICAL LABORATORIES
OCEAN CHEMISTRY DIVISION
COASTAL ENVIRONMENTS GROUP
4301 RICKENBACKER CAUSEWAY
MIAMI, FL 33149 305-361-4312 (PH); 305-361-4447 (FAX)

CHAIN OF CUSTODY

Project Name:	Collected By: Date/Time Collected:	Laboratory #:
Delivered By: Date/Time Delivered:	Received in Lab By: Date/Time Received:	Turnaround Time:

Sample ID	Date Sampled	Time Sampled	Matrix	Bottle Type & Preservation	Sample Volume (ml)	Analyte

Bottle Type: A=Amber Glass Btl; B=Bacteria bag/btl; NC=Nalgene LDPE White Btl; NB=Nalgene LDPE Brown Btl; Vial=V; Test Tube=TT
Preservatives: C=Chloroform; I=Ice; LN=Liquid Nitrogen; U=Unpreserved

Chain of Custody- Continued **LABORATORY #**

Sample ID	Date Sampled	Time Sampled	Matrix	Bottle Type & Preservation	Sample Volume (ml)	Analyte

Bottle Type: A=Amber Glass Btl; B=Bacteria bag/btl; NC=Nalgene LDPE White Btl; NB=Nalgene LDPE Brown Btl; Vial=V; Test Tube=TT
Preservatives: C=Chloroform; I=Ice; LN=Liquid Nitrogen; U=Unpreserved

Chain of Custody- Continued **LABORATORY #**

Sample ID	Date Sampled	Time Sampled	Matrix	Bottle Type & Preservation	Sample Volume (ml)	Analyte

Bottle Type: A=Amber Glass Btl; B=Bacteria bag/btl; NC=Nalgene LDPE White Btl; NB=Nalgene LDPE Brown Btl; Vial=V; Test Tube=TT
Preservatives: C=Chloroform; I=Ice; LN=Liquid Nitrogen; U=Unpreserved

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SAMPLE LOG-IN FORM LABORATORY #		Project Name	

Sample #	Laboratory #	Analyte	Sample Volume	Comments

Analysis Completed:	

Sent by	Carrier	Turnaround

Contact		Phone	
		Email	

	Date	Time	By	To
Recieved			LOT Signed?	

APPENDIX B

FIELD QUALITY CONTROL REQUIREMENTS
DEP-SOP-001/01

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:

- 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.

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

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.

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.