

**SFWMD  
COMPREHENSIVE  
QUALITY ASSURANCE  
PLAN**

**1999**

**WRE INVENTORY #383**



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SSL  
Ivanoff

Comprehensive Quality Assurance Plan #870166G ✓  
for  
South Florida Water Management District  
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Prepared by  
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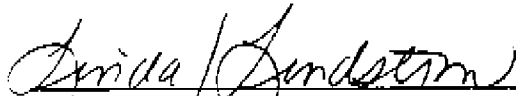
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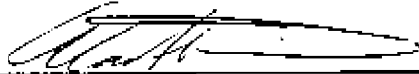
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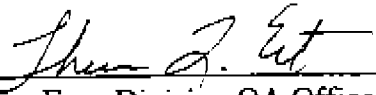
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Quality Assurance Section

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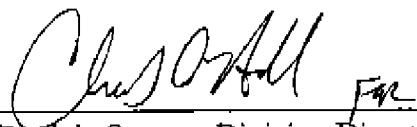
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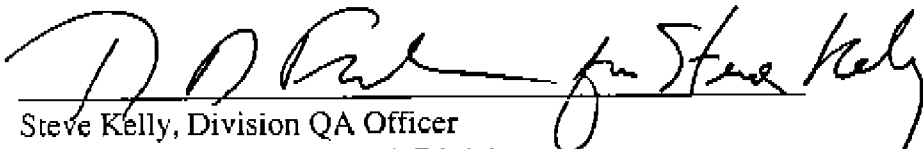
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Quality Assurance Section

**TABLE OF CONTENTS**  
**QA Plan Elements**

Section	Title	# of Pages	Revision Date
1.0	Title Page	3	06/15/99
2.0	Table of Contents	3	06/15/99
3.0	Statement of Policy	1	06/15/99
4.0	Organization and Responsibility	10	06/15/99
5.0	QA Targets For Precision, Accuracy and Method Detection Limits	8	10/27/99
6.0	Sampling Procedures	32	10/27/99
7.0	Sample Custody	16	06/15/99
8.0	Analytical Procedures	3	06/15/99
9.0	Calibration Procedures and Frequency	8	06/15/99
10.0	Preventative Maintenance	4	06/15/99
11.0	Quality Control Checks, Routines to Assess Precision and Accuracy, and Calculation of Method Detection Limits	6	10/27/99
12.0	Data Reduction, Validation and Reporting	10	10/27/99
13.0	Corrective Action	3	06/15/99
14.0	Performance and Systems Audits	14	10/27/99
15.0	Quality Assurance Reports	2	06/15/99

**FIGURES**

Figure #	Description	Page #	Revision Date
4.1	SFWMD Organization Chart	4.4	06/15/99
4.2	Department of Water Resources Evaluation Organization Chart	4.5	06/15/99
4.3	Water Quality Monitoring Division Organization Chart	4.6	06/15/99
4.4	Resource Assessment Division Organization Chart	4.7	06/15/99
4.5	Ecosystem Restoration Department Organization Chart	4.8	06/15/99
4.6	Regulation Department Organization Chart	4.9	06/15/99
4.7	Lake Okeechobee Watershed Water Quality-Okeechobee Service Ctr. Org. Chart	4.10	06/15/99
6.1	Inorganic Surface Water Sampling Procedure	6.17	06/15/99

**FIGURES (con't)**

Figure #	Description	Page #	Revision Date
7.1	Field Trip Check List	7.2	06/15/99
7.2	Sample Submission Diagram for Unfiltered Water	7.3	06/15/99
7.3	Sample Submission Diagram for Filtered Water	7.4	06/15/99
7.4	Chemistry Field Data Log, front page	7.5	06/15/99
7.4	Chemistry Field Data Log, back page	7.6	06/15/99
7.6	Sample Log-In to LIMS	7.7	06/15/99
7.7	Field Measurement Data Input Screen	7.8	06/15/99
7.8	Digestion Log	7.10	06/15/99
7.9	QC Results Log Form	7.11	06/15/99
12.1	Example of Log-in Report and System-generated Header sheet	12.8	06/15/99
12.2	Example of LIMS data report	12.9	06/15/99
14.1	Systems Audit Checklist	14.3	06/15/99

**TABLES**

Table #	Description	Page #	Revision Date
5.1	Laboratory Quality Assurance Objectives	5.2	06/15/99
5.2	Field Quality Assurance Objectives	5.8	06/15/99
6.1	Sampling Capabilities by Major Category	6.1	06/15/99
6.2	Grab Surface Water Quality Sampling Equip.	6.2	06/15/99
6.3	Groundwater Sampling Equipment	6.4	06/15/99
6.4	Soil/Sediment Sampling Equipment	6.5	06/15/99
6.5	Biological Tissues Sampling Equipment	6.5	06/15/99
6.6	Atmospheric Deposition Equipment	6.6	06/15/99
6.7	Trace Mercury Sampling Equipment	6.6	06/15/99
6.8	Macrobenthic Invertebrate Sampling Equip	6.7	06/15/99
6.9	Holding Time and Preservation for Water Inorganics	6.30	06/15/99
6.10	Holding Time and Preservation for Water Organics	6.31	06/15/99
6.11	Holding Times and Preservation for Sediments, Soils and Tissues	6.31	06/15/99
6.12	Holding Times and Preservation for Biologicals	6.31	06/15/99
6.13	Reagent and Standard Storage	6.32	06/15/99
9.2	Solutions Requiring Standardization	9.6	06/15/99
9.3	Laboratory Equipment Calibration	9.6	06/15/99

**TABLES (cont.)**

Table #	Description	Page #	Revision Date
9.4	Laboratory instrument Calibration	9.7	06/15/99
9.5	Field Instrument Calibration	9.8	06/15/99
10.1	Field Equipment Maintenance Schedule	10.2	06/15/99
10.2	Laboratory Equipment Maintenance Schedule	10.3	06/15/99
11.1	Field Quality Control Checks	11.2	06/15/99
11.2	Laboratory Quality Control Checks	11.3	06/15/99
11.3	Procedures Used to Determine Precision and Accuracy	11.7	06/15/99
12.1	Formulas Used for Calculations	12.2	06/15/99
13.1	Corrective Actions for the Laboratory	13.2	06/15/99
13.2	Corrective Actions for In-situ Measurements	13.3	06/15/99
13.3	Corrective Actions Resulting from Field QC	13.3	06/15/99

**APPENDICES**

Appendix ID	Description	# of Pages	Revision Date
A	Color Method SOP	9	03/01/99
B	Silica Method SOP	11	01/13/99
C	Soluble Reactive Phosphate	2	07/14/95
D	Alkaline Phosphatase Method SOP	8	10/01/94
E	Benthic Macroinvertebrate	18	07/14/95
F	Total Inorganic Carbon SOP & Analysis Sheet	6	10/27/99
G	Procedures for Collecting Sediment and Porewater Samples and Monitoring Sediment Deposition Rates in Wetlands	4	08/03/95
H	Standard Operating Procedure for Field Documentation	3	06/15/99



### **3.0 STATEMENT OF POLICY**

This document is a comprehensive quality assurance plan (CQAP) defining sampling and analytical protocols for the South Florida Water Management District (SFWMD or the District). These protocols encompass activities performed for surface water, estuarine systems, ground water, atmospheric deposition, biological tissue and sediment monitoring programs. The Water Quality Monitoring Division (WQMD) Laboratory of the SFWMD is certified by the Florida Department of Health (FDOH) as an environmental laboratory capable of performing metals, nutrients, and general parameter categories 1 & 2.

This CQAP is intended to be used as a reference, training guide, and statement of acceptable procedures to be used by SFWMD personnel collecting and analyzing samples and evaluating the quality and defensibility of the results obtained. It documents the minimum standards to be complied with for these activities and provides a reference for evaluating the procedures used during the time this CQAP is in effect.

The SFWMD is committed to the use of good quality assurance/quality control (QA/QC) management practices to produce data of verifiable quality.

## **4.0 Organization and Responsibility**

### **4.1 Capabilities**

The South Florida Water Management District conducts field sampling for surface water, ground water, atmospheric deposition, sediments, soils and biota. The District's laboratory is capable of performing analyses for inorganic anions, metals, physical properties, and other tests such as TOC and BOD, chlorophyll, periphyton, and macrobenthic invertebrates. Other analyses, including organics, pesticides, and ultra-trace mercury are performed by contract laboratories.

### **4.2 Key Personnel**

The following are key personnel associated with the collection and analysis of samples.

#### Water Resources Evaluation Department:

**Department Director:** Responsible for the allocation of resources throughout the department to meet the needs of the SFWMD for sampling and analytical services and championing the quality assurance program.

#### Water Quality Monitoring Division:

**Division Director:** Responsible for the allocation of resources, training of personnel, collection and analysis of samples, oversees the QA program for the District and reporting of results to meet the needs of the SFWMD for monitoring water quality.

**Field Operations Manager:** Responsible for overseeing field units within the division, ensuring that all mandate requirements are met and that monitoring programs are within compliance. Also serves as a back-up to the division director.

**Supervising Professional-QA Officer:** Responsible for assuring that the laboratory and field personnel adhere to the approved methods of sample collection, analysis, maintenance of the CQAP and laboratory certification, method validation studies, issuance of new methods, the administration of the internal and external laboratory audits, field audits and the review of legislation pertaining to laboratory quality assurance.

**Supervising Professional-Chemist:** Responsible for the management of the laboratory unit, budget preparation and allocation of resources within the laboratory, review of quality control results, review and approval of data, hiring and training of personnel and ensuring adherence to required quality control procedures.

**Senior Chemists:** Responsible for the direct supervision of the assigned shift or group, tracking and maintaining inventory, review of quality control results, review of data, release of samples, hiring and training of personnel and ensuring adherence to required quality control procedures.

**Senior Environmental Scientist-Special Projects, WQM:** Responsible for overseeing sample

collection for: i) ground water, ii) ambient program, iii) ultra-trace mercury and metals, and iv) organics and pesticides. This position is also responsible for special projects monitoring and for maintaining analytical and sampling contracts.

**Staff Environmental Scientists:** Responsible for project management, report generation, data review, and collecting samples.

**Supervising Professional-Field Units:** Responsible for management of field sample and data collection unit, hiring and training of personnel in sampling and QA/QC procedures, budgeting and resource allocation within the unit, design of sampling networks and research projects, review of laboratory data for specific projects.

**Supervising Scientific Associates:** Responsible for the allocation of personnel and equipment for surface water sampling, training of personnel in sampling and QA/QC procedures, review of quality control data, review of analytical results for specified projects and sample collection.

**LIMS Administrator:** Responsible for overseeing the Laboratory Information Management System (LIMS), regulating and training users and LIMS access, interacts with field, laboratory and project personnel in resolving LIMS-related issues.

**Staff Programmer Analyst, WQM:** Responsible for programming applications including LIMS, testing and installing software packages, and maintenance of the LIMS.

**Resource Assessment Division:**

**Division Director:** Responsible for the allocation of resources, training of personnel, collection of samples and supporting the quality assurance program within the division. Also responsible for overseeing reporting functions for various water quality monitoring programs.

**Unit Supervisors and Scientists (Senior Supervising Environmental Scientists and Hydrogeologist, Senior Supervising Engineer, Lead Engineer, Senior Environmental Scientists, Senior Supervising Engineering Associate):** Responsible for reviewing data and preparing reports for various monitoring programs and permits.

**Ecosystem Restoration and Regulation Departments:**

**Department Director:** Responsible for the allocation of resources throughout the department to meet the needs of the SFWMD for sampling and supporting the quality assurance program within their respective departments.

**Okeechobee Systems Research, Kissimmee River Restoration, Everglades Systems Research, Ecologically Engineered Systems Research, Everglades Regulation, Okccchobcc Service Center and Field Engineering:**

**Division Directors:** Responsible for the allocation of resources, training of personnel, collection of samples and supporting the quality assurance program within their respective division to meet the needs of the SFWMD for sampling services.

**Division Representative QA Officer:** Responsible for coordination of all project quality assurance plans and QA reports for the Division, review of quality control results for the projects, conducting field audits and training of division personnel in quality control procedures.

### **4.3 Organization Charts**

The following charts show the organization of the South Florida Water Management District.

Figure 4.1 - SFWMD organization showing the Governing Board, Executive and Deputy Directors and the major departments and offices.

Figure 4.2 - Water Resources Evaluation Department showing the reporting relationships to the Department Director.

Figure 4.3 - Water Quality Monitoring Division through the supervisory levels.

Figure 4.4 - Resource Assessment Division through the supervisory levels.

Figure 4.5 - Ecosystem Restoration Department through the supervisory levels for divisions conducting sample collection.

Figure 4.6 - Regulation Department through the supervisory levels for divisions conducting sample collection.

# SOUTH FLORIDA WATER MANAGEMENT DISTRICT

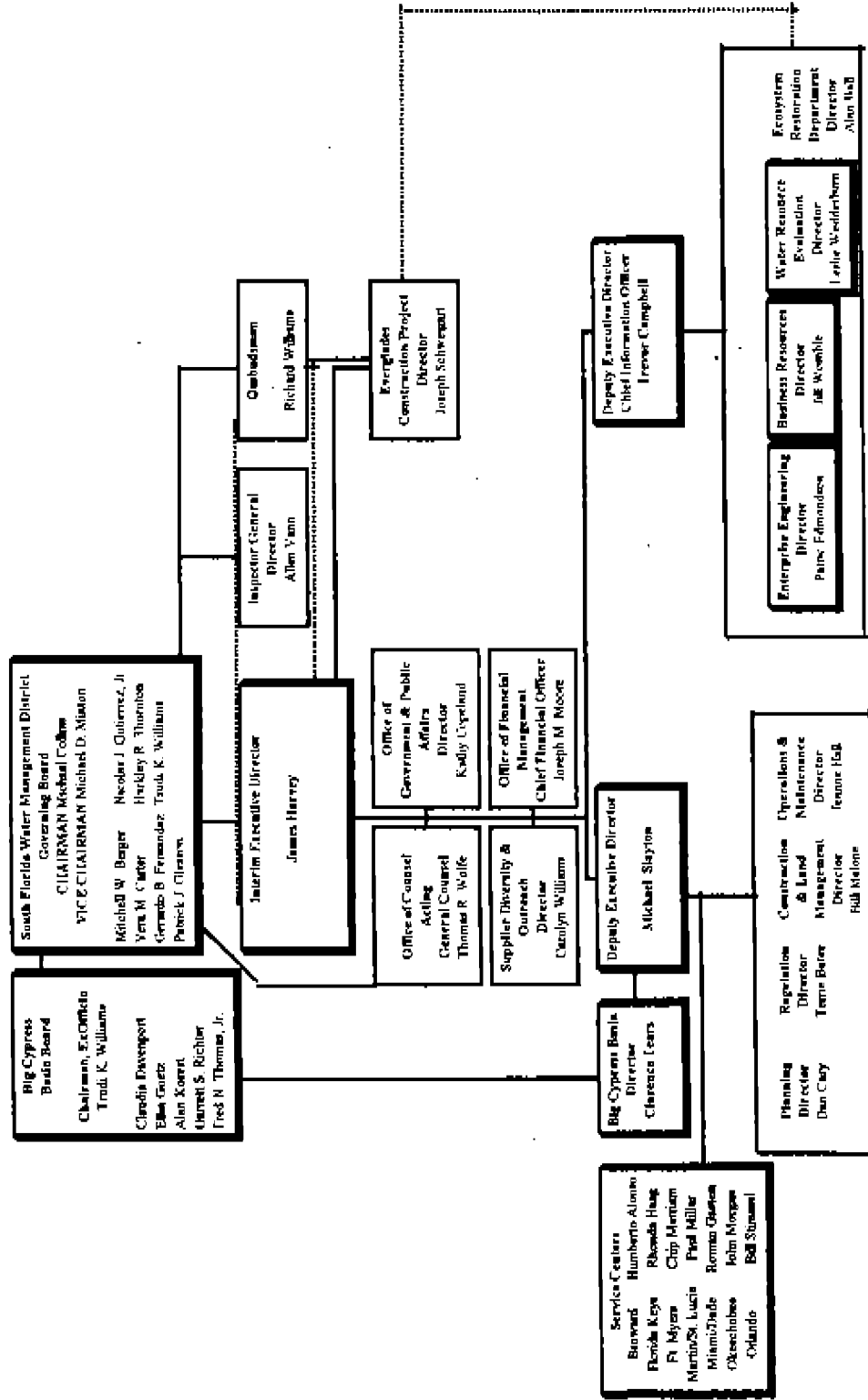


Figure 4.1 – South Florida Water Management District's General Organization

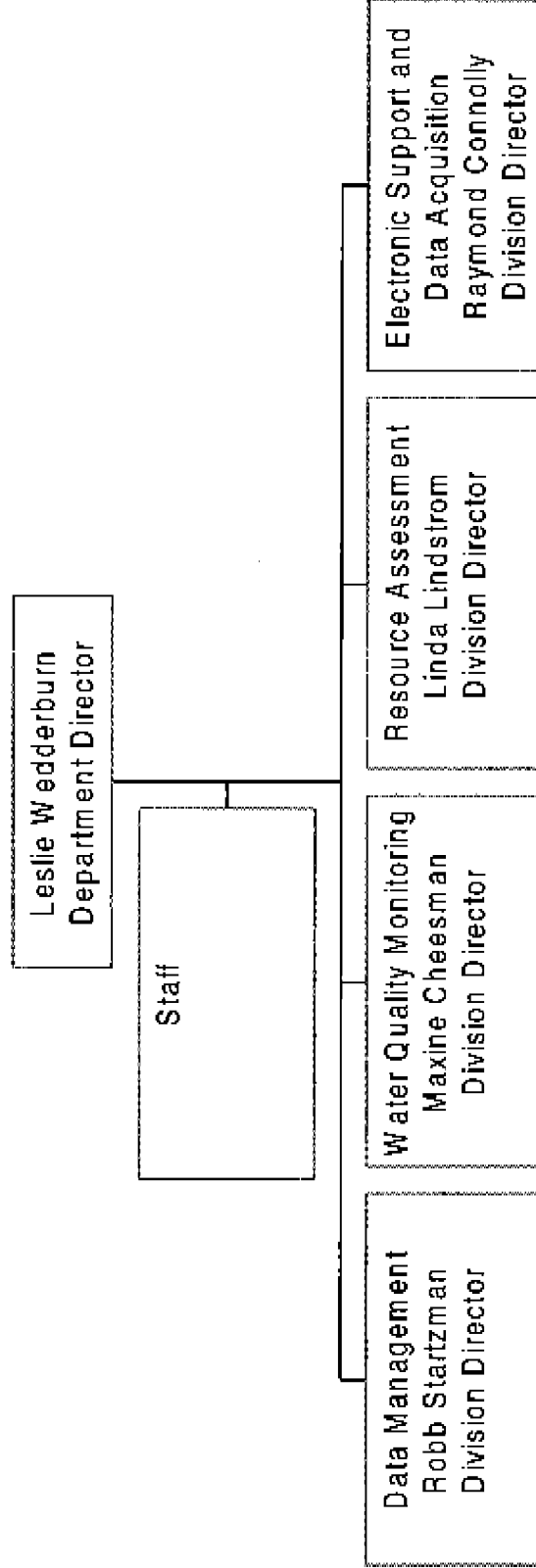


Figure 4.2 Water Resources Evaluation Department

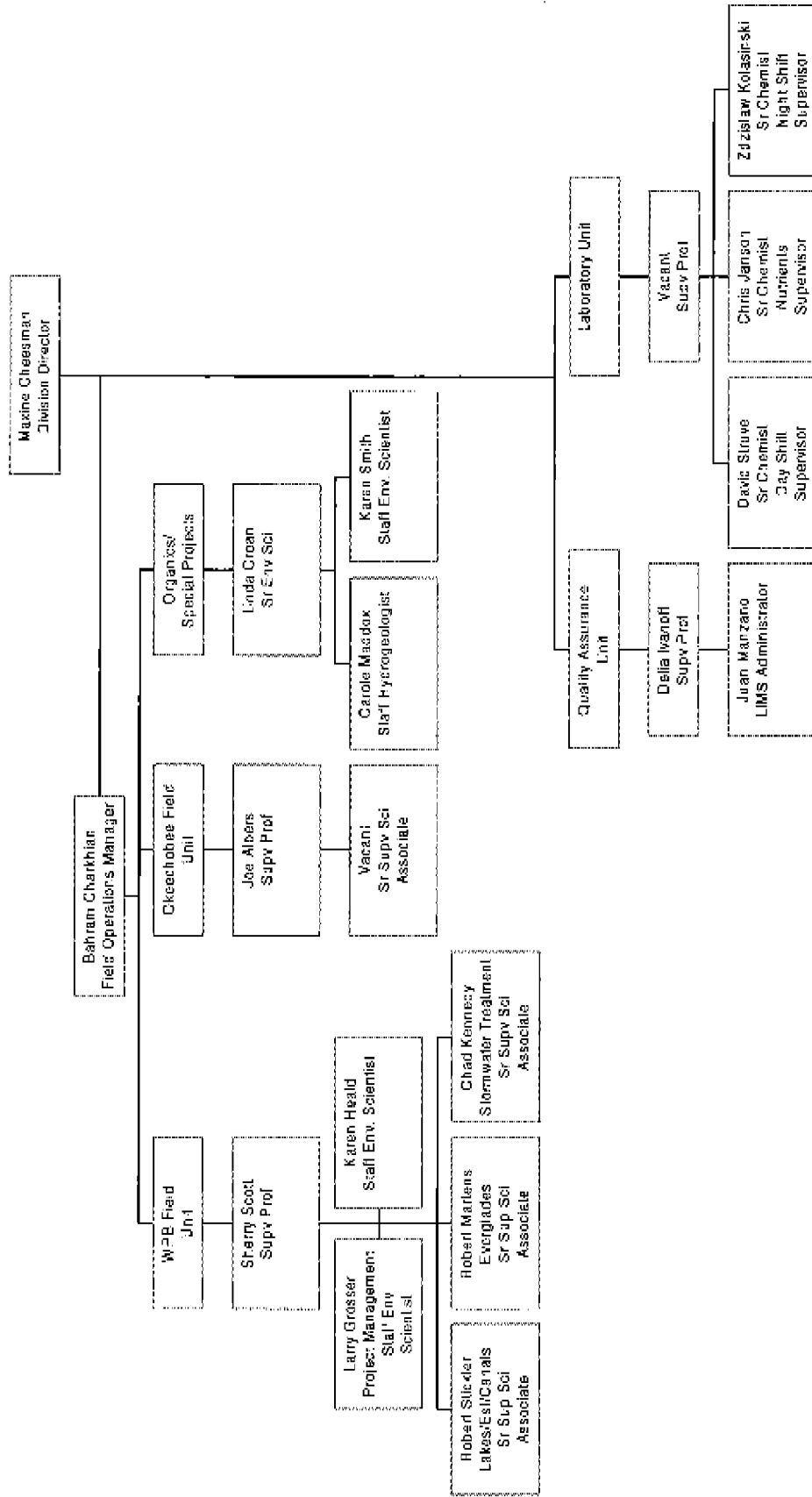


Figure 4.3 Water Quality Monitoring Division

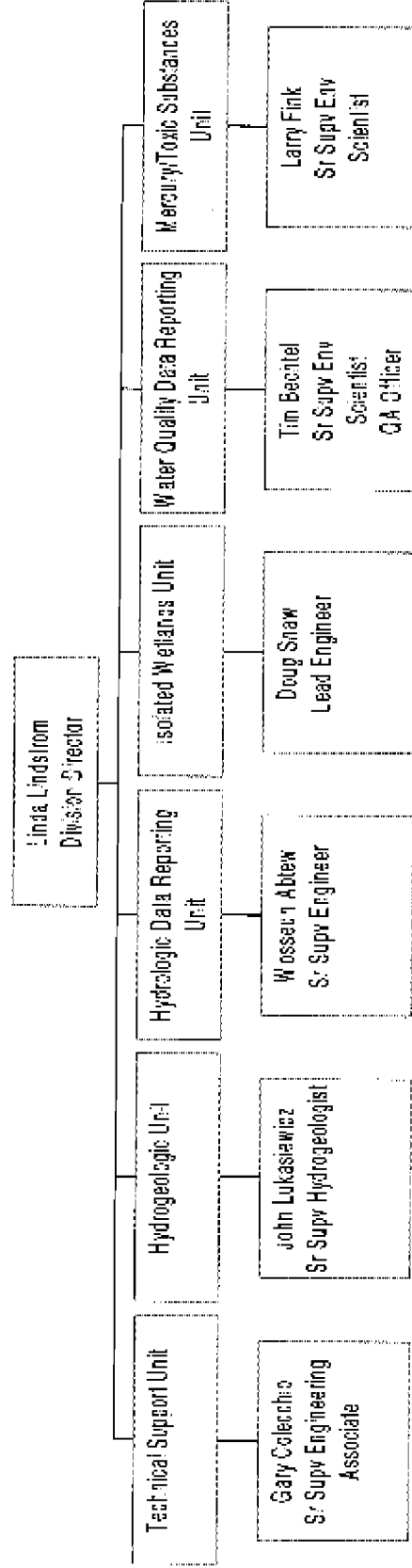
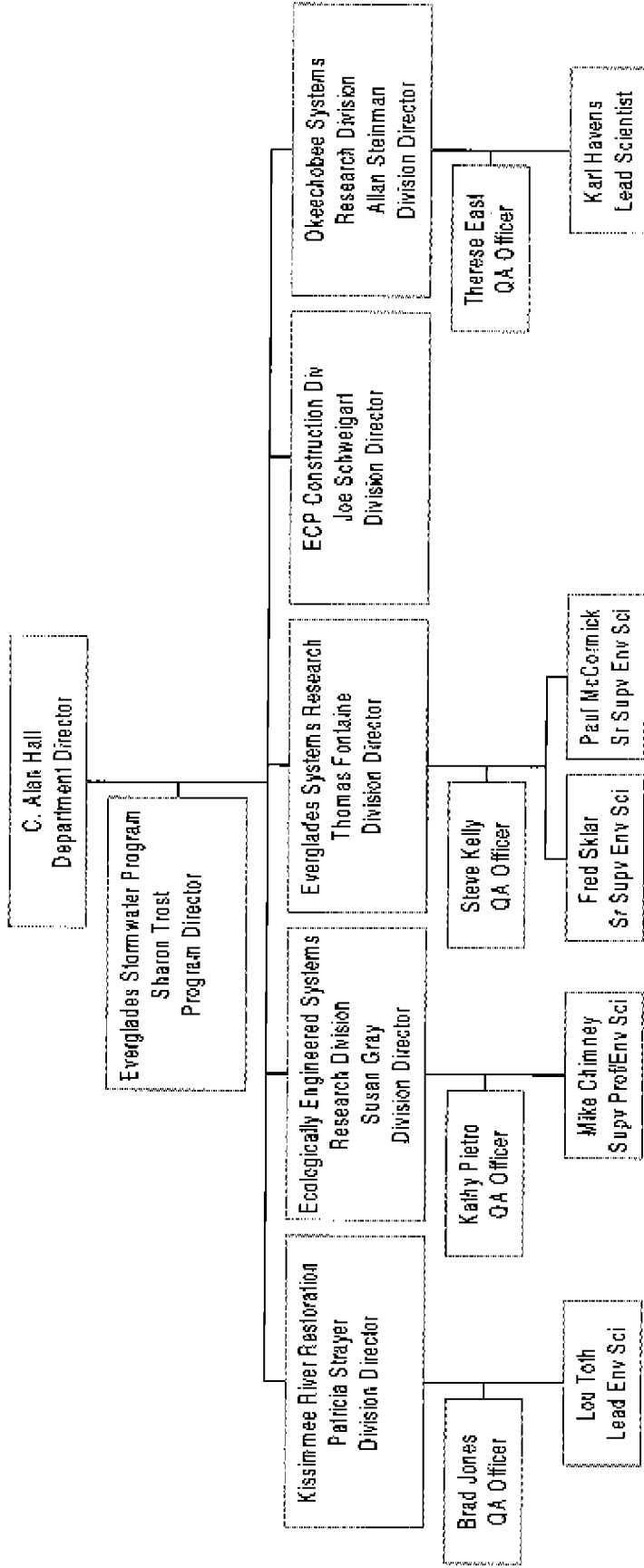


Figure 4.4 Resource Assessment Division





**Figure 4.5 Ecosystem Restoration Department**

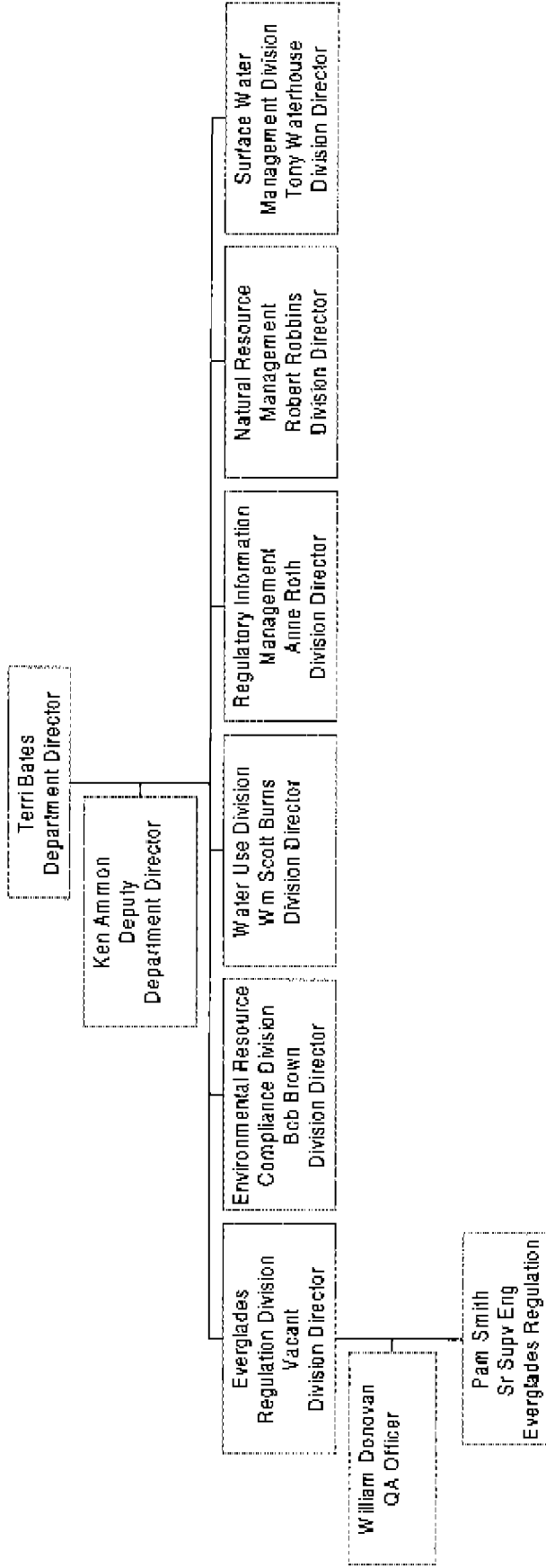


Figure 4.6 Regulation Department

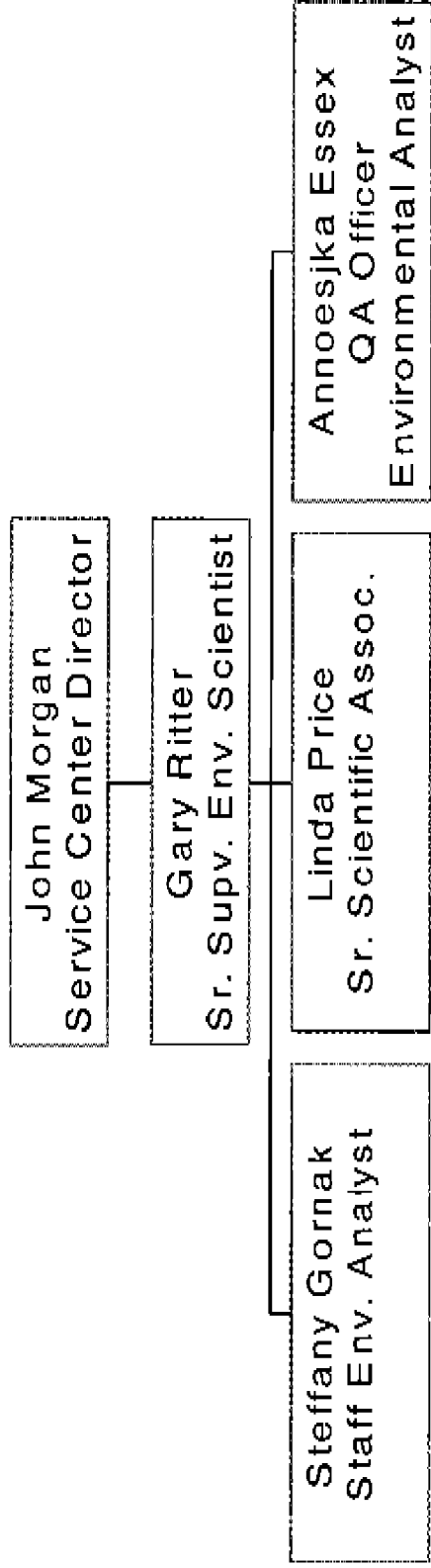


Figure 4.7 Lake Okeechobee Watershed Water Quality Group at Okeechobee Service Center

## **5.0 QA TARGETS FOR PRECISION, ACCURACY AND METHOD DETECTION LIMITS**

Tables 5.1 and 5.2 present the laboratory and field quality assurance objectives used by SFWMD. All MDL values were historically derived using 40 CFR procedure. Accuracy and precision limits were mostly generated from historical data collected in the laboratory and field. Those accuracy and precision targets not derived from historical are specifically marked with a **T** on Table 5.1. These targets were derived either from reference method, from performance validation data, or are currently safe targets to bring up quality performance in areas where they have been poorer in the past. In some cases, there are not enough points to generate limits based on historical data. Limits are evaluated quarterly.

Those derived from historical data are marked with a **H**.

Table 5.1 Quality Assurance Objectives

Minerals

Component	Matrix	Analytical Method #	Precision (% RPD)	Accuracy (% Rec.)	MDL
Specific Conductance	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM2510B	0 - 3	H	0.4 uS/cm
Residue, Filterable (TDS)	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM2540C	0 - 8	H	13 mg/L
Hardness	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM2340B (calculated)	NA	NA	5 mg CaCO <sub>3</sub> /L
Calcium, Dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM3120B SM3111B	0 - 5	H	0.2 mg/L
Magnesium, Dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM3120B SM3111B	0 - 4	H	0.1 mg/L
Sodium, Dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM3120B SM3111B	0 - 8	H	0.2 mg/L
Potassium, Dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM3120B SM3111B	0 - 8	H	0.1 mg/L
Alkalinity	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	EPA 310.1	0 - 7.5	H	NA
Silica, dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM4500-Si D Modified	0 - 10	H	0.01 mg/L
Chloride*	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	EPA 300.0	0 - 10	H	0.1 mg/L
Fluoride	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM4500-F C	0 - 5	H	0.01 mg/L
Sulfate*	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	EPA 300.0	0 - 10	H	0.1 mg/L

\* The use of EPA 300.0 by SFWMD Laboratory for NPDES permit compliance monitoring has been approved by EPA.  
T = target limit other than historical, H=limits based on historical data

Table 5.1 Quality Assurance Objectives (con't)

Nutrients

Component	Matrix	Analytical Method #	Precision (% RPD)		Accuracy (% Rec.)		MDL (mg/L)
			0 - 10	H	90 - 110	H	
Ammonia Nitrogen	Surface H <sub>2</sub> O	SM4500-NH <sub>3</sub> H	0 - 10	H	90 - 110	H	0.009
	Ground H <sub>2</sub> O						
Un-ionized Ammonia	Surface H <sub>2</sub> O	DEP SOP 10/3/83	NA	NA	NA	NA	NA
	Ground H <sub>2</sub> O						
Nitrate	Surface H <sub>2</sub> O	SM4500-NO <sub>3</sub> <sup>-</sup> F (calculated)	NA	NA	NA	NA	0.004
	Ground H <sub>2</sub> O						
Nitrate + Nitrite	Surface H <sub>2</sub> O	SM4500-NO <sub>3</sub> <sup>-</sup> F	0 - 5	H	90 - 110	H	0.004
	Ground H <sub>2</sub> O						
Nitrite	Surface H <sub>2</sub> O	SM4500-NO <sub>2</sub> <sup>-</sup> F	0 - 10	H	90 - 110	T	0.004
	Ground H <sub>2</sub> O						
Orthophosphate	Surface H <sub>2</sub> O	SM4500-P F	0 - 5	H	90 - 110	H	0.004
	Ground H <sub>2</sub> O						
Nitrogen, Total Kjeldahl	Surface H <sub>2</sub> O	EPA 351.2	0 - 10	H	90 - 110	H	0.5
	Ground H <sub>2</sub> O						
Nitrogen, Organic	Surface H <sub>2</sub> O	EPA 351.2, SM4500-NH <sub>3</sub> H (calculated)	NA	NA	NA	NA	0.5
	Ground H <sub>2</sub> O						

T = target limit other than historical, H=limits based on historical data

**Demands**

Component	Matrix	Analytical Method #	Precision (% RPD)	Accuracy (% Rec.)	MDL (mg/L)
Chemical Oxygen Demand	Surface H <sub>2</sub> O	EPA 410.4	0 - 10	T	3.0
	Ground H <sub>2</sub> O				
Organic carbon, Total	Surface H <sub>2</sub> O	EPA 415.1	0 - 15	H	1.0
	Ground H <sub>2</sub> O				
Organic carbon, Dissolved	Surface H <sub>2</sub> O	EPA 415.1	0 - 15	H	1.0
	Ground H <sub>2</sub> O				
Biochemical Oxygen Demand	Surface H <sub>2</sub> O	EPA 405.1	0 - 20	T	2.0
	Ground H <sub>2</sub> O				
Carbonaceous Biochemical Oxygen Demand	Surface H <sub>2</sub> O	SMS210B	0 - 20	T	2.0
	Ground H <sub>2</sub> O				

T = target limit other than historical, H=limits based on historical data

Table 5.1 (cont.) – Quality Assurance Objectives

Trace Metals

Component	Matrix	Analytical Method #	Digestion Method #	Precision (% RPD)	Accuracy (% Rec.)	MDL (ug/L)
Aluminum total and dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM3120B	SW-3015	0 – 10	85 – 115	4.0
Antimony, total and dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM3120 B	SW-3015	0 – 10	90 – 110	2.2
Arsenic, total and dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	EPA 206.2 SM3120B	SW-3015	0 – 10	80 – 120	1.5
Barium, total and dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM3120B	SW-3015	0 – 10	90 – 110	0.2
Beryllium, total and dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM3120B	SW-3015	0 – 10	85 – 115	0.1
Cadmium, total and dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM3120B	SW-3015	0 – 5	85 – 115	0.3
Chromium, total and dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM3120B	SW-3015	0 – 5	85 – 115	0.7
Chromium (VI), total and dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM3500-Cr D	SW-3015	0 – 10	95 – 105	3.0
Copper, total and dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM3120B	SW-3015	0 – 5	85 – 115	1.2
Iron, total and dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM3111B SM3120B	SW-3015	0 – 5	90-110	3.0

T = target limit other than historical, H=limits based on historical data



Table 5.1 Quality Assurance Objectives (con't)

Trace Metals

Component	Matrix	Analytical Method #	Digestion Method #	Precision (% RPD)	Accuracy (% Recovery)	MDL (ug/L)
Lead, total and dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	EPA 239.2 SM3120B	SW-3015	0-10	85-115	0.8
Manganese, total and dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM3120B	SW-3015	0-5	85-115	0.2
Mercury, total	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	EPA 245.1 SFWMD 2140.1	SM3112B	0-10	85-115	0.2
Mercury, trace level	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	EPA 1631 (Mod) SFWMD 2140.2	EPA 1631 (Mod)	0-20	80-120	0.006
Nickel, total and dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM3120B	SW-3015	0-5	85-115	0.5
Selenium, total and dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	EPA 270.2 SM3120B	SW-3015	0-10	85-115	1.0
Silver, total and dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	EPA 272.2 SM3120B	SW-3015	0-5	85-115	0.05
Strontium, total and dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM3111B SM3120B	SW-3015	0-10	90-110	0.3
Thallium, total and dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	EPA 279.2 SM3120B	SW-3015	0-10	85-115	0.5
Zinc, total and dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM3120B SM3111B	SW-3015	0-5	85-115	4.0

T = target limit other than historical, H=limits based on historical data

Table 5.1 Quality Assurance Objectives (con't)

Miscellaneous Analytes

Component	Matrix	Analytical Method #	Precision (% RPD)		Accuracy (% Rec.)		MDL
pH	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM4500H <sup>+</sup> B	0 - 5.0	H	NA	NA	NA
Residue, Non-filterable (TSS)	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	EPA 160.2	0 - 20	T	NA	NA	3 mg/L
Residue, Non-filterable Low Level (LTSS)	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	EPA 160.2	0 - 15	T	NA	NA	0.3 mg/L
Residue, Volatile (VSS)	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	EPA 160.4	0 - 15	T	NA	NA	3 mg/L
Chlorine Residual, total	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	EPA 330.4	0 - 10	T	NA	NA	0.02 mg/L
Inorganic carbon, Total	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SFWMD 3150.2	0 - 10	T	80 - 120	T	1.0 mg/L
Inorganic carbon, Dissolved	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SFWMD 3150.2	0 - 10	T	80 - 120	T	1.0 mg/L
Turbidity	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM2130B	0 - 5	H	90 - 110	H	0.1 NTU
Color	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SM2120B Modified	0 - 5	H	90 - 110	H	1 Pt-Co unit
Alkaline Phosphatase	Surface H <sub>2</sub> O Ground H <sub>2</sub> O	SFWMD 3160.1	0 - 10	H	NA	NA	1 nM/min-mL
Chlorophyll	Surface H <sub>2</sub> O	SM10200H	0 - 15	T	NA	NA	1 mg/m <sup>3</sup>
Macrobenthic Invertebrates	Surface H <sub>2</sub> O Sediments	SM10500	NA	NA	NA	NA	NA

T = target limit other than historical, H=limits based on historical data

Table 5.2 Field Quality Assurance Objectives

Component	Matrix	Analytical Method #	Precision (% RPD)	Accuracy (% Rec.)	MDL
pH	Surface H <sub>2</sub> O	SM4500H <sup>+</sup> B	0 - 5	NA	NA
	Ground H <sub>2</sub> O				
Oxygen, dissolved	Surface H <sub>2</sub> O	SM4500-O G	0 - 20	NA	0.1 mg/L
	Ground H <sub>2</sub> O				
Specific conductance	Surface H <sub>2</sub> O	SM2510B	0 - 5	NA	50 uS/cm
	Ground H <sub>2</sub> O				
Temperature	Surface H <sub>2</sub> O	SM2550B	0 - 3	NA	NA
	Ground H <sub>2</sub> O				
Salinity	Surface H <sub>2</sub> O	SM2520B	0 - 5	NA	0.1 ppt
	Ground H <sub>2</sub> O				
Turbidity	Surface H <sub>2</sub> O	SM2130B	0 - 20	NA	NA
	Ground H <sub>2</sub> O				

## 6.0 SAMPLING PROCEDURES

### 6.1 Sampling Capabilities

The sampling capabilities of SFWMD are shown in Table 6.1. The EPA Region IV Engineering Support Branch Standard Operating Procedures and Quality Assurance Manual (1996) and the FDEP SOP for Laboratory Operations and Sample Collection Activities (DEP-QA-001/92) are the references used for the development of sampling procedures. This reference is available to all field personnel and is referred to in this document as EPA SOP & QAM.

**Table 6.1 Sampling Capabilities by Major Category**

<b>Matrix</b>	<b>Parameters</b>	<b>Matrix</b>	<b>Parameters</b>
<b>Surface Water</b>	Cations	<b>Soils and sediments</b>	Cations
	Inorganic anions		Inorganic anions
	Metals		Metals
	Physical Properties		Physical Properties
	Organics		Organics
	Extractable Organics		Extractable Organics
	Volatile Organics (VOCs)		Volatile Organics (VOCs)*
	Microbiology	<b>Atmospheric Deposition</b>	Cations
	Other (Benthic Macroinvertebrates, chlorophyll)		Inorganic anions
<b>Ground Water</b>	Cations	<b>Biological Tissues</b>	Metals
	Inorganic anions		Physical Properties
	Metals		Cations
	Physical Properties	Inorganic anions	
	Organics	Metals	
	Extractable Organics	Physical Properties	
	Volatile Organics (VOCs)	Organics	
	Microbiology		

\*Includes low level VOC collection following EPA5035 and DEP QAS #98-03 guidelines.

Samples are collected from the least to the most contaminated areas whenever possible, depending on time limitations and distance between sites. Fortunately, the majority of the District sampling sites are ambient water sources with little variation in concentration levels within a sampling trip. Wells are not sampled for organic contaminants if the presence of fuel or free product is suspected. A new pair of powder-free disposable latex/PVC gloves is used at each sampling point for all types of sampling. The preferred order of sample collection is: 1) VOC, 2) POX, 3) TOX, 4) TOC, 5) extractable organics, 6) total metals, 7) dissolved metals, 8) microbiological, 8) inorganics, 9) turbidity and 10) benthic macroinvertebrates.

## 6.2 Field Equipment

The instrumentation, equipment, and supplies used in collection of surface water, groundwater, soil/sediment, biological tissue, atmospheric deposition, trace and ultra-trace mercury, and benthic macro-invertebrates are listed in Tables 6.2 to 6.8, respectively.

**Table 6.2 Surface Water Quality Sampling Equipment**

Category	Equipment Description	Type of Material	Use	Notes
Grab sampling	Vertical sampling bottle, 2.2 L	acrylic	collection	1
	Horizontal sampling bottle, 2.2 L	PVC	collection	1
	Horizontal sampling bottle, 3.2 L	PVC	collection	1
	Plastic bucket	Polyethylene	collection	1
	Sample bottles	Polyethylene, glass, teflon	collection	1
	Filter holders	Acrylic/polypropylene	filtration	1
	Filter units, high capacity, 0.45 µm membrane	Polypropylene housing, nylon membrane	filtration	1
	Disposable filter unit assembly with pre-filter and 0.45 µm membrane	Polypropylene housing, polycarbonate or other suitable polymer membrane	filtration	1
	Pre-filter, 47 mm dia, 1-2 µm pore size	Glass fiber	filtration	1
	Membrane filter, 0.45 µm	Polycarbonate or other suitable polymer	Filtration	1
	Syringe, 60/150 mL or other suitable sizes	Plastic	Filtration	1
	Peristaltic pump	N/A	Collection	1, 4
	Pump tubing	C-flex	Collection	1
	Sampling boom	PVC pipe with LDPE sample bottle attached	Collection	1, 2
	Bailer	Teflon	Collection	3
	Lanyard to support bailer	Teflon-coated stainless steel	Collection	4
	Gloves, short	Latex, powder free	Collection	4
	Subsurface sampler	Stainless steel	Collection	3
	S1000 Traechel syringe	Acrylic	Collection	1
	S1000 Traechel syringe	Teflon	Collection	1
Bottle rack, support for VOC bottles		Collection	4	

**NOTES:**

1. Not suitable for the collection of organics, extractable organics and VOCs.
2. Used to hold tubing at desired depth while collecting sample with the pump.
3. Used to collect VOCs and extractable organics.
4. Does not contact sample.

**Table 6.2 Surface Water Quality Sampling Equipment (Con't)**

Category	Equipment Description	Type of Material	Use	Notes
Auto-samplers	American Sigma Model 700, 800, or 900 autosampler	Polyethylene	Collection	1, 4
	American Sigma Model 6201 autosampler	Polyethylene	Collection	1, 3
	Sample bottle, 2-5 gal.	Polypropylene	Collection	2
	Sample bottles, 1 L	Polypropylene	Collection	2
	Pump tubing/intake tubing	Silicon/PVC	collection	2

Notes:

1. Does not contact sample
2. For inorganic anions, cations, and physical properties with long holding times only
3. Cooled by a refrigeration unit
4. Autosampler bottles are pre-preserved, unit not cooled; validation data for method applicability for nitrogen parameters is currently being evaluated; validation package and CQAP amendment will be submitted to FDEP.

**Table 6.2 Surface Water Quality Sampling Equipment (Con't)**

Category	Manufacturer	Model	Category	Equipment
Multi-parameter unit	Hydrolab	Scout II	Other Field Measuring Device	Turbidimeter
		IV		Secchi Depth Disc
		Surveyor II		Licor spherical equipment sensors
		Surveyor III		
		Surveyor IV		
	YSI	Model 6000 UPG Multiprobe		
		Model 6920 Multiprobe		
		Model 600XL Multiprobe		
		Model 600R Multiprobe		
	Solomat	WP803		

**Table 6.3 Ground Water Sampling Equipment**

Category	Equipment Description	Type of Material	Use	Applicability
Purging Equipment	Centrifugal Pump	Iron/Steel/Rubber	Purge Only	Inorganics/organics
	Suction Hose	Flex PVC		
	Drop Pipe	Teflon/Stainless Steel		
	Check Valve	Teflon		
	Submersible Pump	Stainless Steel/Teflon	Purge Only	Inorganics/organics
	Suction Hose	Polypropylene		
	Drop Pipe	Teflon/Stainless Steel		Organics only*
	Geotech or Masterflex Peristaltic Pump	Aluminum Housing with Stainless Steel Rollers & Plastic Head	Purge	Inorganics/organics
	Suction Hose	Teflon		Organics
	C-Flex			Inorganics
	2 or 3 Gallon Buckets	Polyethylene	Purge Only	Inorganics/organics
	Electronic Water Level Indicator	Teflon/Stainless Steel	Prior to Purge	Inorganics/organics
	Tape measure and chalk		Prior to Purge	Inorganics/organics
Sampling Equipment	Bailer System w/top, bottom, filter adapter, control-flow bottom	Teflon	Collection	Inorganics/organics
	Lanyard	Teflon-coated Stainless Steel	Collection	Inorganics/organics
	Peristaltic Pump	Aluminum Housing with Stainless Steel Rollers & Plastic Head	Collection	Inorganics/organics
	Suction Hose	Teflon	Collection	Organics (except VOCs)
	Suction Hose	C-Flex	Collection	Inorganics
	Sample Bottles	Glass	Collection	Organics
	Bottle Tops with Inflow/Outflow Ports	Teflon	Collection	Organics
	Gloves	Latex, powder-free	Collection	Inorganics/Organics
Field Filtration Equipment	Disposable Filters (QED FF-8200, Meissner or similar) 0.45 micron (1.0 micron used for permit compliance metals only)	Acrylic Copolymer with Polypropylene Housing	Filtration	Inorganics
	Handheld Vacuum Pump	PVC/Tygon Tubing	Filtration	Inorganics, except metals

\* When sampling for organic contaminants, all parts of the apparatus contacting the sample during purge are either teflon, teflon-coated, or stainless steel.

**Table 6.4 Soil/Sediment Sampling Equipment**

Equipment Description	Type of Material	Use	Applicability
Petite Ponar™	Stainless Steel	Collection	All
Scoop/spoon	Stainless Steel	Collection Compositing	All, except VOCs
Bowl/Tray	Stainless Steel	Compositing Homogenizing	All, except VOCs
Core	Stainless Steel	Collection	All
Core	Aluminum	Collection	All, except Al
Core	PVC	Collection	All, except organics
40-mL clear vials, septum-sealed	Glass, rubber septa with silicone face	Collection	Low level VOCs
Top-loading balance, to 0.01 g accuracy	N/A	Weighing sample*	Low level VOCs
Magnetic Stirring Bar	PTFE-coated	Stirring during purging	Low level VOCs
Disposable plastic syringe, 5 mL, with barrel tip cut-off	Polypropylene, rubber flange	Collection	Low level VOCs
EnCore™ sampler	Inert polymer	Collection	Low level VOCs
Core attachment	PVC	Collection	All, except organics
Core stoppers	Rubber	Collection	All, except organics
Gloves (short & long)	Latex, powder free	Collection	All

\*If low level VOC analysis is done by FDEP laboratory, it will not be necessary to weigh samples in the field. Tared vials are used and samples are weighed upon arrival in the laboratory. A complete soil sampling kit is provided by FDEP laboratory (vials, stirring bar, syringe, EnCore™ sampler).

**Table 6.5 Biological Tissues Sampling Equipment**

Equipment Description	Type of Material	Use	Applicability
Shears	Stainless Steel	Collection	Above ground biota
Knife	Stainless Steel	Collection	Above ground biota
Core	PVC	Collection	Below ground biota
Opaque Bags	Plastic	Sample storage	Biota
Soil Sieve (5mm mesh size)	Stainless Steel	Sample processing	
Gloves (short)	Latex, powder free	Collection Processing	



**Table 6.6 Atmospheric Deposition Sampling and Processing Equipment**

Equipment Description	Type of Material	Use	Notes
Aerochem Metric Wet/Dry Precipitation Collector	Aluminum	Collection	2
Aerochem wetfall bucket	PVC	Collection	2
Snap Lids	High Density Polyethylene	Cover Collection Buckets	2
Bucket	Polyethylene	Sample processing	2
Rubber spatula/tweezers/scoop	Plastic	Sample processing	2
Gloves (short)	Latex, powder free	Collection/processing	1
Portable Weighing Scale (Mettler SB12001)	Metal/Plastic	Weigh Wet Samples	1

Notes:

1. Equipment will not contact sample.
2. For inorganic ions, physical properties, aluminum and iron collection/processing only.

**Table 6.7 Low Level Mercury Sampling Equipment**

Equipment Description	Type of Material	Use	Notes
Gloves (long & short)	Plastic	Collection	
Gloves (short)	Latex powder free	Collection	1
Zip-lock bags (small & large)	Plastic	Wrapping bottles/equipment	1
Bottles	Teflon	Collection	
Geopump peristaltic pump	N/A	Collection	1
Pump tubing	Teflon	Collection	
Pump tubing	C-FLEX	Collection	
Filter units, high capacity, 0.45 micron Meissner (CSMFO 45-442) or similar	Acrylic copolymer with polypropylene housing	Filtration	
Screen (100 micron)	Nitex	Pre-screening	
Filter holder	Teflon	hold screen	
Sampling boom	PVC pipe with LDPE sample bottle	Support tubing at desired depth and away from structure	1
Ring stand	Clamps must be non-metal	Support sampling train	1

Notes:

1. Equipment will not contact sample

**Table 6.8 Benthic Macroinvertebrate Sampling Equipment**

The actual equipment used will depend upon the habitats available in the area.

Equipment Description	Type of Material	Use
Hester-Dendy artificial substrates	Tempered hardboard	Collection
Dip nets	Nylon	Collection
Petite Ponar-type Sampler	Steel	Collection
Ekman type grab sampler	Steel	Collection
Sieve (U.S. Standard No. 30)	Steel	Processing
Jars	Glass	Sample Storage
Sorting trays	Stainless Steel	Processing

### 6.2.2 Other Equipment, Tools and Supplies

#### Sample containers

- Polyethylene sample bottles for inorganics sampling only, variable sizes from 60-1000 mL
- 1000 ml amber polyethylene sample bottles - for chlorophyll only
- 125 and 500 mL teflon or amber glass sample bottles (mercury only)
- 60 and 250 mL polyethylene sample bottles (HNO<sub>3</sub> cleaned, trace metals only)
- 125 pre-sterilized Whirl-paks - container for microbiological samples

Note: Sample containers for VOCs, organics, extractable organics, and ultra trace mercury are provided by contract laboratories.

#### Sample preservation supplies

- 50% H<sub>2</sub>SO<sub>4</sub> in plastic dropping bottle
- 50% HNO<sub>3</sub> in plastic dropping bottle
- 50% NaOH, and Zinc Acetate for Sulfide
- pH strips, 0 - 3 range & 11 - 14 range
- Safety goggles
- Acid Spill Kit
- Base Spill Kit
- 10% buffered formalin
- 70-80% ethyl alcohol

Note: Preservatives for VOCs, organics, extractable organics & ultra trace mercury are provided by contract laboratories.

**Field calibration kit for multi-parameter units**

- Certified pH buffers - 4, 7, and 10
- Certified conductivity standards - range appropriate for trip sampling sites
- Ring stand
- Screwdrivers - straight edge and Phillips
- Calibration cup with both hard and soft end caps
- DO membranes and O-rings
- DO and pH electrolyte solutions
- Turbidity Standards
- pH cell caps
- Technical manual and tools

**Coolers** with wet ice (or blue ice for ultra-trace mercury) of sufficient size and quantity to contain all anticipated samples

**QA/QC supplies**

- Analyte free water - for field blanks, equipment blank, and rinsing equipment
- Trip Blanks (VOC and ultra-trace mercury collection)

**Miscellaneous supplies**

- Polyethylene bucket - for inorganic sample processing
- Disposable latex/PVC gloves, powder free (PVC not for organics or VOCs)
- Polyethylene trays - for providing clean working areas (does not contact sample)
- Self-adhesive sample labels
- Waterproof pens
- Clipboard
- Field notebook (bound, waterproof)
- Chemistry field data log sheets
- Watch
- Personal protective equipment
- Field waste container (ex. For nitric acid waste)

**Navigational Aids**

- USGS Quadrangle maps - for site location
- Project location maps - for site location
- WMD low band radio - for communication
- Mark Hurd Aerial Photographs - for site location
- Global Positioning Systems - for site location

### **6.3 Decontamination Procedures**

All sampling equipment is transported to the field pre-cleaned and ready to use. Cleaning procedures are described in Section 6.3.1 through 6.3.10 and are as required by EPA SOP & QAM, Appendix B. All sample collection equipment and unpreserved containers are rinsed three times with sample water before the sample is collected with the following exceptions: VOCs, bacteriological samples (Whirlpaks™), Total Recoverable Petroleum Hydrocarbons (TRPHs), and Oil and Grease.

Analyte-free water is obtained from laboratory or field prep areas which have effective and regularly tested water purification systems. Analyte-free water is generated to provide a source of water in which all interferences and analytes are below detection limits. Field personnel use analyte-free water to prepare field blanks and equipment blanks, and for the final decontamination rinse of field equipment. The reliability and purity of the analyte free water is monitored through the results obtained from the equipment and field blanks. Analyte-free water should be obtained and used as fresh as possible and not stored for more than one week. The District does not provide a decontamination service to its clients.

#### **6.3.1 Laboratory Cleaning**

In the laboratory, the sampling equipment is cleaned using the following procedure:

1. Wash all surfaces thoroughly with tap water and phosphate free laboratory detergent (such as Liquinox). Use a brush to contact all surfaces and remove stubborn debris. Heavily contaminated equipment is disposed of properly.
2. Rinse thoroughly with tap water.
3. Rinse with 10% hydrochloric acid (10% nitric acid if intended use of equipment is for trace metal sample collection only).
4. Rinse thoroughly with analyte free water.
5. Rinse thoroughly with pesticide grade isopropyl alcohol (for equipment used for organic sampling only).
6. Rinse thoroughly with analyte free water.
7. Allow to air dry completely.
8. Cleaned bailers are wrapped in aluminum foil or untreated butcher paper for storage and transportation.

Equipment is properly disposed of if decontamination is not effective. The cleaning procedures used for the field equipment are documented in the equipment logbook and include which equipment was cleaned, the procedure used, and the date and initials of the person performing the cleaning.

#### **6.3.2 Field cleaning procedure for Inorganic Surface Water Sampling**

Sampling equipment for nutrients, major ions and physical parameters that is reused from site to site is rinsed twice with analyte free water and then three times with sample at each sample site

before the sample is collected. Before the next sampling event, all equipment is cleaned as stated in section 6.3.1. The District is currently in the process of validating this cleaning procedure for trace metals. Data from this study is still being collected and analyzed. Evaluation of the data from this study will be presented to FDEP via an amendment of this section of the plan.

### **6.3.3 Field Cleaning Procedure for Organic Surface Water Sampling**

Pre-cleaned and pre-treated 1 L amber glass bottles are supplied by the contract laboratory and are rinsed in the field before sample collection as in 6.3.2. The bottle racks used to support these bottles during collection do not come in contact with the samples but are washed with Liquinox, tap water and D.I. before each trip. A pre-cleaned teflon bailer may also be used in the absence of strong currents or where a discrete sample at a specific depth is not required. The bailer is cleaned according to section 6.3.1, and is used only once in the field. The bailer is rinsed three times with sample water before collecting the sample.

### **6.3.4 Ground Water Equipment**

All ground water sampling equipment is transported into the field pre-cleaned and ready to use. Laboratory cleaning procedures for the field equipment are described in sections 6.3.1. The sampling equipment is used only once in the field and transported back to the lab for cleaning. The identification numbers of the sampling equipment used at each well are recorded in the field notes. All ground water sample collection equipment and sample containers are rinsed three times with sample water before the sample is collected, with the following exceptions: VOCs, and any sample bottles containing pre-measured preservative. After use, the sampling equipment is rinsed with analyte-free water and returned to the sample preparation area for thorough in-house cleaning.

#### **6.3.4.1 Teflon Drop Pipe Decontamination**

Teflon drop pipes are decontaminated in-house according to section 6.3.1.

#### **6.3.4.2. PVC and Polypropylene Hose**

When purging a well with a centrifugal pump, one end of a PVC hose is attached to the pump while the other end is connected to a Teflon drop pipe with a teflon check valve on the bottom end. Only the Teflon drop pipe touches the water in the well. The PVC hose is decontaminated before use in each well by rinsing with dilute Liquinox. The hose is then rinsed with copious amounts of DI water and wiped dry with clean lab-grade paper towels. The PVC hose is not allowed to come into contact with the ground water.

After purging a well, the hose is slowly removed from the well casing while the pump is still running to reduce the possibility of water draining back into the well from the inside of the hose.

#### **6.3.4.3 Filtration Units**

Disposable filtration units (QED, Meissner or equivalent) are purchased pre-cleaned and comes individually packed in plastic bags to prevent contamination prior to use.

#### **6.3.4.4 Teflon Lanyards**

Teflon coated, stainless steel lanyards are decontaminated in-house according to section 6.3.1. Between wells, the lanyards are rinsed with dilute Liquinox, then rinsed with D.I. water before collection. All sampling equipment is rinsed three times with sample water before sample collection.

#### **6.3.4.5 Submersible Pumps**

Submersible pumps are used for purging only and are decontaminated in-house according to section 6.3.1, with the exception of the acid rinse due to the stainless steel construction (the solvent rinse is optional if organics are not sampled). The interior is cleaned between sites by flushing thoroughly with DI water. The attached polypropylene hose is rinsed with dilute Liquinox and D.I. water between wells.

#### **6.3.5 Sediment/Soils Equipment**

The field sampling equipment is cleaned prior to being taken to the field by the following procedure: the dredge, scoop, bowl, and corer (stainless steel) are washed with Lab grade detergent, rinsed three times with tap water, rinsed with analyte free water, rinsed twice with pesticide grade isopropyl alcohol, and rinsed three times with analyte free water. The isopropyl alcohol is containerized for proper disposal. PVC corers are washed with Lab grade detergent, rinsed with tap water, dipped in 10% HCl, rinsed with tap water, then rinsed with DI water and allowed to dry. The corers are bagged in polypropylene bags until taken into the field.

For ultra-trace mercury sample collection, sampling equipment is rinsed twice with D.I. water and finally with MilliQ water. For low level VOC collection, the pre-preserved vials are supplied by the contract laboratory and are not rinsed in the field. The disposable syringes used for low level VOC soil collection are rinsed in the laboratory with isopropyl alcohol.

#### **6.3.6 Sample Bottles and Filtering Equipment**

In the laboratory, the reusable sample bottles (except for trace metals) and reusable filter holders are washed with lab grade detergent, rinsed with tap water, 10% hydrochloric acid, tap water, analyte free water, and finally air dried. Each batch of cleaned re-usable bottles are tested for effective cleaning by performing conductivity analysis on D.I. water contained in at least 5% of the bottles. No further checking is done for pre-cleaned bottles. For both lab-cleaned and commercially pre-cleaned bottles, the equipment blank data is carefully tracked to determine presence of any contamination.

Dry bottles are stored with the caps on and filter holders are stored in a closed container. Disposable bottles, certified pre-cleaned from the vendor, are also used.

Polyethylene trace metal bottles are washed with lab grade detergent, rinsed with hot tap water, soaked in 20% nitric acid overnight, rinsed with analyte free water, and air dried. At the time of sampling, the bottle is rinsed three times with sample water

The Teflon sampling bottles and glass volumetric flasks for total mercury are cleaned by rinsing three times with DI water, filling the bottles with DI water, adding approximately 1ml of digestion reagent (Bromine Monochloride), and allowing bottles to soak for a minimum of 18 hours. Before being used, containers are neutralized by rinsing with approximately 0.2 mL of 30% w/v hydroxylamine hydrochloride per 100 mls of DI water. Containers are then rinsed 5 - 7 times with DI water. Teflon bottles are then shaken dry and capped until sampling. Volumetric flasks are partially filled with DI water for solutions preparation.

Reusable filter holders are soaked in a weak lab grade detergent solution before washing to soften any residues which may be in the filter holders from the previous sampling process according to Section 6.3.1. Reusable filter holders are then washed following the same procedure as inorganic sample bottles. Once assembled, reusable filters may be stored in a sealed plastic bag in a cool, dark place for no longer than 30 days. Disposable filter holders are purchased pre-cleaned and ready for field use. Filtering syringes are washed with lab grade detergent, then rinsed with tap water followed by analyte free water and allowed to air dry.

Clean bottles/equipment are obtained from the lab by field personnel prior to each trip. Bottles for the collection of samples sent to contract laboratories are provided by the laboratory performing the analyses. These bottles have been cleaned by the contract laboratory according to that laboratory's procedures prior to shipment to the District. The contract laboratories must have approved cleaning procedures in their Comprehensive Quality Assurance Plans.

### **6.3.7 Autosamplers**

All autosampler bottles are cleaned in the laboratory using the standard bottle cleaning procedure described in Section 6.3.1 as per EPA SOP & QAM guidelines, Appendix B, Sections B.5 and B.6. Tubing is not cleaned but replaced. The sampler and sampler tubing is dedicated to each site. The sampler is programmed to rinse the tubing twice with sample before collection and then purge the tubing after the sample is taken. The pump and intake tubing for autosamplers is replaced at least quarterly or when first deployed. The entire sampler is cleaned when it is removed from the site for repair or transferred to another site. Pump tubing may be re-used if properly cleaned by soaking in hot water and Liquinox and scrubbing the outside and ends with a small bottle brush. The tubing is then rinsed with tap water, followed by DI water.

### **6.3.8 Atmospheric Deposition Equipment**

Atmospheric deposition buckets are cleaned according to section 6.3.1. Once dry, the buckets are capped and taken to the site. Tare weights of collection buckets are checked at least every three months. Weights are written on the outside of the bucket, using a permanent water-proof marker.

### **6.3.9 Ultra-Trace Mercury Equipment**

Pre-cleaned sample collection equipment (including sample bottles) are supplied by the contract laboratory for ultra-trace mercury collection. Filtration units are disposable and are purchased pre-cleaned. Sample bottles are rinsed three times in the field with sample before the sample is collected. When using the peristaltic pump, a minimum of three sample hose volumes (200 ml) of sample water are flushed through the tubing or filter before the sample is collected. The contract laboratories ship sample bottles and sample trains for the peristaltic pump, clean and in bags, and supply ultra-pure water for blanks, rinsing, and field use. All equipment and supplies taken into the field are kept in sealed plastic bags. Details of decontamination procedure for ultra-trace mercury sample collection are included in SFWMD's current SOP and QAPP for this project.

### **6.3.10 Analyte-Free Water Containers**

The analyte-free water containers are cleaned in the laboratory, at least once a week or when contamination is suspected, using the standard bottle cleaning procedures described in Section 6.3.1 as per EPA SOP & QAM guidelines, Appendix B. Glass containers used for organics sampling must include the isopropyl alcohol rinse of step #5.

## **6.4 Sampling Procedures**

Water sampling locations in the SFWMD are frequently established at water control structures where known flow rates can be combined with chemical concentrations to determine loadings. However, in lakes, rivers, marshes, estuarine systems, storm water runoff, and agricultural point sources, sampling sites and sample depths are chosen based on other criteria as described in the appropriate QAPPs. In any case, the sample must be collected in such a manner as to ensure that it is representative of the water body being studied. A new pair of disposable latex/PVC gloves is used at each sampling point for all types of sampling. In most cases, grab samples of surface water are collected at a depth of 0.5 meters. Sampling depths may vary based on physical condition of the site or project requirements. Except otherwise noted, all samples are preserved according to table 6.9, 6.10, 6.11, 6.12, or 6.13.



### **6.4.1 Sample Rejection Criteria During Field Sample Collection**

The field sample collection personnel are responsible for visually inspecting the sample and rejecting it as necessary. The laboratory personnel receiving the sample are then responsible for inspecting the condition of the sample upon receipt and rejecting it as necessary. Established criteria are detailed below and in Section 7.3.1.

As a general guideline, no samples should be submitted to the lab for which circumstances of collection will result in rejection of data due to factors that may have affected the condition of the sample. In any case, proper and thorough documentation must be done, explaining the reason for rejecting the sample. Upon return to the office, the sampling personnel must notify of the problem the field supervisor, QA officer and project manager, via email.

#### **6.4.1.1 Autosampler and Atmospheric Deposition Samples**

Reject samples that meet any of the following or similar criteria:

- Samples that are obviously contaminated by outside or foreign matter, e.g. dead frogs, lizards, or other animals.
- Samples where the pH is below 1.0, either from insufficient sample volume and/or excessive acid addition.
- Collection line contamination from excessive plant accumulation around the intake, or the intake being submerged in, or directly in contact with, bottom sediments (this may not be readily observable in the field.)
- Cracked or broken sample collection container (only the sample from the damaged bottle should be discarded.)
- Rain samples are a special category of autosampler samples that may be rejected because of gross contamination of the sample, as specified in details in current Atmospheric Deposition Project SOP.
- Samples were obtained from an autosampler which failed during operation such as failure of refrigeration unit, incomplete program, or overflowed containers.

#### **6.4.1.2 Grab samples**

In most cases, if initial grab samples are unacceptable due to any of the above mentioned criteria, or due to lack of water or absence of flow, samples may be obtained from an alternate location. This must be documented in the header sheet and the field notebook.

### **6.4.2 Surface Water (except organics and autosamplers)**

The surface water sampling procedures (except organics and autosamplers) are given in the flow chart in Figure 6.1. The following special considerations are observed when applicable:

1. If a boat is used, the sample is taken from the bow, and/or upwind and upstream from the motor.
2. When wading, the sample is collected upstream from the collector.
3. Care is taken not to disturb the sediment in the immediate sampling area.
4. Pre-preserved containers are not used as collection containers.
5. Intermediate containers are inverted, immersed to the appropriate depth, and turned upright pointed in the direction of flow, if applicable.
6. Samples are preserved according to Tables 6.9 to 6.13.

### **6.4.3 Surface Water - Organics**

Surface water samples for organic analysis are collected directly into the sample bottles using a subsurface grab sampler equipped with a pre-cleaned glass bottle provided by the contract laboratory. All unpreserved containers (except VOCs) are rinsed three times with the sample before final sample collection. The sample containers are immersed, inverted to 0.5 m below the surface, and pointing in the direction of flow, turned upright until full.

When collecting for VOC, the water is poured from appropriate grab sampler, slowly down the edge of the 40 mL Teflon-lined septum glass vial from the pre-cleaned glass bottle to minimize aeration. The vial is filled to the point of creating a convex meniscus. The cap and septum is placed, teflon side down, on the meniscus and sealed. The vial is inverted and lightly tapped on the lid to dislodge any entrapped air bubbles. The absence of air bubbles indicates a proper sample collection. If air bubbles are present, the bottle is opened, additional sample is added and the vial is resealed. Additional sample is added a maximum of three times. If a seal cannot be obtained, the vial, sample, and septum are discarded, a new vial is used and the sampling procedure is repeated. A teflon bailer may also be used in the absence of strong currents or where a discrete sample at a specific depth is not required. Each sample is identified by the project code and sequential sample number. During sample collection, the date, time, location, water movement, weather and site conditions are recorded. The preservation technique and holding times are shown in Table 6.10. Following collection of the sample, the bottles are sealed, tagged or labeled, and placed in wet ice.

The samples, with appropriate sample identification and chain of custody form, are sent to the contract laboratory. The samples are packed in coolers with bubble-wrap or other appropriate packing material to avoid breakage. Samples are kept at 4°C with wet ice. Sample containers for VOC analysis are placed into separate bubble-pack bags for each station. At least one trip blank must be included in each separate cooler containing VOC samples. Coolers are taped shut with shipping tape, labeled appropriately and shipped to the laboratory using common carrier overnight delivery.

### **6.4.4 Surface Water -- Autosamplers**

Water quality autosamplers are used for the collection of daily composite or discrete samples. The choice of whether to use a discrete or composite autosampler depends on the requirements of the project, the facilities available at the sampling site, and the parameters for which samples are to be collected. Data from a validation study, conducted to determine the suitability of current autosampler collection method for nitrogen parameters, is currently being evaluated. Preliminary data has been gathered and the study is expected to continue until Fall 1999. Validation results and appropriate amendment to this CQAP will be sent to FDEP upon completion of the study.

Autosamplers are dedicated to a specific location as long as they are working properly. Volume checks and recalibrations are conducted weekly or at time of sample pick-up to insure accuracy and consistency of samples. If an autosampler fails to perform, the sampler head including the pump hose, electronics, and flow sensor are replaced as required. Sampler intake tubing is

dedicated to a collection site and is replaced at a minimum of every quarter or when the autosampler is first deployed. The tubing may be replaced sooner if algal growth is observed in and around the inflow tubing.

#### **6.4.4.1 Discrete Autosamplers**

The discrete automatic sampler is programmed to rinse the sample collection tubing twice prior to sample collection and to purge the tubing following collection. The samplers are programmed depending on the project requirements. For example, the programming may include collection of daily composites at a rate of 80 ml of sample at 144 minute intervals and addition of the sample to the correct individual sample bottle for a total of 10 samples per 1 liter discrete sample bottle. When collecting for total Kjeldahl nitrogen, total phosphorus, ammonia and nitrate plus nitrite only, 1 mL of 50% sulfuric acid is added to the discrete autosampler bottles before sample collection. The amount of acid is selected to maintain pH between 1.5 to 2 after sample collection. Routinely, samples are poured into sample bottles at the collection site, preservation is checked and samples are immediately placed on wet ice for transport to the analytical laboratory. Additional drops of acid are added at time of pick-up, if necessary to bring the pH to this range. For projects that require manual compositing from discrete bottles, measured aliquot of samples are transferred to properly cleaned plastic bucket, mixed thoroughly, and a composite sample taken and preserved in the field.

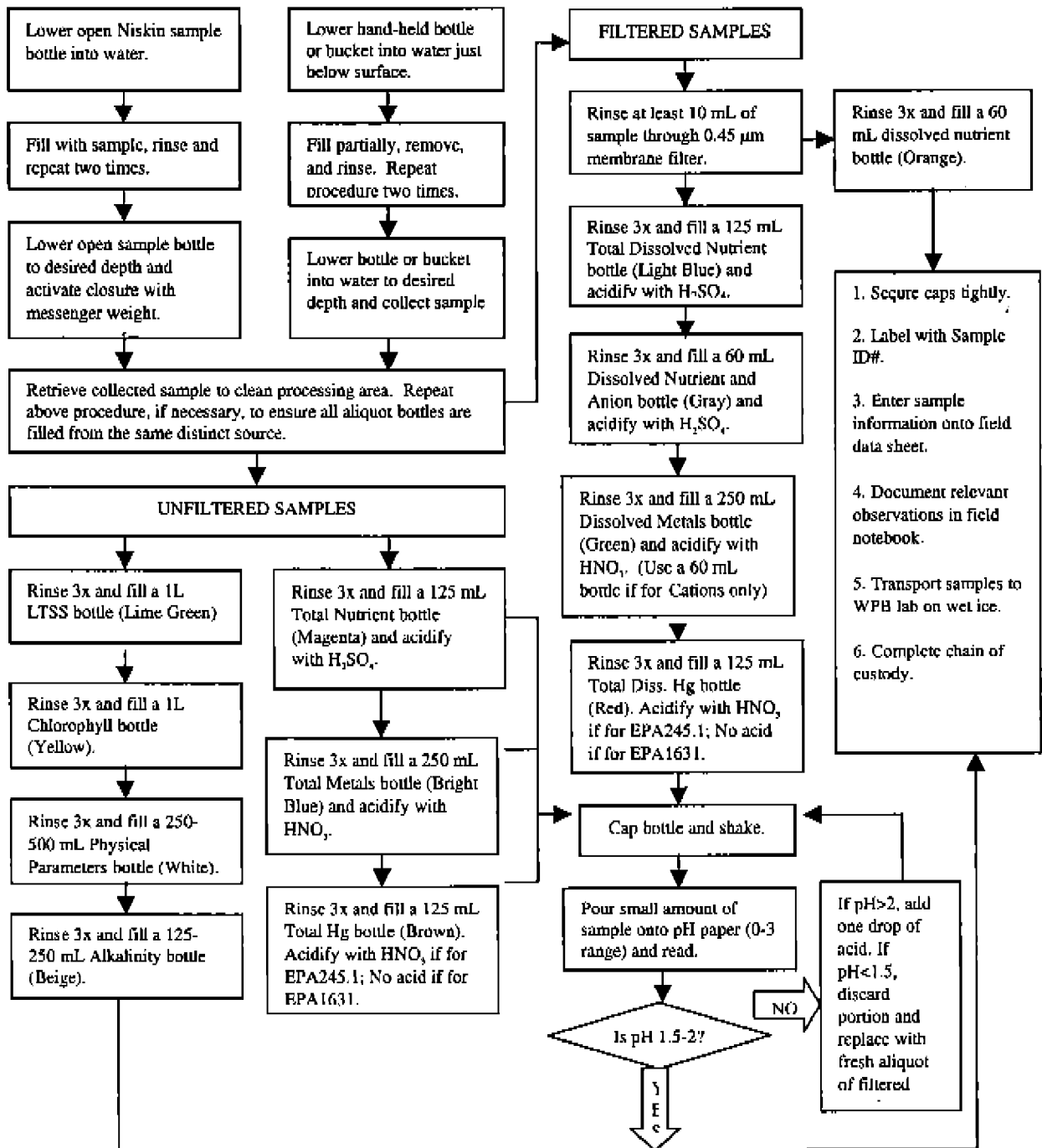
Sampler intakes at water control structures are usually located 0.5 m below the historic low mean water level and off the wing wall. Placement of the sample intake depends of the goals and specifications of the project, or may be determined by the type of structure.

#### **6.4.4.2 Refrigerated Composite Autosamplers**

Most of the composite autosamplers used by the District are installed at pump stations where electrical power is readily available. Autosamplers located at pump stations generally work in synchrony with each of the pumps in the pumping battery. The autosampler is activated once any of the pumps becomes operational, and is usually programmed to collect an aliquot at pre-determined intervals for each operating pump. The aliquot is dispensed into a refrigerated 5 gal polyethylene jug. Generally, the refrigerated autosamplers are deployed for up to one week and samples are collected at the end of a weekly period. Deployment times may vary depending on project requirements as specified in the QAPP. The refrigerated composite sample is homogenized by capping and shaking the bottle. An aliquot is transferred unfiltered to a 125 mL sample bottle for TKN and TPO<sub>4</sub> and another aliquot is filtered into a 60 mL sample bottle, for NO<sub>x</sub> and NH<sub>4</sub> testing. Both aliquots are preserved upon collection in the field as indicated in Table 6.9. As mentioned earlier on this Plan, data to validate the use of autosampler for the collection of nitrogen parameters is currently being evaluated.

### Figure 6.1 Inorganic Surface Water Sampling Procedure

Note: Bottle sizes specified are the most commonly used. Use next size larger bottle sizes if requesting for complete list of analyses for white, orange and beige bottles.



## **6.4.5 Sediment/Soil**

### **6.4.5.1 General Considerations: Duplicate Analyses**

The District collects both grab and core samples for sediment analysis of inorganic and organic analytes. The type of sampling employed depends on the requirements of the project for which the samples are being collected. Field equipment is cleaned prior to the field trip and after each sample according to the procedures described in Section 6.3.5. Whenever possible, sufficient equipment should be pre-cleaned in the laboratory for each trip so that field cleaning will be unnecessary.

Duplicates are collected to measure the variability inherent in the sampling process. Duplicates for sediments are collected from the same sample. Since a true split sediment sample is almost impossible under field conditions, split soil samples are considered duplicates. If analyses for pesticides, extractable organic compounds, or VOCs are to be performed, the sample containers must be glass with teflon lined lids. VOC bottles must have a teflon-lined septum. For other classes of analytes, glass or plastic jars, or other approved containers supplied by sub-contracting laboratories, may be used as sample containers. The containers are completely filled with sample by gently packing the sample into the container with a spoon or scoop to minimize air bubbles trapped in the container in order to minimize sample oxidation that could influence certain test results.

### **6.4.5.2 Grab Samples**

Sediment samples for organics are collected by hand grab using a stainless steel scoop/spoon, stainless steel petite Ponar™ dredge, or stainless steel core. The stainless steel scoop/spoon is utilized only in quiescent shallow waters. The petite Ponar™ dredge is effective over the wide range of circumstances encountered during the collection of sediment samples. The petite Ponar™ dredge can be used on soft or hard bottoms under a variety of flow and depth conditions. Sediment samples from canals are collected mid-stream using a small boat. The dredge is lowered by rope until contact with the bottom is established, then the dredge is slowly retrieved and emptied into a stainless steel bowl/tray. The stainless steel corer is used when collecting shallow sediment samples. Samples for VOCs (high level collection) are taken prior to compositing and placed in appropriate vials and sealed using caps with rubber septa. Each sample (except samples for VOC analysis) is thoroughly mixed in the stainless steel bowl with a pre-cleaned stainless steel spoon. The sediment in the bowl should be scraped from the walls and bottom, rolled to the middle and initially mixed. The mass is quartered, moved to the opposite sides of the bowl, and each quarter individually mixed. Each quarter is then rolled to the center of the bowl and the entire mass is mixed again. This process is continued until the mass is as homogeneous as possible. A pre-cleaned stainless steel spoon or small scoop is used to transfer the required amount of final homogenized material from near the center of the mass into the appropriate sample bottle. This is done quickly to prevent oxidation of metal ions or volatilization of organic compounds. The bottle is filled to its rim.

Low level VOC samples are collected either using an EnCore™ sampler with a T-handle or

using a 5 cc syringe with pre-cut barrel tip and transferring up to 4 cc soil into pre-tared vial containing a small amount of D.I. water and a stir bar. The vials are kept sealed, kept on dry ice, and shipped to the contract laboratory.

#### **6.4.5.3 Core Sampling**

Sediment cores are collected using PVC corers if the sample will not be analyzed for organics. Intact sediment cores are obtained by driving a PVC coring tube to a depth of approximately 50 cm into the soil. Under shallow conditions (water depth < 30 cm) this is achieved using a block of wood to protect the neck of the core tube and then striking the block several times with a hammer such that the core penetrates the soil with minimal compaction. If the water is greater than 30 cm, a PVC coupling should be attached to the coring device. This attachment is comprised of a ball valve and a length of PVC pipe. This is fitted to the neck of the PVC coring tube and a closed ended piece of metal pipe with a diameter larger than the upright PVC pipe is used to pound the core into the sediment. During the insertion, the ball valve should be open. Prior to pulling the core out of the sediment, the ball valve should be closed. The sediment core, with the overlying water, is then labeled, capped at both ends using rubber stoppers, stored out of direct sunlight, and transported to the laboratory. If the sediment surface within the core is at a significantly different depth than the adjacent soil, compaction has occurred, and the core should be discarded.

For ultra-trace mercury collection, buterite tubes are used. If coring is to be done at depths > 30 cm, stainless steel corer is used, with a buterite tube inserted into the corer.

#### **6.4.6 Ground Water**

Ground water wells are purged from shallowest to deepest well, if more than one well is located at a site, and then samples are collected from the least to most contaminated wells whenever possible. The order of collection is: 1) VOCs, 2) Extractable Organics, 3) Total Metals, 4) Dissolved Metals, 5) Inorganics and 6) Radionuclides. The SFWMD does not use temporary well points or dedicated equipment for ground water monitoring. Samples are not collected from wells which contain free product.

A protective covering of visqueen plastic maybe placed on the ground around the well at the sampling site to reduce the potential for contamination. A fresh pair of disposable non-powdered latex gloves are worn at each sample site while purging and another fresh pair worn for collecting samples. All samples are collected using a Teflon bailer which is suspended by a Teflon coated stainless steel lanyard and carefully lowered into the well. Prior to the collection of the sample, the bailer is rinsed three times with sample. The lanyard and bailer are not allowed to touch the ground during sampling or purging.

The bailer, filled with sample, is retrieved from the well and placed on a bailer stand. VOC samples are collected first via a controlled-flow bailer bottom and are poured slowly down the side of the sample vial to minimize sample aeration. The vial is filled to the point of creating a convex meniscus. The cap is secured with the Teflon side of the septum contacting the sample

and no headspace in the sample container. The vial is inverted and gently tapped to locate bubbles. If bubbles are present, the sample in the vial is discarded and sample is recollected and checked for bubbles. Additional sample is added a maximum of three times. If an acceptable sample cannot be collected, the sample, vial and septum are discarded, a new vial and septum are used, and the collection procedure begins again.

To filter a sample, a one piece, molded, in-line disposable filter is attached to the bottom of the bailer with a Teflon adapter. The top of the bailer is attached to a vacuum pump by a Teflon attachment so the bailer can be pressurized to force water through the filter. The filters are 0.45 micron unless a dissolved metals sample is collected for permit compliance, in which case the filter pore size is required to be 1.0  $\mu\text{m}$ . The first 100 mL of sample to pass through the filter is discarded as rinse water, and the last 100 mL of sample water in the bailer is not used since it has been in contact with the air at the top of the bailer. Duplicate samples are collected by sampling from consecutive bailers.

If the analyses are to be performed by a contract laboratory, the bottles are cleaned by the contract lab according to that laboratory's procedures prior to shipment to SFWMD. The contract laboratory must have approved cleaning procedures in their Comprehensive Quality Assurance Plan. VOC vials are supplied by the contract laboratory.

Splits are not routinely collected in the groundwater program. When splits are required to measure the performance between two or more laboratories, splits are collected from the same bailer. For large volume samples that may require more than one bailer load, the first half volume of the first bailer load is poured into the first set of containers and the second half in the second set of containers. Then the first half-volume of the second bailer load is poured into the second set of containers and the second half in the first set of containers, etc., until both sets are full.

The sample bottles are labeled with the date, sample number, and project name before sampling at a site begins; sample time is added to the labels as samples are collected. After collection, the samples are preserved according to Tables 6.9 to 6.13, and immediately placed on ice in a closed container. Exposure of organic samples to sunlight is kept to a minimum. When VOCs are collected, trip blanks are transported with the sample bottles to make certain that the samples have not become contaminated. These trip blanks accompany the samples from the time the empty sample bottles are shipped from the contract laboratory until the samples are analyzed. Trip blanks account for at least 5% of the samples that are analyzed. At least one trip blank must be included in each separate cooler.

#### **6.4.6.1 Wells with In Place Plumbing**

These wells are purged for a minimum of 15 minutes, until three bore volumes have been removed, or until the well has chemically stabilized, whichever is greater. The sample is taken from the faucet closest to the source and before any screens, aerators, or filters. The flow rate is reduced as necessary to avoid any undue disturbance. Unfiltered samples are collected directly into the sample containers from the spigot. Filtered samples are collected by filling a bailer from

the spigot. The bailer is rinsed three times with sample, then filled and pumped through a filter attached to the bottom of the bailer with a Teflon adapter. Sample bottles are rinsed once with sample (unless sample bottles are pre-preserved, or collection is for VOCs).

#### **6.4.6.2 Flowing Artesian Wells**

These wells are purged until three bore volumes have been evacuated, or until the well has chemically stabilized, whichever is greater. The flow of water from the well is adjusted to minimize the aeration and disturbance of samples. Unfiltered and filtered samples are collected directly from the discharging water into a bailer.

#### **6.4.6.3. Monitoring Wells**

The depth to water in each well relative to a measuring point is measured twice using an electronic water level indicator. Both values, which must be accurate to within  $1/10^{\text{th}}$  of a foot, are recorded on the field log sheet. More stringent measurements may be required for specific project programs. These values will later be used to calculate water elevation relative to mean sea level. The same measuring point is used every time the well is sampled. When the wells are surveyed, the survey point is used for the measuring point. Water level measuring devices are rinsed with dilute lab grade detergent and DI water, and wiped dry with a clean lab-grade paper towel before measuring each well.

Prior to collection of samples, a centrifugal pump, a submersible pump or a peristaltic pump is used to purge each well. The choice of an appropriate purge pump is determined by a combination of factors including the total volume of water necessary to be purged, the diameter of the casing of the well, and the depth-to-water. Centrifugal and submersible pumps (or the associated generator) are gas powered. Extreme care must be used when handling and placing these units to minimize on-site contamination. Place them downwind, away from any sampling activities.

The centrifugal pump is connected to a flexible PVC suction hose, which is cleaned prior to use by the method documented in Section 6.3.4.2. Neither the pump, nor the PVC hose comes in contact with the water in the well. The other end of the hose is connected to a rigid three-foot length of Teflon drop pipe, which is equipped with a Teflon check valve at its bottom end to prevent the back flow of purged water into the well. The drop pipe and check valve are cleaned prior to use by the decontamination procedures outlined for other sampling equipment in Section 6.3.1.

The submersible pump is decontaminated as specified in Section 6.3.4.5. It is connected either directly to a polypropylene hose (inorganics), or to a three-foot Teflon drop pipe (organics) before being connected to the polypropylene hose. The hose is cleaned by the method detailed in section 6.3.4.5; the drop pipe is cleaned by the decontamination procedures outlined in section 6.3. The submersible pump is equipped with an internal check valve to prevent the back flow of purged water into the well. The submersible pump with the 150' electrical lead is capable of purging water from as far down as 135 feet (if a well were to be drawn down that far).



When purging a well, the drop pipe or the head of the submersible is lowered to the top of the water column so that the purging process removes all of the standing water. If the water level is drawn down during the purging process and air begins to enter the drop pipe or the head of the submersible, it is lowered to the new water level. If the water level is drawn down too severely, the purge rate is decreased.

The battery powered peristaltic pump is used occasionally to purge low volume wells. If the well will be sampled afterward for inorganic constituents, C-flex tubing is lowered into the water column as well as placed through the pump head. The C-flex is either disposed of or cleaned by rinsing with copious amount of D.I. water between wells. The Teflon tubing is cleaned per the decontamination procedures outlined in section 6.3.1. If the well will be sampled after purging for organic compounds, Teflon tubing is lowered into the water column and connected to the glass bottle with Teflon lid. The lid has two Teflon ports; the Teflon tubing is connected on one port, and the C-flex runs from the other port through the pump head. Sample water never touches the C-flex tubing.

Three standing water volumes, minimum, are removed from the well. The volume of water to be purged is calculated using the following formula:

$$\text{Minimum Purge Volume in Gallons} = (D^2) * (DW-DTW) * 0.1224$$

D = Casing Diameter in Inches  
DW = Depth of Well in Feet  
DTW = Depth to Water in Feet

The constant 0.1224 is a units conversion factor.

The volume of water to be removed from the well must be calculated to provide sufficient purging. The flow rate is estimated by measuring the amount of time required filling a bucket of known volume. The required purge volume is then divided by the estimated flow rate to find the estimated time necessary to purge the well. Flow is measured several times during purging to be certain that it does not change.

Although a minimum of three water column volumes must be purged, the well is not considered to be ready for sampling until the well has chemically stabilized. Temperature, pH and specific conductivity are monitored and readings are recorded on the field log sheet at time intervals equal to one-half of a bore hole volume. A minimum of seven readings are normally recorded – an initial reading, and six more readings recorded at each one-half bore hole volume – until the well has stabilized. Chemical stability readings are made in a flow through chamber to minimize atmospheric contact with the sample. The well is considered to be chemically stable when the last three consecutive readings of temperature, pH, and specific conductivity are within 5% or 0.1 unit for pH readings. The purge volume is also noted on the field log sheet. Only the final readings taken after the well has stabilized are input into the sample results database. The drop pipe is slowly raised out of the well while the purge pump is still running to make certain that all of the water above the drop pipe inlet is purged. This procedure also minimizes the possibility of the back flow of water from the drop pipe or suction hose.

Wells with low hydraulic conductivity sediments that can be purged dry at one liter per minute are not sampled because the water quality is not deemed to be representative of the aquifer water quality. The SFWMD does not sample wells for which recovery cannot be accomplished in four hours or less.

All ground water samples are collected using a Teflon bailer system or a peristaltic pump. When handling bailers or other sampling equipment, clean powder-free Latex gloves are worn. The Teflon bailer is connected to a lanyard with Teflon coated stainless steel line and carefully lowered into the column of well water. The bailer is filled with well water, removed from the well and discarded three times before beginning sample collection.

A minimum of 500 mL of purged well water should be flushed through the lines of the peristaltic pump before inorganic sampling actually begins. Organic sampling with the peristaltic pump would require that the glass sampling bottle, which is connected in-line between the Teflon tubing and the C-flex/pump head, be rinsed three times and the rinse water discarded before filling any sample bottles. This procedure is done as a final rinse of the pre-cleaned sampling equipment or tubing. The lanyard, bailer and tubing are not allowed to touch the ground. After sampling, the equipment is rinsed with DI water and returned to the lab for cleaning.

#### **6.4.6.4 Porewater Wells and Peepers**

Porewater is collected using porewater wells and peepers (Appendix G) for certain mandated projects and other research projects. Once collected, samples are processed and handled according to the QAPP or research SOP for each project.

#### **6.4.7 Biological Tissue**

##### **6.4.7.1 Above Ground Macrophyte Biomass**

Above ground vegetation is clipped at the sediment-water interface with a pair of sheers or knife, and separated into subsamples by species. Each biomass subsample is placed into an individual large opaque plastic bag, labeled, and transported to the laboratory for processing.

##### **6.4.7.2 Below Ground Macrophyte Biomass**

After the above ground vegetation has been removed from the sampling quadrant, a soil core is collected from the quadrant using a soil corer. Each soil core is placed into an individual large opaque plastic bag, labeled, and transported to the laboratory for processing.

#### **6.4.8 Hazardous Wastes/Drums**

The SFWMD does not sample hazardous waste or drums.

#### **6.4.9 Waste Water**

The SFWMD does not sample waste water.

#### **6.4.10 Microbiological**

Microbiological samples are collected and preserved on ice, with extra care in order to prevent sample contamination. The samples are not composited. The personnel collecting the samples do not touch the rims or top of the Whirlpak™ sample containers. It may become necessary to affix the container to a sampling boom in order to effectively grab a representative sample. A Whirlpak™ must be discarded if it is suspected that the top portion has been touched. Microbiological sampling is closely coordinated with the laboratory performing the analyses to ensure that samples are analyzed within holding times.

#### **6.4.11 Oil and Grease**

Oil and Grease samples are collected directly into the sample container without rinsing with sample. Sample containers are not pre-acidified. Sample bottles for Oil and Grease are provided by the contract laboratory.

#### **6.4.12 Trace Metals and Ultra-Trace Mercury Collection using CH/DH**

The SFWMD follow a modified version of the clean hands (CH), dirty hands (DH) technique as specified in *EPA Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*, when collecting low level total and methyl mercury samples in surface water. For surface water collection CH person, using non-powdered latex gloves, touches only clean surfaces (such as new gloves, new plastic bags, or surfaces that have been cleaned in an ultra-clean facility. DH person, using wrist length latex gloves, touches the cooler and the sample bottle covered with two plastic bags. DH opens the outer plastic bag, CH reaches in, pulls up bottle covered with inner plastic bag, and removes the bottle from the inner bag.

CH reaches into the water and collects 100 mL of surface water by immersing the sample bottle about 10 cm under the surface. The bottle is rinsed by shaking the contents (cap on) and dumping the contents away and downstream from the sampling area. This rinse is repeated two more times. The bottle is filled a final time with more than 100 ml and the cap secured tightly by hand. CH then puts the bottle in the inside bag, seals it, and places the inside bag into the outside bag. DH seals the outside bag and places it back inside the container. DH records the sample bottle number, time, site and other information on the field data log sheets, and later transfers the information to the field notebook. Relevant site conditions are recorded into the field notebook. Samples are not acidified in the field, but are kept cool using blue ice. Preservation is done in the laboratory by the laboratory staff receiving the samples.

Samples may also be collected using a peristaltic pump with properly decontaminated sample train. The CH/DH procedure is used. DH removes the sampling train (filter holder with nitex screen, Teflon tubing and C-FLEX tubing-all connected) from the cooler and opens the outside bag. While CH holds the tubing, DH secures it to the sampling boom with tie wraps. DH opens the pump head, CH places the pump tubing inside, and closes the pump head. DH opens the ring stand clamp, CH places the pump tubing inside and DH closes the plastic clamp. CH then changes gloves prior to the sampling event.

To begin sample collection, DH positions the end of the sampling train about 10 cm below the water surface and about one meter from shore. DH starts the pump and begins flushing. DH removes a sample bottle from the cooler and opens the outside bag. CH opens the inside bag and removes the sample bottle. CH opens the sample bottle, empties the contents away from the sampling area and fills the bottle with approximately 50 ml of sample water. The bottle is rinsed by shaking the contents (cap on) and dumping the contents away from the sampling area. This rinse is repeated two more times. The bottle is filled a final time with more than 100 ml and the cap secured tightly by hand. CH then puts the bottle in the inside bag, seals it, and puts the inside bag down inside the outside bag. DH seals the outside bag and places it back inside the cooler.

To prepare a filtered surface water sample, DH stops the pump, removes a filter cartridge from a cooler, opens the bag, CH removes the filter and connects it to the end of the sampling train. DH starts the pump and the filtered sample is collected as above. All equipment is rinsed with sample water at the next site before collecting a sample. To control mercury contamination, CH secures a clean plastic bag to each end of the sampling train for transport between sites. The equipment and supplies are stored inside coolers and bags in a place relatively free of mercury contamination. Dust and human breath (from dental amalgams) contain large amounts of mercury and should be avoided during sample collection. Samples should not be collected in the rain.

#### **6.4.13 Benthic Macroinvertebrates**

The SFWMD follows macroinvertebrate sampling methods as detailed in the Florida Department of Environmental Protection (FDEP) Biology Section Standard Operating Procedures (Appendix E) and in EPA/600/0-90/000, *Macroinvertebrate Field and Laboratory Methods for Evaluating the Biological Integrity of Surface Waters*. The field methods used to study benthic macroinvertebrate communities relate to qualitative, semi-quantitative and quantitative sampling, and are dependent on the data quality objectives of the study. Generally, there are four categories of benthic macroinvertebrate samples collected: cores, grabs, artificial substrates, and miscellaneous. Field equipment is cleaned prior to the field trip and after each sample according to the procedures described in Section 6.3.5.

##### **6.4.13.1 Corers**

Coring devices may be used at various depths in any substrate that is sufficiently compacted so that an undisturbed sample is retained; however they are best suited for sampling homogeneous soft sediments, such as silt, clay or sand. Macrofauna are sampled using single and multiple-head corers, tubular inverting samplers, open-ended stovepipe devices, hand corers and/or box corers. Devices are lowered slowly into the substrate to ensure good penetration and to prevent organisms from escaping. Visual inspection of each sample is necessary to ensure an adequate amount of sample is obtained.

##### **6.4.13.2 Grab samplers**

Grab samplers are designed to penetrate the substrate by gravity and have spring or gravity activated closing mechanisms. They are used to sample a unit area of the habitat. The habitat and substrate type sampled, depth of penetration, angle and completeness of jaw closure, loss of

sample during retrieval, disturbance at the water-sediment interface, and effect of high flow velocities all affect the quantity and species of macroinvertebrates collected by a particular grab. Petite Ponar™ or Ekman grab samplers are typically used; however the type and size of the selected device depends on the substrate composition, water depth, and hoisting gear available. The sampler is lowered slowly to avoid a disturbance of the surface sediment and to ensure the device bites vertically. Upon tripping of the closing mechanism, the sediment is contained and the device is retrieved. The sample is then placed into a suitable container for transporting to the laboratory or is placed directly into a sieving device and processed.

#### **6.4.13.3 Artificial substrate samplers**

Artificial substrate samplers, such as the multiplate (modified Hester-Dendy) sampler, consist of natural or artificial materials of various composition and configuration. They are placed in the water body for a predetermined period of exposure and depth for the colonization of indigenous macroinvertebrates. This type of sampling is used to augment bottom substrate sampling because many of the physical variables encountered in bottom sampling are minimized, e.g. light attenuation, temperature changes, and substrate variation. The samplers are deployed in the euphotic zone of the water column to promote maximum colonization. They are exposed for a preset period of time and retrieved vertically from the water. The samplers are placed in a preservative container and transported to the laboratory for processing.

#### **6.4.13.4 Miscellaneous qualitative devices**

Many devices such as dip nets, bare hands, tongs, and forceps may be used to collect benthic macroinvertebrates. Dip nets are used by sweeping the net through the water or by holding the net stationary against the bottom and disturbing the substrate, causing the benthos to be swept into the net.

Samples collected by any of the aforementioned devices contain varying amounts of fine materials which can be removed by sieving immediately in the field, or in the laboratory. If laboratory sorting can be performed within 24 hours, place samples immediately on ice. If sorting will be delayed, preserve with 10% formalin. After organisms have been removed from detritus, they should be placed into 70% ethanol (Table 6.13).

### **6.4.14 Atmospheric Deposition**

Atmospheric deposition samples are collected according to the National Atmospheric Deposition Program (NADP/MDN) site operation manual. Individuals performing this type of collection should also be familiar with the program's QAPP and current SOP. Samples are preserved according to Table 6.9.

The District uses Aerochem Metrics Wet/Dry Precipitation collectors. These automated collectors are aluminum structures with two 3.5 gallon PVC buckets which serve as receptacles for wet and dry deposition, although dry deposition samples are no longer collected and processed by the District. An aluminum lid covers the wet side bucket under dry conditions. When the humidity sensor detects rain, the lid rotates over the dry side bucket, uncovering the wet side bucket. The wet buckets are collected weekly. The buckets are capped (while using

PVC/Latex gloves) and taken to the laboratory for processing within 24 hours. Clean buckets are placed into the Aerochem collectors. Before clean buckets are placed into the collectors, one bucket from each decontamination lot is checked by pouring one liter of DI water into the bucket, allowing the water to sit overnight (capped) in the laboratory, and processing the water as an equipment blank.

All wet side buckets are weighed using a top loading balance and subtracting the clean bucket tare weight (determined before deployment in the field). Any sample contaminated by non-representative foreign matter such as guano, frogs, insects, lizards, or vegetative material are not processed. The QA SOP for processing atmospheric deposition samples should be followed. Quality control samples (equipment blanks, splits and field blanks) are submitted according to routine QA procedures.

Dry side buckets are inspected for contamination as above, and notes on the presence and nature of any contamination are recorded into a field notebook.

#### **6.4.15 Marsh Sampling by Helicopter**

This section is specific to sample collection when transport by helicopter is necessary due to inaccessibility by other means.

Samples for inorganic analyses are collected in 2 L polyethylene sample bottles for each site and each QC sample. Samples can also be collected directly into an intermediate container or using a peristaltic pump.

##### **6.4.15.1 Surface Water Collection Using Grab Sampler**

1. After helicopter lands, wade out away from helicopter disturbance area, preferably upstream if flow is visible and/or downwind.
2. Be careful to avoid weeds and the creation of turbidity.
3. Measure and record the total depth of the water using a long, rigid, graduated pole.
4. Don clean pair of PVC sampling gloves.
5. If water depth > 20 cm, immerse intermediate sample container(s) in an undisturbed area at middle depth, upstream from the sampling personnel, rinse three times, and fill to the brim.
6. Cap and label the container(s) and place on wet ice.
7. Measure and record Depth, Temperature, pH, Conductivity and DO at middle depth in sampling area using a multi-parameter field instrument.
8. Gather equipment, walk back to helicopter, and place samples in a cooler.

##### **6.4.15.2 Surface Water Collection Using Peristaltic Pump**

###### Platform sampling:

1. After the helicopter lands at the South end of the platform, walk to the North end of the platform, which is the usual upstream side.
2. Set up peristaltic pump and place a screen on the intake end of the tubing (to block large chunks of algae and plant material from flowing into the sample). Place the end

- of the tube into the water column at middle depth being sure not to disturb sediments. Turn the pump on and let the water run for about 10-15 seconds to rinse the tube.
3. Put on plastic gloves and begin to fill unfiltered sample bottles, being sure to rinse the bottle 3 times before collecting sample. Also, make sure to look in the bottle to see if the sample is clean and particulate-free. For filtered samples, place in-line filter on the outflow end of tube and let the water flow through filter for a few seconds. Rinse bottles 3 times and fill.
  4. After all the bottles are full, acidify appropriate samples and place in bag.
  5. Record water depth measurement and Hydrolab readings (once again being sure not to disturb sediments with probe).
  6. Gather equipment, walk back to helicopter, and place samples in a cooler.

#### Pontoon Sampling:

1. The pilot lands the helicopter partially on the vegetation so that it will stay in one place to minimize disturbance to the water column.
2. One person steps out onto the pontoon and attaches the end of the pump tube (which has a screen) to a long pole that extends about 10 to 15 feet from the helicopter. The pole is extended out into the open water and finds a spot that appears undisturbed. The end of the tube is submerged in the water column at middle depth.
3. When an appropriate sampling spot has been found the person in the helicopter turns on the peristaltic pump and begins to sample, making sure the sample is clean and particulate-free. If the sample is not clean, the pole is moved to another spot until a clean sample can be obtained.
4. The procedure for filling sample bottles is the same as above.
5. When bottles are filled, the person on the pontoon records a water depth measurement and Hydrolab readings from the pontoon.
6. Stow equipment properly and place samples in cooler.

#### **6.4.15.3 Sediment Sampling**

Should the trip require sediment collection, samples are processed on site into appropriate containers as per techniques referenced in Section 6.4.4.

#### **6.4.15.4 Sample Processing and Preservation**

Within four hours of sample collection, aliquots are processed from the large intermediate containers into more appropriate containers for lab analyses. Samples are processed and placed into appropriate sample containers and preserved according to the procedure stated in Figure 6.1.

### **6.5 Documentation**

The following is a list of the field records that are maintained.

1. Chemistry Field Data Log
2. Bound field notebook (project specific)
3. Documentation of any significant problem encountered in the field

Established criteria for completion of the field notebook are detailed in Section 7.1 and Appendix H.

## 6.6 Preservation

Holding times and preservation techniques for each parameter are given in Tables 6.9 to 6.12. With the exception of trace metals ultra-trace mercury, atmospheric deposition, and marsh sampling as described in Sections 6.4.12, 6.4.14 and 6.4.15, respectively, samples are preserved in the field at the time of sample collection either by using preservatives provided by the SFWMD laboratory or the contract laboratory. If sample containers are received with preservative from the contract laboratory (VOCs), additional preservative is requested so it is available if needed. ACS reagent grade or better preservatives are used.

For unfiltered samples, the appropriate preservative is added to the sample bottle after the bottle is filled. The bottle is capped and shaken after which a small amount of the sample is poured onto a narrow range pH (0 - 3 pH units) test strip to ensure  $\text{pH} < 2$ . If pH is not  $< 2$ , additional acid is added drop-wise, the bottle is capped and shaken, and the pH is tested again. This procedure is followed until  $\text{pH} < 2$ . The pH is checked on all samples requiring preservative and this amount of acid is added to the equipment blank and field blank. The amount of acid added is recorded in the field notebook. For filtered samples, the acid is added after filtration following the procedure outlined for unfiltered samples. Fresh preservatives are obtained from stocks biweekly or as needed for all sampling trips. Preservatives are taken into the field in polyethylene dropper bottles that are in good physical condition.

## 6.7 Sample Dispatch

Samples to be analyzed by the SFWMD laboratory are submitted to the laboratory by field personnel. The majority of samples are submitted the same day they are collected but all samples are submitted as soon as possible after collection in order to meet recommended holding times.

Samples to be analyzed by contract laboratories are shipped to the laboratory by common carrier overnight delivery the same or next day they are collected. All samples are carefully packed with appropriate material to prevent breakage, and sample chain of custody sheets are included with the samples. Insulated coolers are used for sample shipment and are sealed with shipping tape and tamper proof seal to avoid tampering. If samples must be kept at  $4^{\circ}\text{C}$ , wet ice is used during shipping. For ultra-trace mercury sampling, blue ice is used instead of wet ice.

## 6.8 Field Waste Disposal

All field generated wastes and purge waters are disposed of properly in a manner that will not contaminate the sampling site. The SFWMD does not sample hazardous waste sites so the only field generated wastes are acids and isopropyl alcohol. The isopropyl alcohol is containerized for proper disposal. Acids are diluted and disposed of on site in a location that will not contaminate the sampling area; no concentrated acids are taken into the field during SFWMD sampling trips. The calibration standards for field parameters are flushed into the sanitary sewer.



**Table 6.9 Holding Time and Preservation for Water Inorganics<sup>1</sup>**

Parameter	Holding Time	Preservation	Container & Size
Alkaline Phosphatase	24 hours	Cool, 4°C	Plastic, 125 ml
Alkalinity	14 days	Cool, 4°C	Plastic, 125 ml
Ammonia	28 days	Cool, 4°C, pH<2 (H <sub>2</sub> SO <sub>4</sub> )	Plastic, 60 ml
Biochemical Oxygen Demand	48 hours	Cool, 4°C	Plastic, 500 ml
Carbonaceous Biochemical Oxygen Demand	48 hours	Cool, 4°C	Plastic, 500 ml
Chemical Oxygen Demand	28 days	Cool, 4°C, pH<2(H <sub>2</sub> SO <sub>4</sub> )	Plastic, 125 ml
Chloride	28 days	None required	Plastic, 60 ml
Chlorine, Total Residual	Analyze immediately	None required	Plastic/glass, 250 ml
Chromium VI	24 hours	Cool, 4°C	Plastic, 250 ml
Color	48 hours	Cool, 4°C	Plastic, 60 ml
Fluoride	28 days	None required	Plastic, 500 ml
Inorganic Carbon	14 days	Cool, 4°C	Plastic, 125 ml <sup>2</sup>
pH	Analyze immediately	None required	Plastic, 125 ml
Kjeldahl nitrogen	28 days	Cool, 4°C, pH<2 (H <sub>2</sub> SO <sub>4</sub> )	Plastic, 125 ml
Mercury	28 days	pH<2 (HCL)	Teflon, 125 ml
Metals	6 months	pH<2 (HNO <sub>3</sub> )	Plastic, 250 ml
Nitrate + nitrite	28 days	Cool, 4°C, pH<2 (H <sub>2</sub> SO <sub>4</sub> )	Plastic, 60 ml
Nitrite	48 hours	Cool, 4°C	Plastic, 60 ml
Oil and Grease	28 days	Cool, 4°C, pH<2 (H <sub>2</sub> SO <sub>4</sub> )	Glass, 1 Liter
Organic Carbon	28 days	Cool, 4°C, pH<2(H <sub>2</sub> SO <sub>4</sub> )	Plastic, 125 ml
Orthophosphate	48 hours	Filter immediately, cool, 4°C	Plastic, 60 ml
Total phosphorus	28 days	Cool, 4°C, pH<2 (H <sub>2</sub> SO <sub>4</sub> )	Plastic, 125 ml
Residue, filterable, nonfilterable, volatile	7 days	Cool, 4°C	Plastic, 500 ml <sup>3</sup>
Silica	28 days	Cool, 4°C	Plastic, 60 ml
Specific conductance	28 days	Cool, 4°C	Plastic, 500 ml <sup>3</sup>
Sulfide	7 days	Cool, 4°C, 20 drops Zinc Acetate+ NaOH to pH >9	Plastic, 250 ml
Sulfate	28 days	Cool, 4°C	Plastic, 60 ml
Turbidity	48 hours	Cool, 4°C	Plastic, 500 ml <sup>3</sup>

(1) From 40 CFR, Part 136, Table II (7-1-90)

(2) Not listed in 40 CFR, Part 136, Table II (7-1-90)

(3) 250 ml plastic bottle may be used if BOD is not requested

**Table 6.10 Holding Time and Preservation for Water Organics**

Parameter	Holding Time	Preservation <sup>1</sup>	Container & Size
Volatile (Purgeable) Organics	14 days (preserved with 1:1 HCl), 7 days (unpreserved)	Cool, 4°C	Glass, 40 ml, Teflon lined septum
Base neutral acid extractable compounds	7 days until extraction, 40 days after extraction	Cool, 4°C	Amber Glass, 1 L, Teflon lined cap
Organochlorine Pesticides and PCB's	7 days until extraction, 40 days after extraction	Cool, 4°C	Amber Glass, 1 L, Teflon lined cap

(1) If Residual chlorine is present, Sodium Thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) is added to the sample vial first. The vial is then filled to almost full volume with sample, acid is added, and finally the vial is filled as per procedure.

Note: It is not recommended to mix the two preservatives (and sample) together in an intermediate vessel.

**Table 6.11 Holding Times and Preservation for Sediments, Soils and Tissues<sup>1</sup>**

Parameter	Holding Time	Preservation	Container & Size
Volatile organics (high level)	14 d	Cool, 4°C	Glass, 4 oz. wide mouth with Teflon/silicone septum
Volatile organics (low level)	48 hrs (if unpreserved)	Cool, 4°C	40 mL septum-sealed vial with PTFE lined septa
	14 days (if frozen)	Freeze	
Semivolatile organics	14 days until extraction, 40 days after extraction	Cool, 4°C	Glass, 8 oz. wide mouth with Teflon/silicone septum (50 grams)
Total metals	6 months	Cool, 4°C	Glass or plastic, 8 oz. wide mouth
Mercury	28 days	Cool, 4°C Or freeze	Glass or plastic, 8 oz. wide mouth Plastic, if samples are to be frozen.
Nutrients & Inorganics <sup>2</sup>	Not Specified	Cool, 4°C	Glass, 500 ml or plastic, 8 oz. wide mouth with Teflon lined closure

(1) From Table 5, Chapter 62-160, F. A. C.

(2) From USEPA Standard Operating Procedures and Quality Assurance Manual (Appendix A).

**Table 6.12 Holding Times and Preservation for Biologicals**

Parameter	Holding Time	Preservation	Container & Size
Chlorophyll	(i) 24 hours to filter (ii) 21 days after filtration	(i) Cool, 4°C, dark, filter with MgCO <sub>3</sub> , (ii) Filter frozen (until testing)	Amber Plastic 1-2 L
Benthic Macroinvertebrates	Preserved in the field with formalin, then ethanol in the laboratory or placed on ice and preserved with formalin within 8 hours, then preserved with ethanol	10% buffered formalin, then 70% ethanol	Glass or Plastic

## 6.9 Field Reagent and Standard Storage

**Table 6.13. Reagent, Solvent and Standard Storage**

<b>Chemical</b>	<b>Method of Storage</b>
Sulfuric Acid Nitric Acid Phosphoric Acid	Stored in original containers in vented acid storage cabinet. Acid stocks are stored according to chemical compatibility. Acid preservatives are transported in the field in 25 mL polyethylene dropper bottles.
Isopropyl Alcohol	Stored in original containers in vented solvent storage cabinet. Taken into the field in glass containers carried in a safety carrier.
pH Standards	Stored in cabinet designated for standard and reagent storage. Cabinet is in air conditioned laboratory. Standards taken into the field in polyethylene bottles.
Conductivity Standards	Stored in cabinet designated for standard and reagent storage. Cabinet is in air conditioned laboratory. Standards taken into the field in polyethylene bottles.
Formalin (10%)	Stored in cabinet designated for standard and reagent storage. Cabinet is in air conditioned laboratory. Taken into the field in polyethylene bottles.
Ethyl Alcohol	Stored in original containers in vented solvent storage cabinet. Taken into the field in approved non-combustible containers.
Sodium Hydroxide	Stored in polyethylen dropper bottles as provided by contract labs. Transported to the field in polyethylene bottles. Stored in cabinet designed for standard and reagent storage.
Zinc Acetate	Stored in polyethylene dropper bottles as provided by contract labs. Transported to the field in polyethylene bottles. Stored in cabinet designed for standard and reagent storage.
Hydrochloric Acid	Stored in original container. Used for field decontamination and to preserve mercury samples in the lab.
Analyte Free Water	For inorganics sampling, the analyte free water shall be stored in an opaque HDPE container for a maximum of 2 weeks. For organics (except VOCs) sampling, the analyte free water shall be stored in glass containers for a maximum of 1 week. When VOCs are part of the sampling protocol, analyte free water shall be stored for a maximum of 24 hours. In all cases, avoid excessive sunlight and high temperatures. Keep containers sealed to prevent introduction of possible contaminants.

## **7.0 SAMPLE CUSTODY**

A verifiable trail of documentation for each sample must be maintained from the time of sample collection through the analytical laboratory to the final reporting or archiving of data.

The purpose of sample custody is to provide a clear description of sample and container traceability from sample collection to final sample disposition and to identify those persons responsible for collection and analysis.

### **7.1 Documentation**

Custody starts with the person who prepares for the field trip (Fig. 7.1) and obtains the appropriate size pre-cleaned bottles from the bottle storage area.

The field sheets become a part of the project records maintained by the project manager. Original copies of the Chemistry Field Data Log or header sheets are retained by the laboratory. Original field notes are retained by the project sampling group, copies of field notes are supplied to QA unit for paper and electronic filing. Entries on all records, laboratory and field, are made in waterproof ink. All corrections must be made using a single line through incorrect entry, and the corrections must be initialed and dated by the person making the correction. All field documentation is signed or initialed by the field personnel. Figures 7.4 and 7.5 shows manually used Field Data Log. Laboratory Information Management System (LIMS)-generated log, containing the same information, is used for most projects. The log includes the site name or station code, the date and time of sample collection, the signature of the person relinquishing the samples, the field ID number, the number of samples collected, the intended analyses and preservation requirements, a comment section, and a place for the person who receives and logs-in the sample to sign, date, and record the corresponding laboratory sample numbers.

A guideline in documenting sampling activities and field condition is included in Appendix II. Figures 7.2 and 7.3 show the sample labels. Information on the label includes project code, the date and time the sample was taken, and the sample number. Sample numbers are unique sequential numbers generated by LIMS during pre-log-in. On-going LIMS enhancement would allow the use of barcoding.

In most cases, samples are delivered to the laboratory by the field sample collectors. Common carrier or contractor's courier is used when necessary. Samples with header sheets are placed inside ice coolers and the coolers are sealed with packing tape. The carrier's airway bill or mailing label is used to specify addressee and other information.

The data from the Chemistry Field Data Log, including field measurements, are manually entered into the LIMS as shown in Figure 7.6 and 7.7. This data entry process automatically generates a unique sequential number consisting of the login group hyphenated with the number of the sample for that group. A login group is defined as a group of samples collected by the same collector(s) on a given day, which may include more than one project. This sample number is used to track the progress of the sample through the laboratory.

### Figure 7.1 Field Trip Preparation Checklist

**PROGRAM:** \_\_\_\_\_ **DATE:** \_\_\_\_\_ **PROGRAM CODE:** \_\_\_\_\_  
(Routine / Quarterly / Bi-Annual)

- |   |                                     |
|---|-------------------------------------|
| _____ * Cellular Phone  | _____ * Sign Out Vehicle            |
| _____ * Sign Out Board  | _____ * Gas Vehicle                 |
| _____ * Maps  | _____ * Maintenance Check           |
| _____ * Vehicle Packet/Credit Cards   | _____ * Coolers/Ice                 |
| _____ * Pre-Cleaned Buckets   | _____ * Syringes                    |
| _____ * Filtration Unit _____   | _____ * Pre-cleaned Sampling Bottle |
| _____ * Processing Tray   |                                     |
| _____ * Calibrated Hydrolab   | _____ * Field Data Logs             |
| _____ * Field Notebook  | _____ * Waterproof Pens             |
| _____ * Labels or Tags/Rubber Bands   |                                     |
| _____ * Acids- H <sub>2</sub> SO <sub>4</sub> / HNO <sub>3</sub>  | _____ * Goggles, Gloves             |
| _____ * pH Test Strips  | _____ * 5 Gallons DI Water          |
| _____ * Bottles: 250ml-____, 125ml-____, 60ml-____, 250ml/TM-____, 125ml/Hg-____, 500ml-____, 1 liter-____, |                                     |
| _____ * Bottles: One Liter Bottle for Chlorophyll   |                                     |
| _____ * Stations: Routine / As Specified: _____   |                                     |
| _____ * Keys: _____   |                                     |

#### PERSONAL ITEMS

- |                   |                    |                        |                            |
|-------------------|--------------------|------------------------|----------------------------|
| _____ * Watch     | _____ * Sunglasses | _____ * Drinking Water | _____ * Hat                |
| _____ * Sunscreen | _____ * Rain gear  | _____ * Food           | _____ * Mosquito Repellent |

#### POST TRIP PROCEDURES

- \_\_\_\_\_ \* Check that coolers contain ice and check mark the "samples in ice" box on the log in sheet
- \_\_\_\_\_ \* Sort Samples in Sequence and by Label/Tag Color
- \_\_\_\_\_ \* Place Samples in Refrigerator marked "incoming samples"
- \_\_\_\_\_ \* Sign Chain of Custody Sheet/Get Time Stamp
- \_\_\_\_\_ \* Place Chain of Custody Sheet on the "to be logged in" board
- \_\_\_\_\_ \* Return Clean Bottles to Lab
- \_\_\_\_\_ \* Separate Filter Holders and place in Soak Solution
- \_\_\_\_\_ \* Place Dirty Bottles in Washing area
- \_\_\_\_\_ \* Replace Water in Hydrolab Stand (Tap Water Only!)
- \_\_\_\_\_ \* Clean Out Vehicle
- \_\_\_\_\_ \* Fill Out Trip Ticket/Return Keys
- \_\_\_\_\_ \* Return Field Notebooks to Office; copy field notes and attach to header sheet
- \_\_\_\_\_ \* Report Equipment(Vehicle, Hydrolab, etc.) Problems to Supervisor

Figure 7.2  
Sample Submission Diagram for Unfiltered Water

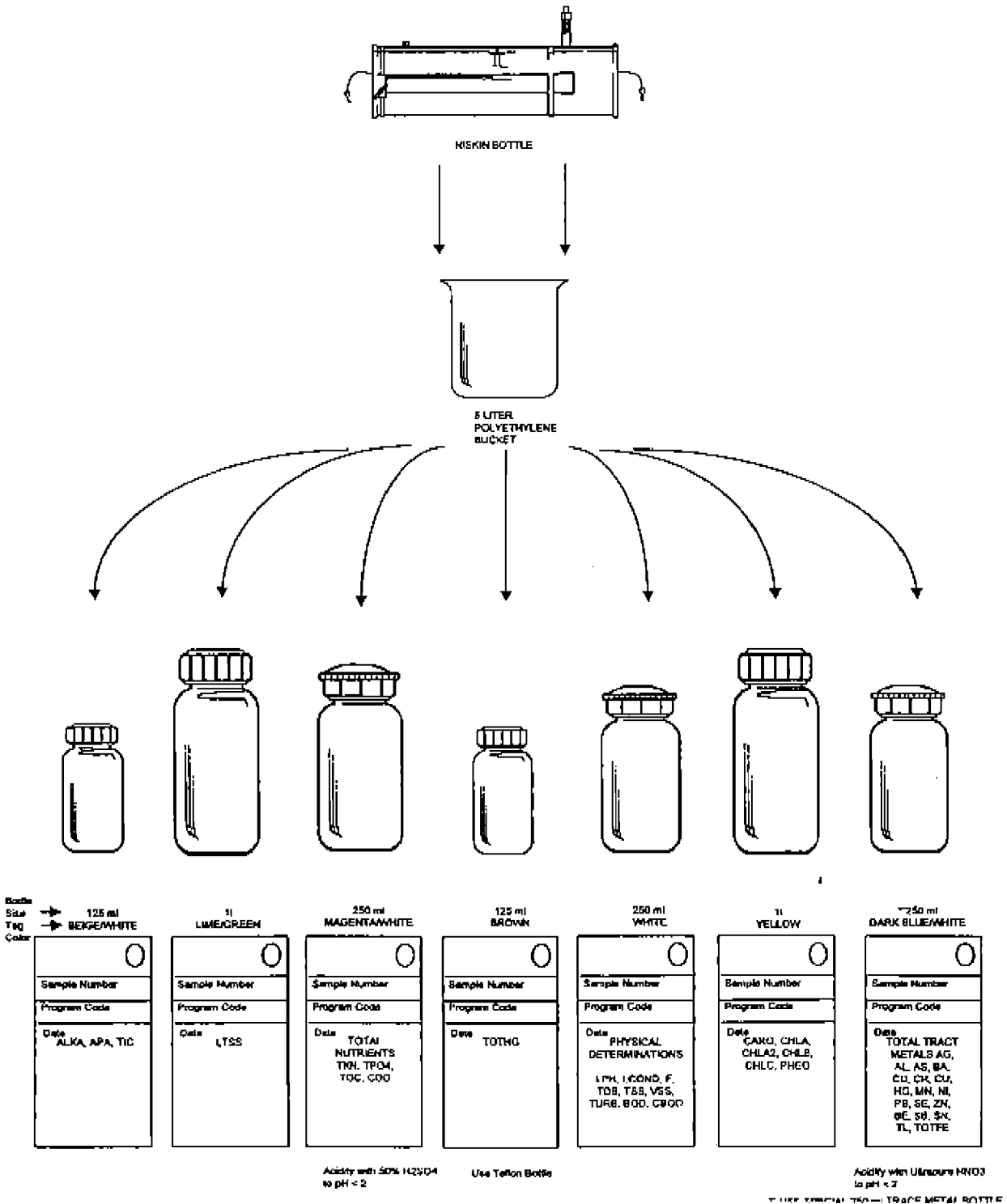
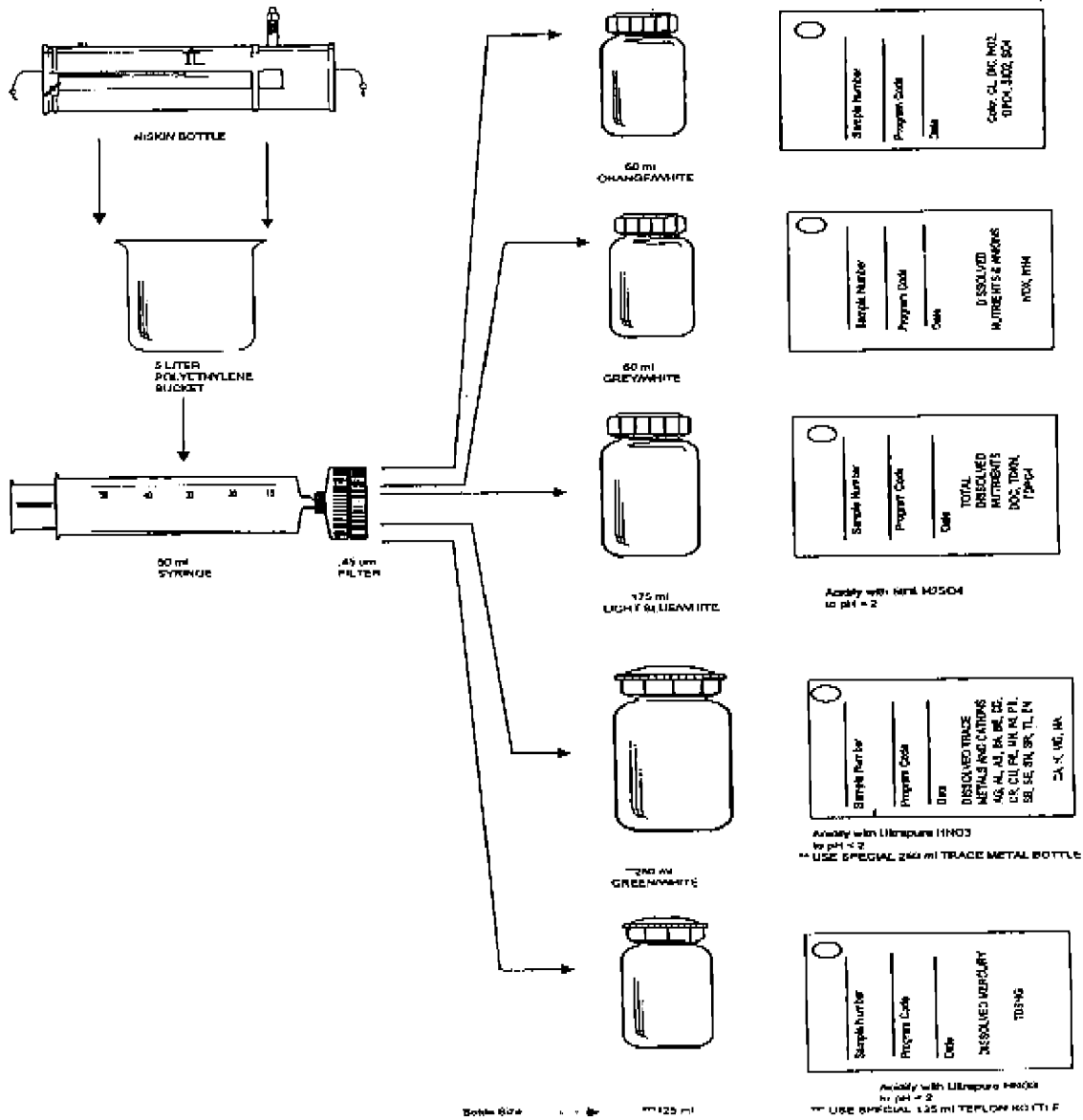


Figure 7.3  
Sample Submission Diagram for Filtered Water







## INFORMATION TABLE

**PROJECT CODE** – The four-letter code for the project name. This code must be registered with the WQMD before the project is initiated.

**DATE SUBMITTED** – The date on which the samples are submitted to the laboratory for analysis.

**DATA COLLECTOR** – The person or persons who performed the sampling trip.

**PROJECT NUMBER** – The SFWMD budget code for the project.

**PERMIT NUMBER** – The SFWMD permit number.

**PROGRAM TYPE** – Specific to EXP-Experimental/Research or MON-Monitoring

### DATA TABLE

**LIMS NUMBER** – (Laboratory use only) The unique number generated by the LIMS system. This number is assigned when the samples are logged in.

**NB** – The number of bottles submitted for the sample.

**SAMPLE NUMBER** – The field sample number. This is assigned on a per project basis by the individual project managers.

**DATE/TIME COLLECTED** – the month, day year, and time the sample was collected.

**STATION CODE** – An eight character or less station code. The station code must be registered with the Water Quality Monitoring Division before sampling is initiated.

**TYPE** – The sample type. Valid codes are as follows:

EB Equipment Blank  
 FB Field Blank  
 FD Field Duplicate  
 RS Replicate Sample  
 SS Split Sample  
 SP Regular Samples  
**MATRIX CODE** – The two or three letter code for the type of material being sampled.  
 SE Sediment  
 SO Soil  
 GW Groundwater  
 SW Surface Water  
 RA Atmospheric Deposition (Rain)  
 SA Sulline  
 BPL Biological - Plant  
 BFI Biological - Fish  
 BAN Biological - Animal  
 BFE Biological - Feathers  
 BIAL Biological - Algae  
 BPE Biological - Periphyton  
 PW Pore Water

**METHOD CODE** – The one, two or three letter code for the method of sample collection.

ACF Auto-Sampler Composite Flow Proportional  
 ACT Auto-Sampler Composite Time Proportional  
 ADF Auto-Sampler Discreet Flow Proportional  
 ADT Auto-Sampler Discreet Time Proportional  
 CDI Composite Depth Integrated  
 CWI Composite Width Integrated  
 CXI Composite Cross Section Integrated  
 CSI Composite Site Integrated – Sediment/Soil Only  
 G Grab  
 GB Grab Bailor  
 GP Grab Purwp  
 BLK Bulk  
 WET Wet (Atmospheric Deposition/Rain)  
 DRY Dry (Atmospheric Deposition/Rain)  
 FP Field Parameters (In Situ Measurements, No sample)

**UD** – The code for upstream/downstream. Valid codes are as follows:

1 Upstream  
 2 Downstream  
 Leave blank for no observation.  
**DS** – The code for discharge. Valid codes are as follows:  
 1 Flow  
 2 No Flow  
 3 Reverse Flow or Backpumping  
 Leave blank for no observation.

**WE** – The code for weather. Valid codes are as follows: Clear Skies Slight Overcast Medium Overcast Very Overcast Drizzle Rain

**DEPTH** – The depth in meters at which the sample was taken.

**TEMP** – The water temperature in degrees centigrade.

**PH** – The pH value in units.

**COND** – The specific conductivity value in umhos/cm.

**DO** – The dissolved oxygen value in mg/l

**SOO** – The depth in meters at which the secchi disk is visible.

**SALINITY** – The salinity value in mg/l.

**REDOX** – The oxidation/reduction potential in mV.

**TDEPTH** – The total water column depth in meters.

**COMMENTS** – Any additional information on the sample.

**Relinquished By** – The signature of the data collector. This signature signifies that all information is checked and sample custody is relinquished.

**Date** – The date the sample custody is relinquished.

**Time** – The time the sample custody is relinquished.

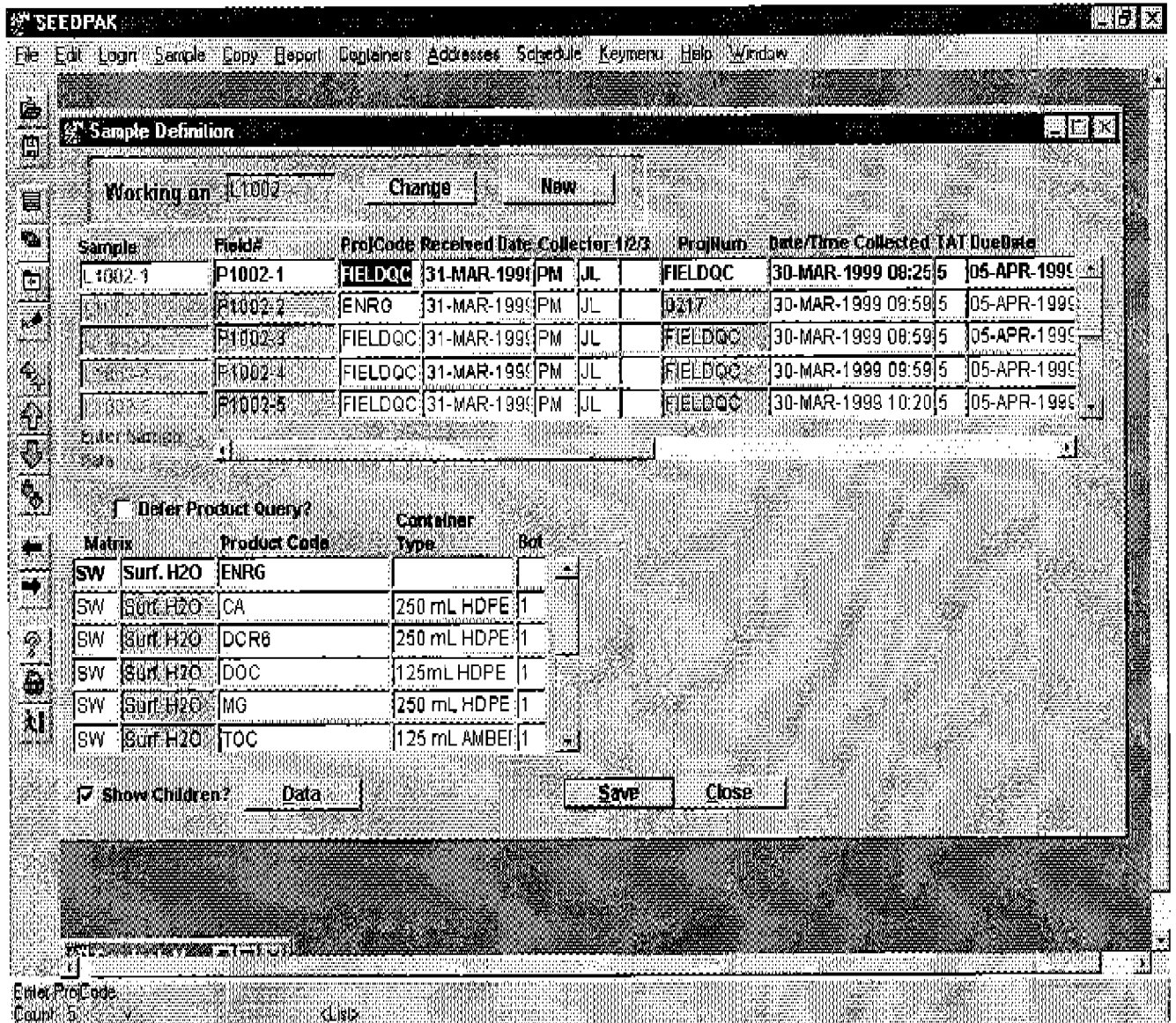


Figure 7.6 Sample Log-In to LIMS

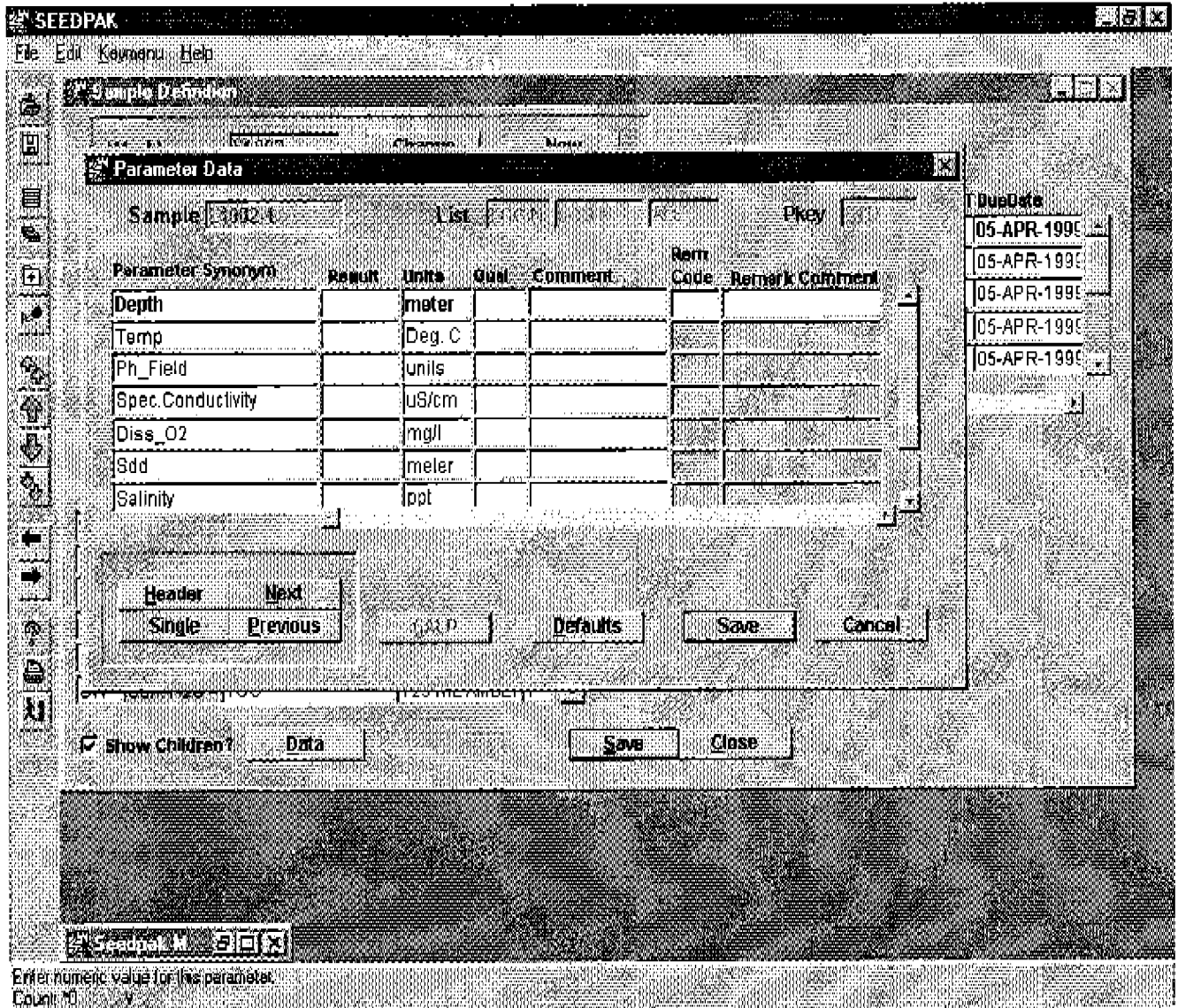


Figure 7.7 Field measurement data input screen

The sample preparation (digestion) records are maintained with the analytical run. A sample of digestion log template is shown in Figure 7.8. The information required is the laboratory sample number, standards, QC samples, dilution factors, person preparing the samples, and the date of preparation. A sample of QC/instrument log template is shown in Figure 7.9.

If samples are collected and sent to a contract laboratory by common carrier for analysis, the custody forms supplied by the contract laboratory are used. Only laboratories that have DEP approved comprehensive quality assurance plans are used as contract laboratories. The pre-cleaned sample containers received from the contract laboratory are delivered to the project manager who is responsible for their secured storage.

## **7.2 Field Custody Protocols**

The samples are labeled at the time of collection using waterproof labels which have been filled out with waterproof pens. The labels are affixed directly to the sample bottles. Some bottles may come with pre-attached labels already affixed to the bottles which may also be used.

Every project is required to be registered in LIMS and DBHYDRO databases and is assigned a unique one to four character project code. The sample field numbers are generated by LIMS during pre-login, and is designated with a letter "P," pre-login batch#, and sample numbers. The field sample (P) numbers are associated with the station (site) code on the Chemistry Field Data Log and in the field notebook. The field sample number can be used to trace a sample through the sample tag, the Chemistry Field Data Log, the field notebook, the laboratory information management system (LIMS), and final data archival.

The field records are maintained and stored by the project manager, who is responsible for maintaining all records of the project for the period of time specified by the Florida standards for record management. The field records which are identified by the project code may include the field notebooks and the Chemistry Field Data Logs.

All physical parameter measurements obtained in the field are written on the Chemistry Field Data Log shown in Figure 7.4 at the time of sample collection. In-situ measurements may include temperature, pH, specific conductivity, dissolved oxygen, oxidation-reduction potential, Secchi disc depth, total column depth, turbidity and salinity. Other information that must be noted on this form includes project code, collector ID, sample number, date and time of collection, station or site ID, types of QC samples collected (when and where collected), depth from which sample was collected, flow conditions, requested parameters, and chain of custody documentation. Beginning and ending times of any composite sampling is noted. Additional information on this form includes upstream/downstream notation, discharge information, weather, sample type, and a comments section. Comment entries may include other information such as field condition, problems with sampling, start of autosampler collection, sample volumes, etc.



# DIGESTION LOG

EPA 351.2

Parameter: TKN/TKDN

Date/Time Started:	
Workgroup #:	
Analyst:	
TKN File #:	

Standard Prep. (date/initials):		QC1:	
Stock NH4/TKN solution lot #:		QC2:	
Organic Check Stock Solution:			

Tube #	Sample ID	Comments	Tube #	Sample ID	Comments
1	S1	10 mg/L	21		
2	S2	5 mg/L	22		
3	S3	3 mg/L	23		
4	S4	1 mg/L	24		
5	S5	0 mg/L	25	WG-6	L_____ +1ml sol A
6	WG-1	Check 1	26		
7	WG-2	QC 1	27		
8			28		
9	WG-4	L_____ +1ml sol A	29		
10	WG-3	QC 2	30		
11			31		
12			32		
13			33		
14			34		
15			35		
16			36		
17			37		
18			38		
19			39		
20			40		

COMMENTS:

Figure 7.7 Digestion Log



# Quality Control Results

Parameter: \_\_\_\_\_

Instrument: \_\_\_\_\_ Analyst: \_\_\_\_\_ Date: \_\_\_\_\_

Method #: \_\_\_\_\_ Workgroup #: \_\_\_\_\_

QC # 1 ID	Value	QC # 2 ID	Value	QC # 3 ID	Value	QC # 4 ID	Value
Range							

	Sample			Spk Sample		Spk value	% Rec.
	ID	value	Factor	Corr. Value	ID		
Spk # 1							
Spk # 2							
Spk # 3							
Spk # 4							
Spk # 5							
Spk # 6							
Range					Spk. Conc		

Set #	1	2	3	4	5	$\% \text{ Rec.} = \frac{\text{Spk Sample} - \text{Corr. Value}}{\text{Spk. Conc}} \times 100$ $\text{RPD} = \frac{\text{value 1} - \text{value 2}}{\text{Mean}} \times 100$	
ID							
Value 1							
Value 2							
Mean							
RPD							
Range							

Std #	1	2	3	4	5	6	7	Correlation Coefficient
Conc								
Abs								
Abs								

Check	True Value	Value	% Rec.	Value	% Rec.	Value	% Rec.
Std							

File Name	Method	Tray	Date

Comments: \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

Note: Attach sample ID table to QC form and copy both for filling in instrument log book.

Figure 7.8 Quality Control and Instrument Log Form

Relevant field observations are noted in a bound waterproof notebook at the time of sample collection. These include sample number, station or site name, date and time, weather, flow conditions, water color, water smell, water clarity, weed conditions, number of drops and type of acid added to each bottle, persons other than sampling personnel at the site, type of purging and sampling equipment used with corresponding ID# (if available), field decontamination performed and if applicable, wave height, bottom conditions, algae description, use of boats and/or other fuel powered equipment. If no sample is collected from a scheduled site, detailed explanation must be noted on the field notebook and entered on the Chemistry Field Log as "NOB" for no bottle.

For monitoring wells, the following information is recorded in addition to any applicable information from the above list: depth to water, calculation for purge volume, determination of volume purged, method of purge, purging rate, date and time the well was purged, and readings taken until the well stabilized.

For wells with in place plumbing or artesian wells, the following information is recorded: plumbing or tap material, flow rate at which the well was purged, time the well was allowed to purge, and the flow rate when the sample was collected.

A monitor well database is kept for all of the wells that are sampled by the SFWMD. This includes the following information: well casing material, well diameter, type of casing, screen diameter, screen type, total depth of the well, casing depth, method of well installation, date of well installation, driller's name, latitude, longitude, measuring point elevation, and land surface elevation. In addition, new wells installed by the SFWMD also have the drilling mud type and name recorded. For sediments, the depth at which the sample is taken is recorded. Drilling/boring information is not used for sampling.

### **7.2.1 Sample Transport**

Following collection of the sample, the bottles are sealed, tagged, and returned to the laboratory. For in-house samples, bottles are placed in designated sample refrigerator. If the samples are for shipment to the contract laboratory, samples, with appropriate sample label and chain of custody form, are packed in coolers with bubble wrap or other appropriate packing material to avoid breakage. Samples for VOC analysis are placed into a separate bubble-pack bag for each station. Chain of custody forms are enclosed in a plastic bag for protection from water damage. Samples are kept at 4°C with wet ice (blue ice for ultra-trace mercury). Coolers are taped shut using packing tape and taken to the SFWMD shipping area for pickup by common carrier. Coolers are shipped to the laboratory overnight, and the shipping receipts are retained. Chain of custody forms are returned to SFWMD with the analytical results.

### **7.2.2 Sample Transmittal**

The Chemistry Field Data Log and examples of the sample tags are shown in Figures 7.2

through 7.4. The Chemistry Field Data Log includes the field ID number, date and time of sample collection, station (site) code, intended analyses (designated by circling desired parameters in figure 7.4), method of preservation, whether or not the samples are still in wet ice, and limited comments about the sample or sample container.

### **7.3 Laboratory Operations**

The samples are brought to the laboratory by the field sampling personnel and those samples to be analyzed by the SFWMD laboratory are placed in the designated refrigerator. The person bringing the samples to the laboratory signs and stamps the Chemistry Field Data Log with the time clock. The Chemistry Field Data Logs are given to the person responsible for logging-in the sample. The information from the Chemistry Field Data Log is entered into the LIMS and a laboratory sample number is generated by LIMS consisting of a login group hyphenated with the number of the sample within the group. For example, L1001-1 is the first sample of the first login group. The person logging-in the samples records the LIMS numbers on the Chemistry Field Data Log, initials and dates the form at the time the samples are logged (in the "received by" section). The LIMS numbers, date logged, and initials of the logger are also maintained in a bound laboratory notebook. A computer-generated list, verified by the data entry technician, is obtained with the respective field and LIMS numbers for each sample.

Labels for each aliquot are generated by LIMS and are manually attached to the sample field tag or directly to the sample container. As each sample is labeled, the technician checks the proper match of field and LIMS numbers, and examines the sample bottle for leakage, cracks, and any other obvious faults. Five percent of the samples (at least one from each batch) are checked for proper preservation. The results of this check are documented in a bound notebook.

#### **7.3.1 Sample Rejection**

The following criteria shall be used to reject samples in the laboratory, discontinuing the analytical process at whatever stage the violation is discovered:

- Cracked or broken sample containers when no alternate container is available.
- Incorrect preservation, including cases when samples were not in ice, and when no procedure exists to render the sample valid.
- A sample that is out of holding time.
- Presence of obvious sample contamination from foreign matter in the sample (animal parts, insects, etc.)
- A sample is obviously mislabeled, e.g. a sample labeled as a blank and vice versa.
- Absence of or incomplete information on the Chemistry Field Data Log.
- Presence of potential hazard that is beyond the normal handling in the laboratory.

Whenever such criteria are discovered, the problem will be documented and approval for rejection of the samples shall be obtained from the lab supervisor and the QA unit.



### **7.3.2 Sample Security, Accessibility, and Storage**

The samples are accessible to the laboratory and field staff during working hours. The doors to the exterior of the building are locked when the last member of the staff leaves for the day. The only persons authorized to be in the laboratory are the laboratory staff and the sampling personnel delivering samples. All visitors must be escorted by a member of the division staff.

Samples are stored in refrigerators designated for sample storage only. No VOCs are stored in the laboratory refrigerators and standard and chemical solutions are stored in separate refrigerators specifically designated for that purpose.

Clearly identified sample digestates are stored on laboratory counters until they are analyzed and are in custody of individual analyst/prep technician during that time.

### **7.3.3 Sample Distribution and Tracking**

The analysts query the LIMS database daily for samples requiring their assigned analyses and generate work groups for these samples. Analysts are required to analyze reworks and the oldest samples on each day's first run. The supervisor receives a daily backlog report listing all samples showing incomplete analyses.

The analysts are responsible for removing the required samples from the refrigerators, analyzing them, and returning them to the refrigerators immediately following analysis. Bound notebooks are used to track digested samples. The person doing the digestion lists the samples, standards and QC samples digested in the batch.

Following completion of the analyses and QA release of the results, the laboratory supervisor generates a sample disposal list. Designated laboratory staff then removes the samples which are included on the disposal list and disposed of by diluting and dumping into the sanitary sewer. The status of the sample is changed from NEED to DONE in the disposal department in LIMS.

### **7.3.4 Interlab Custody**

The SFWMD has only one laboratory and may transfer samples to overflow laboratories when necessary, such as in the event of catastrophic failure. Samples are transported to a contract lab by common carrier or laboratory courier accompanied by the log in sheets and the contract lab's chain of custody. The contract laboratory is responsible for immediately reporting any discrepancy or missing or damaged samples to SFWMD. Final resolution of discrepancies is the responsibility of the District project manager. On-going LIMS enhancement would provide a better tracking of samples sent to contract laboratories and data received from them.

## **7.4 Electronic Data Records**

Instrument data files, including data plots, sample tables, and raw data are stored in individual computer for at least three months. These data are then transferred into diskettes and stored in the laboratory. A LIMS database is used by SFWMD for sample tracking, data storage, and data reduction. Electronic copies of field notes are also maintained.

### **7.4.1 Security System**

The LIMS database has several levels of security. The Staff Programmer Analyst responsible for its operation and maintenance has the highest level of security and can access all information and programs in LIMS. The analysts can enter analytical results, and may modify the sample information or results in LIMS only upon providing Good Automated Lab Protocol (GALP) comments and only before supervisory approval on the data has been done. After that, the analyst must obtain approval from the supervisor and the Laboratory QA Officer to modify results or information. The project managers can only read and print results. User names and passwords are assigned to each person and each level of user corresponds to level of security and permission in LIMS. Back up of both the file system and database is performed daily so that in the event of a catastrophe, only one day of data would be lost. One week's worth of system files is stored in the vault.

### **7.4.2 Electronic Data Transfer**

Data files from instrument PCs are transferred electronically into LIMS. Upon review and final approval, the laboratory QA officer releases the data from LIMS, which are then archived into the District's DBHYDRO database. All data at SFWMD is public information through an on-line database code named REMO that can be accessed directly by registered public users. Requests for data are handled by a designated staff in Water Resources Evaluation Department. For all data transmitted electronically, (e.g. by modem, or diskettes), hard copies are sent via mail following data transmittal.

### **7.4.4 Documentation and Verification**

All LIMS documentation, including project registrations, request for changes, etc., is maintained by the LIMS administrator. Field personnel and laboratory staff are responsible for maintaining the documentation records and the maintenance logs during data collection and analysis. The documentation for all instrument software is located in the laboratory at the instrument. Software problems are included in the maintenance log for the instrument. Software revisions are installed and the records maintained by the laboratory supervisor or the QA unit.

Software is verified by comparing the results generated by the new software to the results from the old software for at least six analytical runs or by other means of calculation. The QC results are also used to show that the software is performing correctly.

Data entry is verified by comparing the results obtained by the instrument software to the results entered into the database. Manual data entry is verified by comparing the results in the database to the results on the data entry forms.

All original hard copies of analytical runs are kept in the QA unit filing area. Any division staff requesting these documents must sign them out and return the documents promptly to the same location.

## **8.0 Analytical Procedures**

The analytical procedures used by SFWMD are listed in Section 5.0.

### **8.1 Field Screening Methods**

A field screening method for soluble reactive phosphate (SRP) is used in the field to determine samples which may be exceeding established limits (see appendix C). Field screening for turbidity is also done for some projects. Data obtained from these field screenings are used only to determine which samples should be sent to the laboratory for testing, based on project requirements.

### **8.2 Laboratory Glassware Cleaning and Storage Procedures**

For physical parameters and nutrients, the laboratory glassware is cleaned by washing with a laboratory grade phosphate-free detergent solution, rinsing with D.I. water, 10% hydrochloric, and finally D.I. water. Once air or oven dried, glassware is stored capped, in cabinets, in the appropriate analytical or digestion area.

Digestion tubes, beakers and other pieces of glassware are washed in a labware washer which has been programmed to follow the above procedure except for the acid rinse. The program is stopped after the first tap water rinse, the glassware is removed from the washer and rinsed with 10% hydrochloric acid and then returned to the washer for the final tap and analyte free water rinses. The glassware is then allowed to either air dry or is placed in a glassware dryer. Once dry, the glassware is stored in clean drawers in the appropriate analytical or digestion area.

A complete supply of glassware is dedicated for use in the metals laboratory. Pipettes are soaked in 1% lab grade detergent (Liquinox<sup>TM</sup> or equivalent), and cleaned in a pipette washer using three volumes of D. I. water followed by soaking in 20% HNO<sub>3</sub> for 24 hours minimum, and washing with three volumes of analyte free water. Volumetric flasks and glassware dedicated to major cation analyses are rinsed three times with analyte free water after each use, air dried, and stored in cabinets in the appropriate analytical or digestion area. Glassware dedicated to trace metals is rinsed with analyte free water after each use, soaked in 20% HNO<sub>3</sub> bath, rinsed with analyte free water, allowed to air dry, and stored separately from other glassware in the metals analysis area. Polyethylene or Teflon trace metal bottles are soaked in 20% nitric acid for a minimum of 24 hours, analyte free water rinsed, and stored in cabinets in the metals area filled with analyte free water.

### **8.3 Laboratory Method Modifications**

The color procedure has been modified for use in the laboratory. The samples submitted to this laboratory are from natural surface and ground water sources within the boundaries of the SFWMD.

The color in the samples is due primarily to vegetative decay and not from industrial sources. Measurement of the color at 465 nm gives results comparable to those measured visually by technicians. Use of an autoanalyzer, with a colorimeter, eliminates the natural variation in color perception found in the human eye and allows the lab to consistently report results regardless of

which technician performs the analysis. Calibration of the instrument is done using known concentrations of platinum cobalt solution. The procedure used is given in Appendix A.

Silica analysis is done using a method developed and validated by Alpkem for use in Rapid Flow Analyzers. The adopted method reduces saltwater interferences. A copy of the modified method is included in Appendix B.

Alkaline phosphatase activity (APA) is measured using the Methylumbelliferyl Phosphate (MUP) assay (Pettersson and Jansson, 1978). The procedure is included as Appendix D.

Total and dissolved inorganic carbon (TIC/DIC) is determined using a high temperature combustion and infrared detection system following the EPA 415.1 for total organic carbon. Method was developed based also on alkalinity method (EPA 310.1). A copy of the procedure, which has been validated and approved by FDEP, is included as Appendix F.

Trace mercury sample preparation and analytical procedure are modifications from EPA1631; validation package has been submitted and the method has been approved by FDEP. Same validation package will be sent to EPA for approval on its use for NPDES monitoring.

#### 8.4 Laboratory Reagent Storage

**Table 8-1. Reagent and Chemical Storage**

<b>Chemical</b>	<b>Method of Storage</b>
Mineral acids (sulfuric, nitric, hydrochloric and phosphoric acids)	Stored in original containers in vented cabinet designed for acid storage. Storage is done based on chemical compatibility.
Liquid bases	Stored in original containers in a vented cabinet designed for corrosive storage.
Organic solvents	Stored in original containers in a vented cabinet designed for flammable storage in the outside storage area.
Compressed gases	Stored in original containers in the compressed gas storage area in the outside storage area.
Dry chemicals	Stored in original containers segregated by reactivity in the dry chemical storage area.

As each chemical is received, it is dated and initialed by the person unpacking it. When a new container is opened for use, it is dated and initialed by the person who opened it.

#### 8.5 Waste Disposal

The laboratory has a designated hazardous waste storage area outside the laboratory. The process wastes containing mercury, phenol, chromium, and acetone are collected for disposal by a hazardous waste company. As each waste is generated, the volume is entered on a monthly hazardous waste report. When the volume collected reaches a specific level set by Risk Management, the waste is removed by a commercial waste hauler and disposed of according state and federal regulations.

Any small amounts of reagents are transferred to the hazardous waste storage area as they expire

or are no longer needed. The waste disposal company then picks them up for proper disposal.

Concentrated acids and bases are neutralized or diluted in the laboratory then poured down a drain with copious amounts of water; diluted acids or acid solutions are poured directly down a drain into the lab drainage system with copious amounts of water where the waste passes through a neutralization tank on the way to the sanitary sewer system. Samples are disposed of by washing them into the sanitary sewer system with copious amounts of water. Nitric acid is disposed of according to local, state and federal regulations.

## 9.0 Calibration Procedures and Frequency

Listed on Tables 9.4 and 9.5 are the calibration procedures and frequency used for the laboratory and field instrumentation, respectively.

### 9.1 Instrumentation Lists

#### 9.1.1 Laboratory Instrumentation

<u>Manufacturer</u>	<u>Model and Description</u>
Hach	Model 2100 AN Turbidimeter Model 18900 Ratio Turbidimeter Model 45600 COD Reactor
Fisher Scientific	Model 50 Ion Analyzer pH Electrodes Model AB 15 pH Meter Model 21K/R Marathon Centrifuge Model 307A BOD Incubator Model SPT - III Stereoscope
Orion	Combination Fluoride Electrode Model 162 Conductivity Meter Model 960 Autochemistry System pH Electrode with ATC
Mettler	P160 Top Loading Balance AE163 Analytical Balance (2)AE100 Analytical Balance
Bausch & Lomb	Spectronic 501 Visible Spectrophotometer
Dionex	4000i Ion Chromatograph DX500 Ion Chromatograph
Alpkem	(3)RFA300 Rapid Flow Analyzer with PC workstation (3)RFA500 Rapid Flow Analyzer with PC workstation
Perkin Elmer	1100B Flame Atomic Absorption Spectrophotometer Z5100 Furnace Atomic Absorption Spectrophotometer Optima 3000XL ICP Spectrometer Lambda 6 UV-VIS Spectrophotometer
Shimadzu	Model 5050A Total Organic Carbon Analyzer

### 9.1.1 Laboratory Instrumentation (cont.)

<u>Manufacturer</u>	<u>Model and Description</u>
Rosemount Dohrmann	DC-190 Total Organic Carbon Analyzer
Millipore	Cytofluor 2350 Fluorescence Measurement System
Barnstead	Model 2250 Autoclave
YSI	Model 59 DO Meter Model 5905 DO Probe
Thermolyne	(4) Model 9000 Oven Furnatrol II Muffle Furnace Type 37900 Culture Incubator
CEM	MDS-2100 Microwave Digester
Tecator	(2) Digestion System 40, 1016 Digester
Ultra Lum	Ultra Violet Digestion Cabinet
Lachat	Quickechem 8000 Mercury Analyzer Quickechem 8000 Automated Ion Analyzer (2) BD-46 Digestion Blocks
Powers Scientific	(2) Refrigerator
Amerikooler	Refrigerator
Jordan	Refrigerator
Market Forge	Autoclave



## 9.1 Instrumentation Lists (cont.)

### 9.1.2 Field Instruments

<u>Manufacturer</u>	<u>Model and Description</u>
Hydrolab	Model 4031 pH, Conductivity, ORP, and Temperature Meter Model 4041 pH, Conductivity, DO, and Temperature Meter Surveyor II pH, Conductivity, DO, Temperature, Salinity, Surveyor III pH, Conductivity, DO, Temp., Salinity ORP, Turbidity and Depth Meter Surveyor 4 pH, Conductivity, DO, and Temperature Meter
Solomat	WP803
YSI	Model 58 Dissolved Oxygen Meter Model 6000UPG Multiprobe pH, Conductivity, DO, Temperature,
EH	Turbidity Model 600XL Multiprobe pH, Conductivity, DO, Temperature, EH
HF Scientific	Model DRT-15CE Turbidity Secchi Depth Disc
Licor	Spherical Quantum sensors

## 9.2 Standard Receipt and Traceability

Standard stocks are received by the laboratory staff, initialed, dated, and stored in the designated area. The preparation dates of in-house primary stock solutions are recorded in a log book along with the following information: analyte, concentration, supplier, date opened, expiration date and date of disposal. Only one bottle of each purchased analyte stock solution may be in use at one time. Purchased stock solutions are replaced according to expiration date or sooner if the stock is depleted. Manufacturer's certificates of analysis and/or records of traceability for purchased stock solutions are filed in a notebook according to analyte or analytical category. Preparation logs are maintained for each standard stock. Working calibration standards are prepared at a frequency pre-determined for each analyte, based on the stability of the chemical. Such frequency is specified in individual SOP and in Table 9.1. The standard sources and preparation are given in Tables 9.1 and 9.2.

The calibration procedures for laboratory and field instruments are given in Tables 9.3 to 9.5. QC check standards from a different source than the calibration standards are used to check the initial calibration for both laboratory and field instruments. Calibration information including the date and time of calibration, technician, standards used, standard results and temperature, and instrument for the field is recorded in the field note book.

Calibration information for the laboratory is recorded in the QC log and includes the date of analysis, standard values, instrument response values for the standards, correlation coefficient, results of continuing and initial calibration, precision and accuracy results, and samples analyzed.

**Table 9.1 Standard Sources and Preparation**

Instrument Group	Standard Sources	How Received	Source Storage	Preparation from Source	Lab Stock Storage	Preparation Frequency
Atomic Absorption/Emission	Spec/JT Baker/NIST/EM Scientific	Solutions of 1000 mg/L and 10,000 mg/L	Room temperature	Primary stocks (>1 mg/L) prepared from source Working stocks	0.2% HNO <sub>3</sub> at room temp. NA	Weekly or as needed Daily/Weekly
Continuous Flow & Ion Chromatograph	Commercial lab supplier	Dry, ACS reagent grade	Room temperature	Primary stocks, 1000 mg/L prepared from source Working stocks	Refrigerator NA	Monthly Daily/Weekly
Organic Carbon/Inorganic Carbon	Commercial lab supplier	Dry, ACS analytical grade	Room temperature	Primary stocks, 1000 mg/L prepared from source Working stocks	Refrigerator NA	Monthly Daily/Weekly
Alkaline Phosphatase	Sigma Chemicals	Dry, Enzymatic grade	Room temperature	Primary stocks, 10 micro Molar in Tris Buffer Working stocks	Room temperature NA	Monthly Daily/Weekly
pH Standards	Commercial lab supplier	pH 4,7,10 solutions	Room temperature	NA	NA	Replace on expiration
Conductivity Standards	Commercial lab supplier	200, 720, 1413, 2000 uS	Room temperature	NA	NA	Replace on expiration
Turbidity	Hach	Sealed Gel Standards	Room temperature	NA	NA	Annual replacement
Color	Commercial lab supplier	500 Pt-Co units	Room temperature	Working stocks	NA	Weekly
Analytical balances	Commercial lab supplier	1 g and 100 g Class S weights Entire set of class S weights	Dessicator, room temperature	NA	NA	Daily Monthly
Mercury	Commercial lab supplier	10 mg/ml NIST/NBS traceable standard	Room temperature	Primary stocks 100mg/l & 1000ug/l prepared from source. Working Stocks	Room temperature Room temperature	Weekly or as needed Daily

**Table 9.2: Solutions Requiring Standardization**

Test	Standard sources	How Received	Source Storage	Preparation from Source	Standardization and Criteria	Standardization Frequency	Preparation Frequency
Alkalinity Titration	Commercial Lab Supplier	0.02 N Sulfuric Acid	Acid Storage Cabinet	Used as is from supplier (certified)	Normality checked with 0.05 N sodium carbonate; must be within 5% of expected value	Weekly and each time a new lot is used	Used as is from Supplier

**Table 9.3: Laboratory Equipment Calibration**

Equipment	Calibration	Acceptance Criteria	Frequency
Analytical Balance	1 g and 100g weight, class S weights	All weights within 2 % of known value	Daily
	Entire set of Class S weights	All weights within 2 % of known value	Monthly
Autoclave	Semi-annual external maintenance and calibration Autoclave Tape/Strips	NA	Semi-Annually
BOD Incubator	Temperature recorded from a calibrated thermometer. Adjustments made as needed	Indicates acceptable set-up condition $\pm 1^{\circ}\text{C}$	Each use (for Total P digestion) Each time of use
Ovens	Temperature recorded from a calibrated thermometer. Adjustments made as needed	$\pm 1^{\circ}\text{C}$	Daily
Refrigerators	Temperature recorded from a calibrated thermometer. Adjustments made as needed	$\pm 1^{\circ}\text{C}$	Daily
Mercury Thermometer	Checked with a NIST(NBS) certified thermometer	$\pm 0.5^{\circ}\text{C}$	Semi-Annually
Digital Thermometer	Checked with a NIST(NBS) certified thermometer	$\pm 0.1^{\circ}\text{C}$	Quarterly

**Table 9.4 Laboratory Instrument Calibration**

Instrument	# Standards Initial Calib.	Accept/Reject Criteria - Initial Calibration	Frequency	# Standards Cont. Calib.	Accept/Reject Criteria - Cont. Calibration	Freq.
Atomic Absorption/Emission	3-5	Corr. Coefficient >0.995	Daily prior to use or failure of cont. calibration	1-5	Concentration within 5% of known value (mid-range)	Every 20 samples
Continuous Flow	5 - 7	Linear Corr. Coefficient >0.998	Daily prior to use or failure of cont. calibration	1-7	Concentration within 5% of known value (mid-range)	Every 20 samples
Silica only	5 - 7	Quadratic Regression Corr. >0.998	(same)	1 - 7	(same)	
Ion Chromatograph	5	Corr. Coefficient > 0.998	Daily prior to use or failure of cont. calibration	1	Concentration within 5% of known value (mid-range)	Every 20 samples
Carbon Analyzer	3	Concentration within 5% of known value	Daily prior to use or failure of cont. calibration	1-3	Concentration within 5% of known value (mid range)	Every 20 samples
pH Meter	3	pH 7 = 0 +/- 5 mV; pH 4 = 177 +/- 10 mV; Eff = 1.00 +/- 0.05	Daily prior to use or failure of cont. calibration	1-3	Concentration within 5% of known value (mid-range)	Every 20 samples
Conductivity Meter	3	Concentration within 5% of known value	Daily prior to use or failure of cont. calibration	1-3	Concentration within 5% of known value (mid-range)	Every 20 samples
Turbidimeter	3	Concentration within 5% of known value <sup>1</sup>	Daily prior to use or failure of cont. calibration	1-3	Concentration within 5% of known value (mid-range)	Every 20 samples
Visible Spectrophotometer	5	Linear Regression Corr. Coefficient >0.998	Daily prior to use or failure of cont. calibration	1	Concentration within 5% of known value (mid-range)	Every 20 samples
Fluorometer	5	Linear Regression Corr. Coefficient >0.998	Daily prior to use or failure of cont. calibration	1-3	Concentration within 5% of known value (mid-range)	Every 20 samples

(1) Gel standards are checked monthly with Formazin control solutions of the same concentration. (i.e. 1.8, 18.0 and 180 NTU)  
Note: These are minimum calibration requirements. A more stringent calibration requirements may be followed if more stringent than specified on this plan.

**Table 9.5. Field Instrument Calibration**

Instrument	Multi-parameter Component	# Standards Initial Calibration	Accept/Reject Criteria-Initial Calibration	Frequency	# Standards Cont. Calibration	Accept/Reject Criteria Continuing Calibration	Frequency
Multi-parameter unit <sup>1,3</sup>	pH	2 (pH 7 & pH 4 or 10) <sup>2</sup>	Reading within 0.1 pH unit	Daily prior to use or failure of cont. calibration	1	Concentration within 5% of known value	At the end of the day or within 24 H of initial calibration
	Conductivity	1 (within expected sample range) <sup>4</sup>	Concentration within 5% of known value	Daily prior to use or failure of cont. calibration	1	Concentration within 5% of known value	At the end of the day or within 24 H of initial calibration
	Temperature	1	Temperature within $\pm 0.5^{\circ}\text{C}$ of known value. Thermometer calibrated to NIST thermometer.	Daily	1	Temperature $\pm 0.5^{\circ}\text{C}$ of NIST thermometer.	Quarterly <sup>5</sup>
Licor Spherical Quantum Sensors		N/A	N/A	Semi-Annual (factory calibration)	N/A	N/A	N/A – Factory Calibration
Turbidity meter		1	Reading within 5% of known value	Daily	1	Concentration within 10% of known value	Daily prior to use
	Automatic Samplers	Correct sample volume verified by using graduated cylinder	Volume within 5% of programmed volume	Daily prior to use	NA	NA	Daily or weekly prior to deployment of instrument.

<sup>1</sup> All multi-parameter units have automatic temperature compensation for pH, conductivity and DO measurements. Meters are checked with NIST traceable thermometers.

<sup>2</sup> Each unit is calibrated with a pH 7 buffer. Buffer pH 4 or pH 10 solution is also used.

<sup>3</sup> The calibration check is conducted weekly for instruments deployed in the field.

<sup>4</sup> YSI recommends calibration at 1000  $\mu\text{S}/\text{cm}$ . A standard in the expected range of the samples is then checked for the 5% compliance.

<sup>5</sup> The thermometer that is used in the daily check is either purchased as certified to an NIST thermometer or checked by comparing a low temperature reading ( $-40^{\circ}\text{C}$ ) and a high temperature reading ( $40^{\circ}\text{C}$ ) quarterly. If the difference is more than  $0.5^{\circ}\text{C}$ , the thermometer is discarded. If the difference is constant at the two readings and  $<0.5^{\circ}\text{C}$ , the thermometer is used with the application of a correction factor.

## **10.0 Preventative Maintenance**

Preventative maintenance is a necessary part of a successful quality assurance program. Time must be allocated to clean and maintain all equipment used for the collection and analysis of a sample. Equipment which is not operating properly may give unreliable results.

### **10.1 Equipment Maintenance**

Field and laboratory equipment maintenance procedures are outlined in Tables 10.1 and 10.2, respectively. Maintenance that cannot be performed by SFWMD personnel is done by the manufacturer or its designee, and several of the instruments are covered by manufacturer's service contracts.

### **10.2 Maintenance Documentation**

The field equipment maintenance activities are documented in bound notebooks assigned to each instrument. Service reports for repairs that cannot be done by SFWMD personnel are kept on file by the Technician Supervisor.

The laboratory equipment maintenance activities, as listed in Table 10.2, are documented in a separate bound notebook for each instrument. Service reports for repairs that cannot be done by SFWMD personnel are kept on file in a notebook located at the instrument.

### **10.3 Contingency Plans**

The SFWMD has replacements for most critical instruments which can be used in the event of a breakdown. Instrument service contracts are maintained on all major pieces of equipment and response time is typically 48 hours. Overflow laboratories are contracted to provide analytical services in the event of a catastrophic failure.

**Table 10.1 Field Equipment Maintenance Schedule**

<b>Instrument</b>	<b>Specific Activity</b>	<b>Frequency</b>
Hydrolabs (all models)*	DO probe membrane and electrolyte changed	Quarterly/As needed
	Conductivity sensors are sanded with emery cloth	Quarterly
	pH and reference electrodes cleaned with methanol	Quarterly/As needed
	pH reference electrode refilled with 3M KCl	Quarterly/As needed
	Outside surfaces cleaned and rinsed with analytic free water	Daily
Y S I Multiprobe Instruments*	pH/Redox combination probe cleaned with Isopropanol, cotton swab and rinsed w. D.I. water	Monthly/As needed
	DO membrane and electrolyte solution changed	Monthly/As needed
	DO sensors sanded w/ provided sanding disk	As needed
	Conductivity probe cleaned w/ dilute Liquinox & soft brush, rinsed thoroughly w/ D.I. Water	Monthly/As needed
Licor Sensors	Returned to Factory for Calibration	Semi-annually
Pumps (Gorman Rupp 2HP or Honda Centrifugal)	Check oil and add if needed	Before use
	Drain pump of water, rinse inside thoroughly with water	After use
	Wipe clean of mud and grease	After use
	Change oil & filter	Quarterly
	Change spark plugs & adjust carburetor	Quarterly
Autosamplers	Check battery charge & replace as needed	Before use
	Check programming	Before use
	Check pumping volume with a graduated cylinder	Weekly
	Check indicating desiccant & change as needed	Weekly
	Change pump tubing	Quarterly
	Clean liquid sensor	Quarterly
Acrochem Collectors	Clean intake tubing strainer	Quarterly or as needed
	Check temperature of sensor plate by touching	Before use
	Remove & cap collection buckets	Weekly
	Apply a few drops of water to sensor plate to check lid operation	Before use
	Check for snug fitting lid over collection bucket	Before use
	Check temperature of sensor plate after operation to see if warm to the touch	Before use
	Wipe top and bottom of lid & air dry	Before use
Install clean collection buckets	Weekly	
Honda Generator	Rinse, wipe outside surfaces	After use
Peristaltic pump	Rinse with D.I. water, wipe surfaces	After use
	Charge battery	As needed
Submersible pump	Wash all Teflon components of pump head with Liquinox, D.I. water, HCl and final D.I. rinse	Monthly or as needed

\* For long-term deployed multi-parameter units, internal batteries must also be changed once a year or according to manufacturer's specifications.



**Table 10.2 Laboratory Equipment Maintenance Schedule**

<b>Instrument</b>	<b>Specific Activity</b>	<b>Frequency</b>
Flame Atomic Absorption	Check gases	Before each use
	Preventative maintenance	Semiannually
	Nebulizer cleaned ultrasonically in Liquinox™ solution, rinsed with tap water, dipped in 10% HNO <sub>3</sub> , rinsed with DI water.	Biweekly when in use
	Burner head soaked in Liquinox™ solution.	After each use
Graphite furnace AA	Check gases	Before each use
	Preventative maintenance	Semiannually
	Windows inspected and cleaned with isopropyl alcohol.	Before each use
	Tubes and platforms inspected and changed	As needed
	Furnace decontamination as recommended by manufacturer	Weekly or as needed
Atomic Emission / ICP	Check pump & system tubing	Before each use
	Inspect Torch & RF coil for deposits or moisture and clean if necessary	Before each use
	Inspect filters	Monthly
	Clean nebulizer	Biweekly
	Flush torch with 5% HNO <sub>3</sub> then DI	After each use
	Pump air through spray chamber	After each use
Flow Analyzers Alpkem RFA300 Alpkem RFA500	Inspect all tubing and fittings	Before each use
	Wash manifold/flow cell	Before and after each use
	Inspect filters	Weekly
	Replace pump tubes	Biweekly
	Clean rollers & grease	Monthly
	Preventative maintenance	Semi-annually
Ion Chromatograph	Check tubing and fittings for leaks	Before each use
	Clean columns and change bed supports	Monthly
	Preventative maintenance	Semi-annually
Carbon Analyzer	Check/replace O-rings	Weekly or as needed
	Change acid	Daily
	Replace copper & glass wool	6 months
	Replace gas filter	As needed
	Inspect/replace combustion tube and catalyst	6 months or as needed

**Table 10.2 Laboratory Equipment Maintenance Schedule (con't)**

<b>Instrument</b>	<b>Specific Activity</b>	<b>Frequency</b>
pH Meter	Rinse electrode with DI water	Before and after each use
	Add reference solution	As needed
Conductivity Meter	Rinse electrode with DI water	Before and after each use
Dissolved Oxygen Meter	Rinse probe with DI water	Before and after each use
	Probe membrane and electrolyte changed	Quarterly or as needed
Turbidimeter	Clean cuvettes	Before each use
	Adjust calibration	Annually
Spectrophotometer	Clean flowcell / cuvette	Before and after each use
	Change pump tubes (if using sipper)	As needed; at least monthly
Fluorometer	Service maintenance	Annual or as needed
Ovens	Check temperature	Daily when in use
Refrigerators	Check temperature	Daily
Analytical Balances	Clean weighing compartment	After each use
	Clean interior/exterior	Monthly
	Calibration check against class S weights	Monthly or as needed
	Calibration service & inspection	Semi-annually
TKN digestion blocks/ COD Reactor	Check temperature	Weekly
	Clean blocks	Monthly or as needed
Centrifuge	Clean holder	After each use
	Clean walls	After each use
Autoclave	Check water level	Before each use
	Clean interior and replace water	Before each use
	Check pressure during operation	During each use
BOD Incubator	Check temperature	Twice daily when in use
Lachat QuikChem <sup>R</sup> Mercury Analyzer	Clean surfaces and detectors	Before and after each use
	Flush pump tubes	Before and after each use
	Replace pump tubes	Biweekly or as needed
	Clean detectors	Before and after each use
	Clean rods/moving parts	Monthly
	Check discoloration of Perma Pure Dryer	Semi-annually
	Replace inner membrane of Perma Pure Dryer	Annually
Ultra-Lum UV Digester	Wipe down interior and exterior	Daily or as needed
MDS - 2100 Digester	Check door, seals and cleaning	Monthly
	Wipe microwave cavity	Monthly
	Clean cavity exhaust outlet	Weekly

## **11.0 Quality Control Checks, Routines to Assess Precision and Accuracy, and Calculation of Method Detection Limits**

Data quality assessment is based on the precision and accuracy checks in the field and laboratory. The definitions of each type of quality control checks can be found in DER QA-001/90, Appendix C.

### **11.1 Field Quality Control Checks**

The field QC checks are given in Table 11.1. The DEP QC procedures confirm the precision of the sampling techniques, that the equipment is clean and addresses the effects of the sample handling and transport. All QC samples are processed, preserved, handled as and submitted to the laboratory along with routine samples for a given trip. Field QA/QC requirements are applied on a trip basis, independent of projects. Additional QCs, other than minimum required, maybe collected to satisfy specific QAPP requirements.

The field QC check samples consist of the following:

#### **Field Blank (FB)**

A D.I. water sample poured directly into the sample container on site, preserved and kept open until sample collection is completed for the routine sample at that site.

#### **Replicate Sample (RS)/Field Duplicate (FD)**

Two or more samples collected simultaneously from the same source. RS or FD data are used to evaluate sampling precision. FDs are also used to evaluate field variability.

#### **Split Sample (SS)**

Two or more samples that are taken from the same sample collection event; all bottles are filled from the same sample collection device or sample composite. SS are usually collected for inter-laboratory comparison with one part of each portion of the split sent to each laboratory in the comparison study. Splits may also be collected and submitted to one laboratory to assess analytical precision.

#### **Equipment Blank (EB)**

To evaluate the effectiveness of lab decontamination, EBs are collected before sample collection begins. EBs are also collected at a rate of one every 20 samples thereafter, or more often according to the requirements of the sampling event. After field cleaning of sampling equipment, the final DI water rinse is collected and analyzed as an EB. EBs are prepared by pouring 1 L of DI water into the sample collection container and through each piece of sampling equipment. For trips requiring more than 1 L of water, the volume required to fill the sample bottles may be used. This volume will vary by project and must be documented in the field logbook. In cases when peristaltic pump is used, the water should be pumped through the entire sampling train in accordance with the project SOP, then collected as an EB. The EB is processed, preserved and handled as a routine sample.

#### **Trip Blank (TB)**

Analyte free water blank (VOCs and ultra-trace mercury only) prepared before sample containers are transported to the field. Trip blanks remain unopened and are handled in the same manner as the samples.

**Table 11.1 Field Quality Control Checks**

Type	# Samples per Trip	Frequency (All Parameter Groups)
Equipment Blank, Pre-cleaned Equipment.	>20	1 blank prior to sampling on-site and 1 blank for every 20 additional samples (or portion of 20 samples)
Equipment Blank, Field Cleaned Equipment.	>20	1 blank for every 20 samples taken from field cleaned equipment
Trip Blank (VOC and Ultra-trace Mercury Collection)	1 or more	1 for each volatile organic method per cooler used to transport samples
Field Duplicate/Replicate	1 - 10	1 field duplicate/replicate + 1 split
Split Samples	11-20	2 field duplicates/replicates + 2 splits
	21-30	3 field duplicates/replicates + 3 splits
	>30	1 for every 10 samples
Field Blank	1 - 20	1 field blank
	21-40	2 field blanks
	>40	1 for every 20 samples
Field Measurements QC Check Standards. (multi-parameter instruments only)	1 or more	1 at the end of the day or within 24 hours of initial calibration
Field Measurements (Single parameter instruments)	1 or more	Every 4 hours and at the end of the day

## 11.2 Laboratory Quality Control Checks

The laboratory QC checks are listed in Table 11.2. These requirements are minimum standards for the operation of the laboratory; additional QC checks may be performed to further assess the operation of individual procedures, or if requested by a supervisor, the QA unit, or the DEP or DHRS.

**Table 11.2. Laboratory Quality Control Checks**

Type	Frequency (All parameter groups)
Method Reagent Blank	1 per sample set (batch)
Matrix Spikes (spike added prior to sample preparation)	At least 1 per run and 1 per 20 samples analyzed; if more than one matrix, 1 from each matrix.
Quality Control Check Samples (PE)	Blind Performance Evaluation Samples- analyzed in duplicate at least semiannually*
Quality Control Check Standards (QC)	Analyzed at the beginning of each analytical run to verify standard curve. One QC is also analyzed at the end of the analytical run.
Duplicate Samples (Dup or Rpt)	At least 1 per run and 1 per 20 samples analyzed; if more than one matrix, 1 from each matrix.
Spike Duplicate (SpkDup)	Used in place of Dup or Rpt when analyte is suspected to be <10xMDL for a reasonable precision assessment, ex. Trace metals, Hg, NO <sub>2</sub> .
Continuing Calibration Standard (CCV)	1 per 20 samples in an analytical set (at least one in each batch is at a concentration of 1-2 times the PQL).

\* If blind QC data is not acceptable, results are reported to DEP in the QA Report.

## 11.3 Species Identification

The SFWMD maintains the following in-house specimen collections for species identification:

1. Herbarium
2. Estuarine larval fish, zooplankton and benthic invertebrates
3. Phytoplankton (photographic reference record from the Caloosahatchee River)

Plant species and freshwater fish identification are done in-house. Verification of identifications by outside experts is done on an as needed basis.

Estuarine species identification is done in-house. A reference sample is made for each species collected. The reference samples and 5-10% of the samples collected are set aside for identification by an outside expert. Species identification for freshwater invertebrates is done in-house using an in-house type specimen collection. The reference samples and 5-10% of the samples collected are set aside for identification by an outside expert. Ten percent of all sorting and identification is confirmed by a different SFWMD staff member. Counts should agree within 10%.

## 11.4 Routine Methods Used to Assess Precision and Accuracy

### 11.4.1 Definitions

Accuracy can be defined as the agreement between the actual obtained result and the expected result. QC check samples having a known or "true" value are used to test for the accuracy of a measurement system.

Precision can be defined as the agreement or closeness of two or more results and is an indication that the measurement system is operating consistently and is a quantifiable indication of variations introduced by the analytical system over a given time period.

### 11.4.2 Reportable Data for Field QC Samples

The formulas used to calculate the precision and accuracy of the QC checks are:

Percent Relative Standard Deviation for precision of routine, split and replicate samples.

$$\%RSD = \frac{S}{X} * 100 \quad \text{where } S = \text{Standard Deviation, and } X = \text{mean}$$

Relative Percent Differences for precision of duplicates.

$$RPD = \frac{\text{abs}[A - B]}{A + B} * 200 \quad \text{where } A \text{ and } B \text{ are the analytical values for the two duplicate samples}$$

The QC data is kept in spreadsheets and LIMS database, and maybe transformed into QC charts. Quarterly QC limits are supplied to the laboratory staff and used as guide by the laboratory analysts and supervisors in accepting analytical runs. The formulas for calculating control limits are based on the standard deviation of at least 6 measurements and preferably 20 measurements for each type of sample. The standard deviation is calculated according to the following formula:

$$s = \left[ \frac{\sum(X_i - X)^2}{(n-1)} \right]^{1/2}$$

where  $X$  is the mean,  $X_i$  is an individual value, and  $n$  is the number of values.

$$\text{Mean} = X = \frac{\sum X_i}{N}$$

The warning limits for field parameters are 2s while control limits are 3s from the mean.

Acceptability criteria for blanks (FB, EB) is currently set at 2x MDL. Blanks that do not pass this criteria are confirmed through rework and if confirmed, data for the blank and associated samples that maybe affected (values < 3x blank value) are flagged.

### 11.4.3 Reportable Data for Laboratory QC Samples

The precision and accuracy of each parameter are measured on a daily basis. The field blanks, splits, and replicates are analyzed as routine samples.

Accuracy may be quantified by comparing results obtained for QC check samples to their true values and calculating a percent recovery using the following equation:

$$\% \text{ Recovery} = \left[ \frac{\text{Experimental}}{\text{Known}} \right] * 100$$

The values obtained for a matrix spike are used to evaluate any matrix interference. Spike recovery is calculated using the following equation:

$$\text{Percent Recovery} = \%R = \frac{[\text{matrix spike}] - [\text{sample}]}{[\text{spike}]} * 100$$

Accuracy data, obtained from QC and spike recoveries, may be used as an indication of analytical bias. The target control limits for accuracy are calculated for each analyte, based on quarterly performance, or are a default value of 90-110% of the known true value.

To determine the precision analyses performed in the SFWMD laboratory, one sample is chosen at random from each group of 20 samples as the repeat (or replicate) sample for each parameter. Each replicate sample is then analyzed twice during the analytical run, and the precision of the analysis is calculated from the precision of the replicate determinations analyzed during the run using the following equation:

$$\text{RPD} = \frac{\text{abs}[A - B]}{A + B} * 200 \quad \text{where A and B are the analytical values for the two duplicate samples}$$

On a daily basis, the results obtained for each of the quality control checks used are compared to the acceptable limits for precision and accuracy. Target limits are set based on prior performance or at a default value of 10% of the known true values.

The procedures used to determine precision and accuracy are given in Table 11.4.

### 11.4.4 Method Detection and Practical Quantitation Limits

The method detection limits (MDLs) are determined by the procedures in 40 CFR Part 136, Appendix B. They are updated annually and when necessary due to equipment or procedural changes. See Tables 5.1, 5.2 & 5.3 for current MDLs.

The practical quantitation limit (PQL) is 12 times the pooled standard deviations derived from the procedures to determine the MDL, or roughly 4 times the MDL.

**Table 11.4 Procedures Used to Determine Precision and Accuracy**

<b>Method</b>	<b>Purpose</b>	<b>Concentration Level</b>	<b>Method References</b>
Matrix Spike	Accuracy	Low Level Mid Level High Level	Nutrients, Trace Metals, Anions, Cations
Duplicates	Precision	Low Level Mid Level High Level	All parameters
Replicate for analytical run	Precision	Mid Level High Level	All parameters
QC Check Samples (PE)	Accuracy	Low Level Mid Level High Level	All parameters
QC Check Standards (QC)	Accuracy	Low Level Mid Level High Level	All parameters for which a sample is available
Method Reagent Blank	Accuracy	Low Level	Total Nutrients and Total Metals
Mid-Range Check Standard	Precision and Accuracy	Mid Level	Nutrients, Trace Metals, Anions and Cations



## **12.0 Data Reduction, Validation and Reporting**

### **12.1 Data Reduction**

#### **12.1.1 Field Reportable Data**

All field measurement data are directly read from the instruments. These measurements include pH, specific conductance, dissolved oxygen, temperature, ORP, salinity, turbidity, and depth. The data are automatically temperature-compensated for pH, specific conductance, and dissolved oxygen. The cell constant for specific conductance is determined by the manufacturer. The field technician does not perform any calculations on field data.

The technician responsible for data entry inputs all field data from the Chemistry Field Data Log into the computer.

#### **12.1.2 Laboratory Reportable Data**

Data for pH, specific conductance, turbidity, and fluoride are directly read from the instrument and entered into LIMS. The pH and conductivity meters have automatic temperature compensation. The conductivity cells constants are checked before each analysis and verified monthly. Data from all other instruments are calculated using individual instrument PCs with vendor-supplied software or calculation programs. No calculations are performed using a single point reference or internal standard. Table 12.1 shows the formulas used to calculate specific parameters. The analyst is responsible for running the computer programs which provide the results in the appropriate concentrations and entering those results into the database.

Every analytical package include raw data and calculated results from the instrument, strip chart, plots or chromatograms, and QC report. Data reports are identified with the date, the computer file name if applicable, method #, and the initials of the analyst. The computer files are named using the instrument code, date, and sequential file number for the day.

### **12.2 Data Validation**

#### **12.2.1 Laboratory Data Integrity**

The Analysts/Supervisors are responsible for checking the raw data entries and calculations for correctness. The analysts ensure that instruments are performing properly, that instrument responses are within the normal range, and that the QC checks are met prior to accepting data. On a daily basis, the supervisors are responsible for ensuring that all data were generated following the standard operating procedure and within the guidelines of this plan. The QA Officer periodically checks sample preparation logs and instrument/analytical logs for adherence to QC protocols and sample identification. The QA Officer is also responsible for checking the analytical performance through quality control charting and reports this to the laboratory supervisors and division director.

**Table 12.1 Formulas Used for Calculations**

Parameter	Formula
Alkaline Phosphatase Activity (APA)	Linear regression for the calibrant (methylumbelliferone, MU) $\text{APA, nM/min/mL} = \frac{\text{MU conc. at time 0 } (\mu\text{M}) - \text{MU conc. after 30 minutes } (\mu\text{M})}{(30 \text{ minutes} \times 0.9 \text{ mL})} \times 1000$
Alkalinity	(volume of titrant, mL) x N x 50,000/ml sample
Ammonia	linear regression, computerized calculation
Ammonia, unionized	Ammonia value X chart value (pH & Temp)
Biochemical Oxygen Demand/ Carbonaceous Biochemical Oxygen Demand	$(\text{DO}_{(\text{initial})} - \text{DO}_{(5 \text{ day})} - \text{Seed Correction})/P$ where P = decimal volumetric fraction of sample used Seed Correction = DO loss in seed control X f f = ratio of seed in sample to seed in control
Calcium, dissolved	Linear regression, computerized calculation
Chemical Oxygen Demand	Linear regression, computerized calculation
Chloride	Linear regression, computerized calculation
Chlorine Residual, total	1 ml of FAS titrant = mg/L Cl
Inorganic Carbon, total and dissolved	Computerized, mean of 2 Repeats, multiple point calibration
Iron, total and dissolved	Linear regression, computerized calculation
Nitrogen, total Kjeldahl	Linear regression, computerized calculation
Magnesium, dissolved	Linear regression, computerized calculation
Nitrate + nitrite	Linear regression, computerized calculation
Nitrite	Linear regression, computerized calculation
Nitrate	Computer calculation, (Nitrate + nitrite) - Nitrite
Total phosphorus	Linear regression, computerized calculation
Organic Carbon, total and dissolved	Computerized, Total - Inorganic, mean of 2 Repeats, multiple point calibration
Orthophosphate	Computer generated linear regression
Potassium, dissolved	Computer generated linear regression

**Table 12.1 Formulas Used for Calculations (con't)**

<b>Parameter</b>	<b>Formula</b>
Residue, filterable	$\frac{\text{Final Weight-Tare, g} \times 10^6}{\text{Volume, ml}}$
Residue, nonfilterable	$\frac{\text{Final Weight-Tare, g} \times 10^6}{\text{Volume, ml}}$
Residue, volatile	$\frac{\text{Nonfilterable Final Weight-Weight}(550^\circ\text{C}), \text{g} \times 10^6}{\text{Volume, ml}}$
Silica, dissolved	Quadratic regression, computerized calculation
Sodium, dissolved	Linear regression, computerized calculation
Strontium, dissolved	Linear regression, computerized calculation
Sulfate	Quadratic regression, computerized calculation
Trace metals	Linear regression, computerized calculation
Hardness	Computerized calculation $2.497 \times [\text{Ca}] + 4.118 \times [\text{Mg}]$
Chlorophyll	<p> <math>\text{Chl. a} = 11.85(\text{OD}664) - 1.54(\text{OD}647) - 0.08(\text{OD}630)</math>  <math>\text{Chl. b} = 21.03(\text{OD}647) - 5.43(\text{OD}664) - 2.66(\text{OD}630)</math>  <math>\text{Chl. c} = 24.52(\text{OD}630) - 7.6(\text{OD}647) - 1.67(\text{OD}664)</math>  <math>\text{Pheophytin} = (26.7(1.7 \times \text{OD}665 \text{acidified})) - \text{OD}664</math>  <math>\text{Carotenoids} = 4.0(\text{OD}480)</math>  <math>\text{Chl. a corrected} = 26.7(\text{OD}664) - \text{OD}665(\text{acidified})</math> </p> <p>Where:            OD(wavelength) = absorbance (wavelength) - Abs. at 750 nm in non-acidified sample            and results are multiplied by volume of extract and divided by the volume of sample filtered in ml<sup>3</sup></p>

## **12.2.2 Field Data Integrity**

The QA Officer for each division is responsible for checking calibration integrity by checking the calibration logs and comparing present values to historical values and the sample custody integrity by checking the paperwork to ascertain that only trained personnel collected samples and that they were preserved and transported correctly. The Project Manager is responsible for checking raw data entries and calculations by reviewing the records for accuracy and use of proper formulas.

Staff from Water Quality Monitoring Division audit field activities of both District and contractors, provide feedback to field personnel and/or project managers, and ensure that corrective measure is taken to correct any deficiencies.

## **12.3 Specific Data Validation Procedures**

### **12.3.1 Laboratory Data Validation**

Each analyst is responsible for the first step in the validation process. It is his/her responsibility to follow the procedures correctly, perform the quality control checks, and report any discrepancies to his/her supervisor and/or the laboratory QA Officer. A real time QC charting program is currently being developed to aid the analysts and their supervisor in identifying potential analytical problems on a daily basis.

The laboratory supervisors are responsible for ensuring that QC checks are met, investigating any discrepancies, determining the cause, and ensuring that corrective measures are taken to solve the problem. The supervisors are also responsible for the review of all data to identify obvious anomalies. The laboratory QA Officer or designated staff is responsible for regular tracking laboratory performance through QC plots, and providing feedback to the laboratory staff and division director. The QA Officer must update the acceptable quality control limits for all parameters quarterly.

Listed below are the minimum QC checks required in the laboratory .

#### **Method Reagent Blank**

This is analyzed to ensure that no significant amount of the analyte is present on the background that could potentially affect the quality of analysis. A method reagent blank must not have detectable level of analyte. Troubleshooting must be initiated if recovery for this blank is greater than MDL.

#### **Matrix Spike Sample**

Matrix spikes are indication of accuracy of analysis and is an assessment of potential matrix interference. Spiking level must be adjusted depending on the approximate concentration level of the analyte in the samples being analyzed. As a guide, spiked sample result must be within 50-85% of the highest calibration standard. If the result is outside the current acceptable limits, the spike must be prepared again and re-analyzed. If the value is outside the range again, a matrix

problem is suspected and it is noted in the database that the sample exhibits matrix interference.

In limited cases, method of standard addition is used to determine analyte concentration when matrix interference is present.

### **Quality Control Check Standards**

If the result is outside the current acceptable limits, the run is stopped and the instrument re-calibrated. If necessary, new calibration standards are prepared and the instrument is checked for leaks, cracks in tubing, correct reaction temperature, correct wavelength or filter, and correct calculation procedure in the computer.

### **Blind Quality Control Check Samples**

If the results for these blind samples are incorrect, the entire procedure is checked for errors. The analytical results are reported in the quality control report.

### **Replicate or Duplicate Samples**

This is used to assure that analytical precision is maintained throughout the analytical run. At least one replicate is run for each analytical run and every 20 samples thereof. Matrix samples are used for this purpose unless it is anticipated that the analyte concentration in the batch of samples being analyzed are too low for a reasonable estimate of precision. If the analyte concentration is <10 times the MDL, then a spiked matrix duplicate maybe used instead. Field duplicates and splits are treated as individual samples and are not considered analytical duplicates.

### **Continuing Calibration Verification**

At least one standard solution is analyzed every 20 samples to confirm that the calibration curve remains constant throughout the analytical run. The recovery, calculated as % of initial instrument response, must remain within 5%, otherwise, the run or the affected portion of the run is re-analyzed.

## **12.3.2 Field Data Validation**

The field sampling personnel are responsible for following the sampling procedures, reviewing the Chemistry Field Data Logs, and filling out all forms correctly and completely. The field project manager or senior scientific associates are responsible for reviewing field data submitted to the laboratory for data entry for accuracy, initial data review following analysis, and review of the field quality control results for adherence to established standards. The Staff Environmental Scientist or Senior Environmental Scientist is responsible for reviewing all data for his/her project(s) to assure that the data quality objectives for the project(s) are being met.

Below is a list of field QC checks used to validate the field collected data and the sample collection process and the required corrective measure if not met:

### **Quality Control Check Standard**

A QC check standard is used to check the calibration of the instruments. Results must be within

the established acceptable limits, otherwise, the instrument must be re-calibrated or required maintenance be performed.

**Equipment Blank (EB)**

This is an indication of the effectiveness of sample equipment decontamination. If EB concentration >2x MDL, the sample is reworked for confirmation. If confirmed, the blank is flagged and the associated samples that may have been affected are also flagged.

**Field Blank (FB)**

An FB is used to measure the amount of environmental contamination that maybe present at time of collection. Same criteria and corrective action as EB is applied.

**Field Duplicates (FD) or Replicate Sample (RS)**

A FD or RS is collected and analyzed to evaluate the precision of the sample collection process.

**Field Split Sample (SS)**

A SS is collected and analyzed to assess the combined precision of the analysis and processing of the samples in the field. It is also used to evaluate inter-laboratory performance between two or more laboratories.

**Trip Blanks (TB)**

A TB is used for VOC sample collection to evaluate potential shipping/handling contaminants and problems.

**12.3.3 Project Data Validation**

The Project Manager is responsible for the final review of data. The laboratory QA Officer is responsible for review of the laboratory QC data and the field quality control data. The Project Manager is responsible for review of all supporting documentation and review of the data to ensure that data quality objectives of the project is met.

**12.4 Data Reporting**

**12.4.1 Analytical Data Reporting**

All data from automated instruments are collected through and stored in the instrument PC. A limited amount of data is manually entered into LIMS. Hardcopy of the analytical report is generated. After the analyst reviews the data, the results are reported into LIMS. In most cases, this is done through electronic transfer of file from the instrument PC to LIMS. The analyst retrieves the LIMS loading report and validates that the data reported are the same as what is in the analytical report. The analyst may initiate a rework of part of or the entire run at this point. The analyst may also enter new data or perform changes at this point, but a Good Automated Laboratory Practice (GALP) comment would be required. If the data are acceptable and upon completion of the QC log, the analyst approves the data in LIMS.

The laboratory supervisors review reported data both through visual inspection of the report package and by means of automated computer programs to ensure detection of aberrant data (e.g. reversals). Rework of part of or the entire run maybe initiated if QC criteria are not met. If all criteria are met, the supervisor approves the data in the system. Further automation of the LIMS system is underway that would incorporate more automated checks, automatic notification of the supervisors for any data outliers, and customized reports.

Data report package consisting of the original raw data (including charts or plots in some cases), LIMS data loading report, and QC result log is submitted to the QA unit. Preliminary result and log-in information reports are generated by the LIMS and sent to the project managers and field supervisors on a weekly basis. Examples of these reports from LIMS is given in Figures 12.1 and 12.2.

After the QA staff reviews and approves the data, any correction on the data may only be performed by the LIMS administrator. A formal request for correction with a valid reason indicated on the request is required.

#### **12.4.2 Data Release from the Laboratory**

Final comprehensive data review is done by the QA unit. This level of review incorporates both field and laboratory criteria, historical project-specific trends, resolution of anomalies, and review of field notes. If all criteria are met, the samples are released and archived into the District's historical database (DBHYDRO). If any of the criteria are not met, the data are qualified prior to release using the qualifier codes in Table 4 of Chapter 62-160 FAC, then archived.

Reports generated from LIMS are considered preliminary. Requests for data reports from LIMS must be made through the LIMS administrator. Data users should use data that are in DBHYDRO for reporting purposes.

South Florida Water Management District, DMS Certification #16077  
 Logia Summary Report  
 Jun 11, 1999 02:16 pm  
 Logia Number: 112541  
 Matrix: SW Surf. B20  
 Collector: JCF

Project: M08

Logia #	Project	Logia	Start	End	Time	Day	Temp	Wind	Humid	Cloud	Wind	Temp	Wind	Humid	Cloud	Wind	Temp	Wind	Humid	Cloud	
112541-1	M08	10-JUN-1999 09:00	711	1	1	89	EXP	0	1	1	1	1	1	1	1	1	1	1	1	1	
Comments:																					
112541-2	M08	10-JUN-1999 11:14	CM07X	1	1	89	EXP	0	1	1	1	1	1	1	1	1	1	1	1	1	
Comments:																					
112541-3	M08	10-JUN-1999 09:21	711	1	3	89	EXP	0	1	1	1	1	1	1	1	1	1	1	1	1	
Comments:																					
112541-4	M08	10-JUN-1999 09:21	711	1	3	88	EXP	0	1	1	1	1	1	1	1	1	1	1	1	1	
Comments:																					
112541-5	M08	10-JUN-1999 09:18	711	1	3	85	EXP	0	1	1	1	1	1	1	1	1	1	1	1	1	
Comments:																					
112541-6	M08	10-JUN-1999 09:14	711	1	3	83	EXP	0	1	1	1	1	1	1	1	1	1	1	1	1	
Comments:																					
112541-7	M08	10-JUN-1999 09:10	711	1	3	81	EXP	0	1	1	1	1	1	1	1	1	1	1	1	1	
Comments:																					
112541-8	M08	10-JUN-1999 10:04	713	1	3	84	EXP	0	1	1	1	1	1	1	1	1	1	1	1	1	
Comments:																					

Page 1

Signature: \_\_\_\_\_  
 Date: \_\_\_\_\_

Figure 12.1 An example of log-in report, showing a system-generated header sheet and logged in field information.



South Florida Water Management District, DMS Certification #46077  
WATER CONSERVATION AREA MATERIAL BUDGET

Project:	P11110-1	CAMP	CAMP	CAMP	CAMP	CAMP	CAMP	CAMP	CAMP
Lab Sample:	L11370-1	L11370-2	L11370-3	L11370-4	L11370-5	L11370-6	L11370-7	L11370-8	L11370-8
Field No.:	P1111-1	P1111-2	P1111-3	P1111-4	P1111-5	P1111-6	P1111-7	P1111-8	P1111-8
Station:	SSA	SSA	SSA	SS	SS	SS	SS	SS	SS
Sample Type:	SW	SW	SW	SW	SW	SW	SW	SW	SW
Date Collected:	11-MAY-1999	11-MAY-1999	11-MAY-1999	11-MAY-1999	11-MAY-1999	11-MAY-1999	11-MAY-1999	11-MAY-1999	11-MAY-1999
ALFA	mg/L	ND							
APA	mg/min-mt	ND							
CA	mg/L	ND							
CAR0	mg/ml	ND							
CHLA	mg/ml	ND							
CHLA2	mg/ml	ND							
CHLA3	mg/ml	ND							
CHLC	mg/ml	ND							
CL	mg/L	ND							
CO	mg/L	ND							
COLCM	units	ND							
DCS	ug/L	ND							
DIC	ug/L	ND							
DOC	ug/L	ND							
F	mg/L	ND							
L	ug/L	ND							
LCOMD	units/cm	ND							
LPH	units	ND							
LTSS	ug/L	ND							
NO	ug/L	ND							
NA	ug/L	ND							
NO1	ug/L	ND							
NO2	ug/L	ND							
NO3	ug/L	ND							
OP04	ug/L	ND							
PH20	ug/L	ND							
PH07	ug/L	ND							
SO4	ug/L	ND							
TDNH	ug/L	ND							
TDPO4	ug/L	ND							
TDN	ug/L	ND							
TDNHQ	ug/L	ND							
TDHAL	ug/L	ND							
TDAS	ug/L	ND							
TD8A	ug/L	ND							
TD8E	ug/L	ND							
TD8D	ug/L	ND							
TD8C	ug/L	ND							
TD8B	ug/L	ND							
TD8A	ug/L	ND							
TD8H	ug/L	ND							
TD8G	ug/L	ND							
TD8F	ug/L	ND							
TD8E	ug/L	ND							
TD8D	ug/L	ND							
TD8C	ug/L	ND							
TD8B	ug/L	ND							
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TD8F	ug/L	ND							
TD8E	ug/L	ND							
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TD8C	ug/L	ND							
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TD8E	ug/L	ND							
TD8D	ug/L	ND							
TD8C	ug/L	ND							
TD8B	ug/L	ND							
TD8A	ug/L	ND							
TD8H									

## **12.5 Data Storage**

Electronic files of data are retained on the instrument's PC drive for up to six months or until capacity is reached. Files are then transferred to floppy disks and retained in the laboratory for up to three years. Hardcopy information is retained in the division for a maximum of two years. After that it is sent to warehouse records storage and will be microfilmed if storage for longer than three years is needed. The records that will be retained are the plots, chromatograms, data files, Chemistry Field Data Logs, manual data entry records, daily QC reports, instrumentation logs and LIMS back up tapes.

The magnetic tapes used for weekly back-up of the LIMS are maintained in two sets. One set is kept in an in-house vault for immediate access and one set is sent to secure storage outside the SFWMD for recovery in the event of a catastrophic event.

Archived records are indexed based on date for hard copy laboratory records, and by project for field notebooks and results in the water quality database. The Project Manager is responsible for the storage of all project data for at least three years.

### **13.0 Corrective Action**

Corrective action is required in those cases when the acceptance criteria for QC measures are not met. The specific corrective actions for each type of quality control measure are given in Tables 13.1, 13.2 and 13.3.

The analyst or field sample collector is responsible for assessing each QC measure and initiating corrective action according to Tables 13.1 and 13.2, respectively. The QA officer and the supervisors are responsible for approving the corrective action taken or for initiating further steps to solve the problem.

Corrective action may be initiated by external sources or events, which may include performance evaluation results, performance audits, system audits, split sample results, and laboratory/field comparison studies. DEP recommends that corrective action be initiated as a result of systems or performance audits, split samples, or data validation review.

Problems requiring corrective action and corrective actions taken are documented in detail in one of the following: QC result log, analysis logbooks, digestion logbooks, or instrument maintenance logs depending on the nature of the problem and how it was solved. The supervisor will report the problem to the appropriate QA Officer who has the responsibility for determining if the solution is acceptable and, if not, what further steps should be taken.

**Table 13.1 Corrective Actions for the Laboratory**

<b>QC Activity</b>	<b>Acceptance Criteria</b>	<b>Recommended Corrective Action</b>
Initial Instrument Blank; Method Reagent Blank	< MDL response and value	Prepare new blank and re-start analysis. If same response is obtained, determine cause of contamination (reagents, calibration standards, environment, equipment failure, etc.) and eliminate the source of contamination.
Initial Calibration Standards	Correlation coefficient >0.995 for cations and metals, >0.998 for all other analyses Accuracy within established limits	Re-analyze standards. If same response is obtained, re-optimize instrument and re-start analysis. If same response is obtained, prepare new standards and re-start analysis.
Quality Control or Check Standards	Accuracy within established limits	Re-analyze QC check standard. If same response is obtained, prepare new primary and calibration standards. If that fails, check against an alternate QC source. Obtain approval from QA officer or staff. Discard unacceptable QC once confirmed and document findings on QC result log.
Continuing Calibration Standards	Within 5% of initial instrument response	Recalibrate and re-analyze the affected portion of the run.
Replicate/Duplicate Sample	Precision within established limit	Determine and eliminate cause of problem (baseline drift, carryover, etc. ). Re-analyze all affected samples.
Matrix Spikes	Accuracy within established limits	Re-make spike and re-analyze. If acceptable, re-analyze affected portions of run. If not acceptable, spike a different sample. If second sample spike is acceptable, analyze first sample by standard addition. If second sample is not acceptable, spike all samples in that LIMS group in order to check for matrix interference.

Note: Data for QC samples and affected samples are flagged if the problem is noted after the sample has expired or if no other action is possible to validate the data.

**Table 13.2 Corrective Actions for In-situ Measurements (Field Parameters)**

QC Activity	Acceptance Criteria	Recommended Corrective Action
Initial Calibration Standards	Value within 5% of expected value or within established limits	Re-analyze standards or use another stock solution. If confirmed, perform the necessary troubleshooting to optimize instrument.
QC Check Standards / Re-calibration standards	Value within 90 - 110 % known true value or within established limits	Re-analyze standards or use another stock solution. If confirmed, perform the necessary troubleshooting to optimize instrument.

Note: Data for QC samples and affected samples are flagged if the problem is noted after the sample has expired or if no other action is possible to validate the data.

**Table 13.3 Corrective actions resulting from field quality control checks**

QC Check	Acceptance Criteria	Recommended Corrective Action
Equipment Blank (EB) Trip Blank (TB) Field Blank (FB)	< 2 x MDL or less than established acceptance limits	Laboratory should reanalyze blanks. If confirmed, QA investigates the source of error, lab and field collection staff should check recorded cleaning procedures. Data for QC sample and other samples that may possibly be affected and related parameters are flagged accordingly. Current criteria to qualify potentially affected samples is that results would be less than 3 times the highest positive blank concentration. If second analysis is acceptable, samples that may have been affected in first run should be re-analyzed.
Field Duplicate (FD) Replicate Sample (RS) Split Samples (SS)	Precision within established limits (only if values >PQL)	Laboratory should re-analyze duplicates to confirm. If confirmed, data for affected samples are flagged for failing field precision criteria. If re-analysis shows field collection to be acceptable, re-analyze all samples analyzed with the questionable result from the original run.

Note: Data for QC samples and affected samples are flagged if the problem is noted after the sample has expired or if no other action is possible to validate the data.

## **14.0 Performance and Systems Audits**

Audits are an essential part of the QA program for both laboratory and field operations. Systems audits are conducted to measure compliance with the comprehensive and project quality assurance plans. Performance audits are conducted to evaluate the quality of the data outputs with respect to mandatory limits or the laboratory's own performance standards.

### **14.1 Systems Audits**

A systems audit is used to evaluate the entire measurement system both in the field and laboratory. It is a detailed review of each component of the sample collection process from equipment cleaning, through submission of the samples to the laboratory, and the laboratory process from sample log-in to archival of the results. Each element must be evaluated for conformance to appropriate methodology, approved procedures and the appropriate QA Plans. A list of any deficiencies discovered must be made and subsequently addressed to correct, improve, or modify the system as necessary. Immediate feedback must be provided to field and laboratory personnel.

#### **14.1.1 Internal Systems Audits**

Systems audits are performed using the forms shown in Figure 14.1. Audits are conducted semi-annually by the WQMD QA Officer or designated QA staff.

#### **14.1.2 External Systems Audits**

There are no regularly scheduled external systems audits. The SFWMD will submit to audits conducted by the DEP QA Section and FDOH auditors.

### **14.2 Performance Audits**

Performance audits are used to evaluate the routine quality control program of the laboratory.

#### **14.2.1 Internal Performance Audits**

Internal performance audits are conducted semi-annually by the WQMD QA Officer or designated staff. The audit may consist of any or all of the following: re-submission of previously analyzed samples under a different LIMS number, preparation of additional QC samples, samples split with another laboratory, and submission of spiked samples, all of which are blind to the analysts. For certain parameters or projects, performance audits may be conducted more frequently to comply with specific permit, QAPP, or regulatory guidelines.

An audit may be conducted at any time on a suspect parameter in addition to the semi-annual audits for the entire laboratory. A performance audit on a parameter is mandatory when 10% of the analytical runs for that parameter fail one or more quality control criteria. The results of the performance audits are included in the quarterly quality assurance reports issued to the Division Director by the WQMD Quality Assurance Officer.

### **14.2.2 External Performance Audits**

The laboratory participates in three external performance audit programs. They are:

1. Florida Environmental Laboratory Certification Program administered by FDOH
2. United States Geological Survey's round robin study, Denver, semi-annually
3. Phosphorus round robin studies, coordinated by FDEP, semi-annually
4. Low-level mercury round robin study, coordinated by FDEP for the South Florida Mercury Science Program

FIGURE 14.1 - SYSTEMS AUDIT CHECKLIST

**South Florida Water Management District  
Water Resources Evaluation Department  
Water Quality Monitoring Division**

**INTERNAL SYSTEMS AUDIT CHECKLIST**

PROJECT NAME, FREQ: \_\_\_\_\_

CODE, #,TYPE, DIV.: \_\_\_\_\_

AUDIT LOCATION: \_\_\_\_\_

(County/sites visited) \_\_\_\_\_

PROJECT MANAGER: \_\_\_\_\_

DIV/ TELEPHONE #s: \_\_\_\_\_

SAMPLING/LAB PERSONNEL: \_\_\_\_\_

*responsibilities*

AUDITOR(S): \_\_\_\_\_

DIV/ TELEPHONE #s: \_\_\_\_\_

VISITOR(S): \_\_\_\_\_

REF. SOP/QAP'S: \_\_\_\_\_

AUDIT DATE: \_\_\_\_\_

REPORT DATE: \_\_\_\_\_

APPLICABLE PAGES:

\_\_\_\_\_  
\_1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25\_\_\_\_\_

SIGNATURE OF AUDITOR: \_\_\_\_\_

Copies to: MC/ DI/ (ProjMgr)/ (FldSupv)/ (AE)/ (AE)/ (AE)

Original to: \_\_\_\_\_



**PART I. FIELD AUDIT CHECKLIST**

**A. PLANNING AND PREPARATION**

- 1. Has this **Project** been **audited** previously? Y N  
If yes, by **whom**? \_\_\_\_\_
- 2. Have the field sampling **personnel** been **audited** previously? Y N  
If yes, by whom? \_\_\_\_\_
- Was a **briefing** held with the project participants? Y N
- 4. Was this project conducted under the proper **QAPP** or **SOP**? Y N
- 5. Was there a written list of sampling **locations** and **descriptions**? Y N
- 6. Was there a **map** of sampling locations available to field personnel? Y N
- 7. Was **sampling scheduled** with field tech supervisor in advance (minimum 1 wk)? Y N
- 8. Were **analyses scheduled** with laboratory in advance (minimum one week)? Y N
- 9. Were **additional instructions** given to participants (ie. changes in Project Plan)? Y N
- 10. Was sampling **team** organized, experienced, efficient, knowledgeable? Y N
- 11. Did the sampling **team** have a clear understanding of the project goals or objectives? Y N
- 12. Was field **equipment** well-organized and ready for use? Y N
- 13. Was sampling **equipment** selected according to proper protocols? Y N
- 14. If not, did all selected **equipment** meet the **material construction** and **parameter restriction** requirements of the CompQAP? Y N  
 material construction       parameter restrictions
- 15. Were proper **communication/ notification** procedures in place should office and field staff need to contact one another? Y N
- 16. In the event of malfunction or loss, were **extra supplies/equipment** taken into field? Y N
- 17. Were all relevant **safety protocols** and equipment prepared (i.e. fuel, PFD's, fire extinguisher, acid spill kit, safety glasses, drinking water, etc.)? Y N

List any deficiencies noted during Planning and Preparation activities:

\_\_\_\_\_

**B. DECONTAMINATION**

- 1. Did all sampling equipment arrive at the site **precleaned** and ready for use? Y N
- 2. Was sampling equipment wrapped with aluminum foil, untreated butcher paper or otherwise **protected** from contamination? Y N  other \_\_\_\_\_
- 3. Was sampling equipment **precleaning** documented properly? Y N
- 4. Was all sampling equipment immediately **rinsed** with DI water after each use? Y N
- 5. Was all equipment that was used only once, site specific, **tagged** with the sample location? Y N
- 6. Were all aspects of proper field decontamination **protocols** followed as per the CompQAP? Y N
- 7. Were all **pumps precleaned** and/or field cleaned per CompQAP? Y N
- 8. Was all **tubing precleaned** and/or field cleaned per CompQAP? Y N
- 9. Is **fresh DI** available for the crew? Y N  
source \_\_\_\_\_ date acquired \_\_\_\_\_

List any deficiencies noted during Decontamination activities:

\_\_\_\_\_

**C. GENERAL SAMPLING PROCEDURES**

- 1. What mode of **transportation** was used to access sampling locations? \_\_\_\_\_
- 2. Were sampling **locations** properly selected? (Instructions and/or directions properly followed?) Y N
- 3. If applicable, were any **devices** (i.e. GPS, flow meter, depth meter) needed to assist in locating sampling sites? Y N  
type \_\_\_\_\_
- 4. Were samples collected for **all required analyses**? Y N

5. Was sampling equipment **protected** from possible contamination prior to sample collection? Y N
6. Were samples/sampling equipment **segregated** from personal gear as appropriate? Y N
7. Were clean disposable latex or vinyl **gloves** worn during sampling? Y N
8. Were **gloves changed** for each sample station? Y N
9. Were **gloves changed** during sampling event? If yes, explain conditions. Y N
10. If equipment was **cleaned** in the field, were proper procedures used? Y N
11. What field **instruments** were used? \_\_\_\_\_
12. Were **calibration procedures** documented in the field notes? Y N
13. Was a **calibration check** conducted within 24 hours or at the end of the sampling day for Hydrolabs or similar multi-parameter field instruments? Y N
14. Which **field-metered parameters** were collected?  
 pH       temperature     conductance     DO       turbidity       salinity  
 OVA       Other: \_\_\_\_\_
15. Were readings truly **representative** of the medium being sampled? Y N
16. For which **parameters** were samples collected? \_\_\_\_\_ (attach C-O-C)
17. Were **methods of collection** consistent with governing CompQAP guidelines? Y N
18. Were sample containers **appropriate** for project (or as specified in QAP)? Y N
19. Were **sample containers rinsed** with sample prior to filling? Y N
20. Were samples **chemically preserved** at the time of collection? Y N
21. Was the **preservative amount** recorded in the field notes? Y N
22. Was the **pH** of preserved samples checked to insure **proper preservation**? Y N
23. Were **samples iced** at the time of collection? Y N
24. Were disposable or lab-cleaned **filter units** used for processing the sample? Y N
24. What **pore size** is the filter? \_\_\_\_\_
25. Was filtering equipment **pre-rinsed** with sample? Y N
26. Were **filters bagged** or otherwise kept free from possible contamination? Y N
27. Were disposable filters **discarded** properly after use? Y N
28. Were samples processed on a **clean tray/surface**? Y N
28. Was **waste material** containerized and maintained separate from samples and equipment? Y N
29. Were **ambient field conditions** recorded in the field notes? Y N
32. Were proper **safety precautions** followed to ensure no damage or injury to the crew, the general public or any of its equipment? Y N If No, explain in deficiencies section below.

List any deficiencies noted during General Sampling activities:

---

#### D. SURFACE WATER SAMPLING

1. What **procedures** were used to collect the surface water samples? \_\_\_\_\_
2. Were the surface water samples taken **before** the sediment samples, if applicable? Y N
  1. Was a **Niskin** or horizontal bottle used for sample collection? Y N  
type and size? \_\_\_\_\_
  2. Was sample collected or processed in a **polyethylene bucket**? Y N
  3. Was a **pump** used for sample collection? Y N  
type and size? \_\_\_\_\_
  4. Was the **pump** properly **cleaned** before and between sites? Y N
  5. Was the pump **tubing** properly **cleaned** before and between sites? Y N
  6. Were samples collected **upstream** from the sampler, vehicle, or water control structure? Y N
  9. Were samples taken from locations considered to be more **stagnant** or **well-mixed**?
  10. Were **flow measurements** taken/recorded? Y N
  11. Were there any man-made **structures** or impoundments in the vicinity (dams, weirs, holding ponds)?  
Y N If so, how were sampling locations chosen relative to them?

Notes:

12. List all surface water **sampling equipment**.

Notes:

13. Did this equipment meet the material construction and parameter restriction **requirements** of the CompQAP? Y N

material construction       parameter restrictions

14. Was a **boat** utilized? Y N

Was it fuel-powered?       Were samples taken from the bow, and/or upwind-upstream-upcurrent from the motor (to avoid fumes, effluent, or prop wash from the motor)? Notes:

15. Were any samples collected by **wading**? Y N

Was wading appropriate for location?       Did sampler face upstream while collecting samples?

Was care taken not to disturb sediments?

Notes:

16. Were samples for **specific parameter groups** taken properly? Y N

(Consult CompQAP sections noted below for detailed requirements.)

- **organics** samples (Section 6.4.2)
- **biological tissue** samples (Section 6.4.6)
- **microbiological** samples (Section 6.4.9)
- **Oil & Grease** samples (Section 6.4.10)
- **low level trace Mercury** samples (Section 6.4.11)

- **benthic macroinvertebrates** samples (Section 6.4.12)

- **radiological/radon** samples (consult DEP Sections 4.2.2.6 & 7)

- **cyanide** samples (consult DEP Section 4.2.2.8)

**List any deficiencies noted during Surface Water Sampling activities:**

---

**E. AUTOMATIC WATER SAMPLING**

1. Were **autosamplers** used? Y N type and size? \_\_\_\_\_

2. Were samples **composited**? Y N

3. **How** were samples composited? \_\_\_\_\_

4. Was sample collection method consistent with CompQAP or Project QAP/SOP in order to achieve a truly **representative** sample? Y N

5. Were autosampler bottle(s) **capped and shaken** well before compositing or processing? Y N

6. Was **tubing changed** within the last three months? Y N

7. Were **preventative maintenance** protocols followed and documented? Y N

8. What method of **preservation** was used for sample integrity? \_\_\_\_\_

9. What method of **collection frequency** was used? (ie. flow/time proportional, and trigger) \_\_\_\_\_

10. Was **deployed equipment secured** against outside contamination and/or vandalism? Y N

11. What other forms of **electronic equipment** were used? \_\_\_\_\_

12. Were any **electronic counters** reset to zero? Y N

13. What is the depth of the **intake tubing**? \_\_\_\_\_

14. Were any **physical parameters** measured? Y N

15. Were clean bottles **replaced** into the autosampler? Y N

16. Were the new bottles **acidified**? Y N

17. Was the level of **acidification proper**? Y N

18. Was the **preservation** (temperature or pH) of the automatic sample checked for proper level? Y N

19. Was a **dessicant** within the autosampler checked? Y N

20. Was the autosampler and its **program checked** for any **malfunctions** in the period of time since its last inspection? Y N

21. If problems were encountered, how were they **resolved**? \_\_\_\_\_

22. Was any sample **discarded**? Y N

23. Were any of the samples **flagged**? Y N

24. Was the autosampler **restarted** prior to leaving the site? Y N

25. Was the autosampler **recalibrated** prior to leaving the site? Y N

26. How was the **calibration performed**? \_\_\_\_\_
27. Were the calibrations **documented** properly? Y N

List any deficiencies noted during Automatic Water Sampling activities:

---

#### F. WASTE WATER SAMPLING

1. What **procedures** were used to collect the waste water samples? \_\_\_\_\_
2. List type and name of all **sampling and measuring equipment** used. \_\_\_\_\_
3. For what **parameters** were samples being analyzed? \_\_\_\_\_
4. Were sampling containers and methods **appropriate** for parameter type(s)? Y N
5. Were sampling containers and methods **consistent** with approved QAPP/SOP or CompQAP? Y N
6. Were sampling **locations** selected properly? Y N
7. Were any **physical parameters** measured? Y N
8. Were proper **safety precautions** followed to prevent contamination to sample personnel? Y N
9. Were **autosamplers** used? Y N type and size? \_\_\_\_\_
10. Were samples **composited**? Y N
11. **How** were samples composited? \_\_\_\_\_
12. Was sample collection method consistent with CompQAP or Project QAP/SOP in order to achieve a truly **representative** sample? Y N
13. Were autosampler bottle(s) **capped and shaken** well before compositing or processing? Y N
14. Was **tubing changed** within the last three months? Y N
15. Were **preventative maintenance** protocols followed and documented? Y N
16. What method of **preservation** was used for sample integrity? \_\_\_\_\_
17. What method of **collection frequency** was used? (ie. flow/time proportional, and trigger) \_\_\_\_\_
18. Was deployed equipment **secured** against outside contamination and/or vandalism? Y N
19. What other forms of **electronic equipment** were used? \_\_\_\_\_
20. Were any **electronic counters** reset to zero? Y N
21. What is the depth of the **intake tubing**? \_\_\_\_\_
22. Were any **physical parameters** measured? Y N
23. Were clean bottles **replaced** into the autosampler? Y N
24. Were the new bottles **acidified**? Y N
25. Was the level of **acidification proper**? Y N
26. Was the autosampler and its **program checked** for any **malfunctions** in the period of time since its last inspection? Y N
27. If problems were encountered, how were they **resolved**? \_\_\_\_\_

- 
28. Was any sample **discarded**? Y N
  29. Were any of the samples **flagged**? Y N
  30. Was the autosampler **restarted** prior to leaving the site? Y N
  31. Was the autosampler **recalibrated** prior to leaving the site? Y N
  32. How was the **calibration performed**? \_\_\_\_\_
  33. Were the calibrations **documented** properly? Y N

List any deficiencies noted during Waste Water Sampling activities:

---

#### G. GROUNDWATER SAMPLING

1. Was a **pump** used for sample collection? Y N
2. If a pump was used, what **type**? \_\_\_\_\_
3. Was the pump properly **cleaned** before and between sites? Y N

Section 14.0

10/27/99

Page 8 of 14

4. Was the **pump tubing** properly cleaned before and between sites? Y N
  5. Was sample collected in polyethylene **bucket**? Y N
  6. Was sampling conducted from **least- to most-contaminated** area, if known? Y N
  7. Were sample containers **appropriate** for this project? Y N
  8. Were **well measurements** taken properly? Y N
    - measuring device decontaminated between wells
    - measuring device has .1' sensitivity (not necessary if for purge volume calculations only)
    - taken from same reference point on casing
  9. Were **well volumes** determined accurately? Check random calculations in logbook. Y N
  10. Were **wells purged** prior to sampling? Y N  bailer  pump
  11. If by **bailer**, was it constructed of the **proper material**? Y N
    - Teflon  HDPE  Stainless Steel  Other
  12. If by **pump**, were all materials/restrictions met per CompQAP? Y N
    - above-ground pump: proper tubing material and foot valve/continuous pumping
    - submersible pump: proper body and tubing material and check valve
  13. If protocol #12 not met because of improper material construction, was the "**polishing**" procedure implemented properly (1 well volume purged with appropriate sampling device)? Y N
  14. Were wells sufficiently **purged** before sampling? Y N
    - measured volume  time/flow rate (estimate only)  pH/temperature/conductance
    - combination -
  15. Were **bailers** used for sampling? Y N
    - Teflon  Stainless Steel  Other
  16. Were fuel-powered units placed **downwind** from sampling and decontamination activities? Y N
  17. Did non-dedicated sampling pumps meet the **material construction** and **parameter restriction** requirements of the CompQAP? Y N
    - above ground pump  submersible pump
  18. Did dedicated sampling pumps meet the **material construction** and **parameter restriction** requirements of the CompQAP? Y N
    - above ground pump  submersible pump
    - if not, why not: \_\_\_\_\_
  19. Was sufficient **information** known about these pumps (construction, placement, age, tubing type(s), packers used, check valves, etc.)? Y N
  20. Did sample tubing material meet the **material construction** and **parameter restriction** requirements of the CompQAP? Y N
    - Teflon  HDPE (high density polyethylene)  Tygon  Other \_\_\_\_\_
  21. Was sufficient **clean tubing** available? Y N
    - tubing not reused  tubing decontaminated between each well (NOT recommended)
  22. Was **tubing decontaminated** per requirements in the CompQAP? Y N
  23. Were **pumps decontaminated** per requirements in the CompQAP? Y N
  24. Were **dissolved constituents** taken properly? Y N
- List parameters filtered: \_\_\_\_\_
- List the kind of filters and pore size: \_\_\_\_\_
- Briefly describe the setup: \_\_\_\_\_
25. Was a **dissolved trace metals** sample collected? Y N
    - was a **total metals** sample also collected?  was a 1.0 micron filter used for these dissolved constituents only?
  26. Was the **bailer and lanyard** (line) prevented from coming in contact with the ground surface? Y N
  27. Was wetted bailer **lanyard** treated properly? Y N
    - disposable line discarded  reusable line decontaminated properly
  28. Were samples for **specific parameter groups** taken properly? Y N  
(Consult CompQAP sections noted below for detailed requirements.)
    - **organics** samples (Section 6.4.2)
    - **biological tissue** samples (Section 6.4.6)
    - **microbiological** samples (Section 6.4.9)
    - **Oil & Grease** samples (Section 6.4.10)

- low level trace Mercury samples (Section 6.4.11)
  - benthic macroinvertebrates samples (Section 6.4.12)
  - radiological/radon samples (consult DEP Sections 4.2.2.6 & 7)
  - cyanide samples (consult DEP Section 4.2.2.8)
29. Were purge and rinse waters disposed of properly? Y N

List any deficiencies noted during Groundwater sampling activities:

---

## H. SOLID MATRIX SAMPLING

### Soil Sampling

1. Were grab samples taken from these soil regimes? (Check all that apply) Y N  
 surface     shallow subsurface     deep subsurface
2. Were areal or depth composite samples taken from these soil regimes? (Check all that apply) Y- N  
 areal     surface     shallow subsurface     deep subsurface  
 depth     surface     shallow subsurface     deep subsurface
3. Was appropriate equipment used for each regime? Y N    List for each -  
surface:     spoon     shovel     trowel  
shallow subsurface:     hand/bucket auger     shovel/post hole diggers     powered device  
deep subsurface:     split spoon     shelby tube
4. Did equipment meet the material construction and parameter restrictions as listed in the CompQAP? Y N  
 material construction     parameter restrictions

### Sediment Sampling

1. Were surface water samples taken prior to sediment samples? Y N
2. Were areal or depth composite samples taken from sediments? Y N  
 areal     depth
3. Was the proper equipment used for the particular substrate at the site? Y N  
 coring device for soft materials or high flow situation     dredge device for hard substrate  
 spoon, trowel, or coring device used at water body margin
4. Did equipment meet the following requirements, as listed in the CompQAP? Y N  
 material construction     parameter restrictions

### General

1. Was sampling conducted from least- to most-contaminated area, if known? Y N
2. Were sample containers appropriate for project and matrix as specified in CompQAP? Y N
3. Was an attempt made to collect representative samples from the location? Y N  
Note any sampling bias. Notes:
4. Was each non-volatile sample mixed thoroughly before being transferred to its container? Y N  
 VOCs taken separately (see below)     appropriate tools and tray used for mixing  
 homogenize by mixing, dividing, remixing     transfer sample to container with minimal headspace  
 clean container and rim carefully (good seal)     gloved fingers did not come in contact with sample  
 cap tightly
5. Were all tools used for the mixing/homogenization phase of the proper material? Y N
6. Were VOC (all volatile parameters) samples taken properly? Y N  
 transfer sample directly from sampling device to container     fill the vial/wide mouth container with sample  
 tamp the sample with glass rod or equivalent     refill and tamp sample down until no headspace exists  
 clean vial and rim carefully (good seal)     gloved fingers did not come in contact with sample  
 cap tightly with teflon septum facing sample
7. Did composite sample collection meet the requirements listed in the CompQAP? Y N  
 sample aliquots of identical size (important)     follow mixing schedule as listed in #4 above  
 origin and size of aliquot is documented     aliquoting done in a systematic manner
8. Was sampling equipment properly decontaminated before arrival and between each sampling site? Y N

List any deficiencies noted during solid matrix sampling activities:

---

**I. ATMOSPHERIC DEPOSITION SAMPLING**

1. What **procedures** were used for Atmospheric Deposition collection? \_\_\_\_\_
  2. Were procedures **consistent** with governing SOP or CompQAP? Y N
  3. Were both **wet and dry** precipitation buckets utilized? Y N
  4. Were buckets maintained **capped** before deployment? Y N
  5. Were previously deployed buckets **sealed** immediately? Y N
  6. Were sample buckets **secured** and kept clean in vehicle? Y N
  7. Were buckets **labeled** with all relevant information? Y N
  8. Were **field conditions** adequately documented in the field log? Y N
  9. Was preventative maintenance and **cleaning** performed as specified in the SOP or CompQAP? Y N
  10. Was deployed equipment **secured** against outside contamination and/or vandalism? Y N
  11. How were samples ensured to be **representative**? \_\_\_\_\_
  12. Was balance **calibration** performed? Y N
  13. Was tare weight **legible** on the buckets? Y N
  14. Was tare weight determined within the last **quarter**? Y N
- 

15. Was **bucket** Equipment Blank performed? Y N

16. List any deficiencies noted during atmospheric deposition sampling activities:

17. \_\_\_\_\_

**J. OTHER SAMPLING**

1. What other **types** of samples were collected during this investigation? \_\_\_\_\_
2. What **procedures** were used for the collection of these samples? \_\_\_\_\_
3. Who or what **directed** this additional sampling? \_\_\_\_\_
4. Is sampling **covered** by a governing SOP or CompQAP? Y N
5. Is sampling **consistent** with SOP and CompQAP guidelines? Y N
6. For what **duration** will this sampling continue? \_\_\_\_\_
7. Was deployed equipment **secured** against outside contamination and/or vandalism? Y N
8. Were samples for **specific parameter groups** taken properly? Y N  
(Consult CompQAP sections noted below for detailed requirements.)
  - **organics** samples (Section 6.4.2)
  - **biological tissue** samples (Section 6.4.6)
  - **microbiological** samples (Section 6.4.9)
  - **Oil & Grease** samples (Section 6.4.10)
  - **low level trace Mercury** samples (Section 6.4.11)
- **benthic macroinvertebrates** samples (Section 6.4.12)
- **radiological/radon** samples (consult DEP Sections 4.2.2.6 & 7)
- **cyanide** samples (consult DEP Section 4.2.2.8)

List any deficiencies noted during Other sampling activities:

---

**K. FIELD QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)**

1. Were **Trip Blanks (TB)** taken properly? Y N
  - analyte free water prepared before containers are transported into the field
  - at least 1 Trip blank for each volatile organic method per cooler used to transport samples
2. Were any **Trip Spikes (TS)** utilized? Y N
  - analyte free water spiked with known amount of stock in the laboratory
  - carried along on trip and handled like routine samples; not opened

3. Were **Equipment Blanks (EB)** taken properly? Y N

Precleaned Equipment Blank (PCEB)

- processed in the field, at the sampling location     DI water poured through EACH piece of sampling equipment  
 filtered, handled and preserved as a routine sample     1-20 samples, a minimum of 1 taken\*  
 21 or more samples, taken at 5%

Field Cleaned Equipment Blank (FCEB)

- processed in the field, at the sampling location     after field cleaning of sampling equipment, the final deionized water rinse is collected as FCEB  
 5-20 samples, 1 FCEB taken\*     21 or more samples, taken at 5%

\* = if less than 5 samples taken, an EB or FCEB is required; if any field cleaning is conducted, take a FCEB

NOTE: At least 1 EB is always required

4. Were **EBs** collected to maximize any site influences? (FCEBs taken after sampling) Y N

5. Were **Split Samples (SS)** taken properly? Was an attempt made to secure two identical samples? Y N

- water: pour all sample water into large vessel and then pour out aliquots for real and split sample (not VOC)  
 water: fill sample containers from consecutive sample volumes from the same sampling device; if the sampling device does not hold sufficient volume, then:

- fill container A half full, then fill container B half full
- waste whatever is in the sampling device and retrieve a full sampling device
- fill container B to the top, then fill container A to the top

- soil: true splits for soil cannot be accomplished, follow protocol for duplicates

6. Were **Field Duplicates (FD)** and/or **Replicate Samples (RS)** taken properly? Y N

- samples collected at the same time from the same source     water: FD from consecutive volumes  
 soil: FD from same source and sampling device volume     1-10 samples, 1 is required  
 11-20 samples, 2 are required     10% of samples thereafter

7. Were **Field Blanks (FB)** taken properly? Y N

- DI water poured directly in sample containers without filtration or the use of other equipment  
 Preserved and maintained open during routine sample processing  
 1-20 samples, 1 is required     5% of samples thereafter

8. Were field meters **calibrated** prior to the first sample? Y N

- one at the end of the day or within 24 hours of initial calibration

9. Were the proper type and number of calibration **standards** used? Y N

- pH buffer    2 to bracket expected sample pH  
 temperature    checked against field grade thermometer  
 conductance    KCl    at least 1 near sample conductance  
 DO    air calibration  
 turbidity    gel or formazin    1 near expected sample value  
 OVA    SPAN gas    1 canister  
 Other    method \_\_\_\_\_

List any deficiencies noted during field QC activities:

---

**L. SAMPLE CONTAINERS AND PRESERVATION**

1. Were analytical **services** scheduled in advance? Y N
2. Were sample **containers** well-organized, properly prepared, protected from contamination, and ready for use? Y N
3. Was **documentation** available for the sample containers? Y N
4. Did any samples require **special handling** (e.g. samples with less than 24 hour holding times)? Y N
5. Were appropriate **fresh preservatives** available (type, grade, recent date)? Y N
6. Were the proper **tools** used to dispense preservative (dropper, disposable pipette, ampuls)? Y N
7. Were preservative containers **appropriate** for the reagent and in good physical shape? Y N
8. Were sampling staff knowledgeable of proper preservative **handling** (suitability, safety, etc.)? Y N
9. Were all samples **preserved properly**? Y N
10. Was chemical preservation **verified**? Y N



- with close-range pH-paper       sample not contaminated with pH-paper  
 all chemically-adjusted samples verified during first visit  
 1 sample from each parameter group that is chemically-adjusted during subsequent visits  
 VOC samples never opened after collection, an additional *dummy* sample can be tested for proper pH

Please note that it is the sampling team's responsibility for proper sample preservation.

11. Were samples put on wet ice for shipment to the laboratory? Y N  
 12. Was **sufficient ice** used to keep samples at 4C? Y N  
 13. Were coolers packed to **isolate** sample or parameter groups (especially VOC) and to minimize breakage/damage? Y N  
 14. Were coolers **taped shut** to prevent damage, contamination and/or loss? Y N

List any deficiencies noted regarding containers or during preservation activities:

#### M. SAMPLE CUSTODY AND DOCUMENTATION

1. Were samples properly **handled** during collection? Y N  
 2. Was each sample container **labeled** correctly? Y N Did it include the minimum:  
 field ID number  
 additional information as required (parameter, date, sampler ID, time, preservation, etc.)  
 the tag or label **must not** come in contact with the sample  
 3. Did the Field ID number meet the minimum requirements as described in the CompQAP? Y N  
 EACH sample container must have a unique field ID number or code  
 4. Were all entries into the notebook made in **waterproof ink**? Y N  
 5. Were **errors** deleted correctly (one line through)? Y N  
 6. Was the required **minimum information** properly documented in a bound notebook and/or field sheets? Y N  
 names of all personnel and visitors       date and time of sample collection  
 ambient field conditions       specific description of sample location  
 field ID for each sample container  
 field measurement data  
      when measurements were taken  
      time of meter calibration  
      concentration of standard and acceptance criteria  
 sample sequence  
 preservation  
      preservative name  
      pH verification  
      amount/quantity of preservative added, if field preserved  
      amount/quantity of additional preservative is added, if pre-preserved  
 purging and sampling equipment used       field decontamination performed  
 field QC samples collected; when, where, type       use and location of fuel powered units  
 composite samples  
      number of samples that make up the composite  
      approximate amount of each subsample  
 signature of sampler       time/date of completion  
 7. Was additional information collected for **monitor wells**? Y N  
 well casing composition and well diameter       water table depth and total well depth  
 calculation used to determine purge volume       total amount of water purged  
 date well was purged       beginning and ending purge times  
 measurement data for stabilization       drilling/boring method and drilling mud used  
 8. **Other matrices** have specific items that must also be documented.  
 samples taken from taps or wells with in-place plumbing  
 surface water samples: depth samples were taken  
 automatic wastewater (effluent) samples  
      composite type (continuous, flow proportioned, etc.)  
      beginning and ending times for timed composites  
 sediments and soils

- depth from surface sample was taken
- drilling or boring method
- drum or container sampling
  - type of drum, description of contents and markings
  - if stratified, what layers were sampled
- 9. Did information in notebook and sample label **match** custody records? Y N
- 10. Did the lab transmittal sheets (COC or sample transmittal) include the required information? Y N
  - site name and address                       date and time of sample collection
  - name of sampler responsible for sample transmittal                       Field ID#s
  - number of samples                       intended analyses                       preservation
  - comments section                       common carrier ID                       signature of sampler
  - time/date relinquished
- 11. How were samples **transported** to the laboratory?
  - Hand delivered \_\_\_\_\_  Common carrier \_\_\_\_\_
- 12. Was **delivery time** appropriate for sample holding time(s)? Y N
- 13. Was a **copy** of the Chain-of-custody included with shipment? Y N
- 14. Did Chain-of-custody record indicate **method** of transport? Y N
- 15. Was the Chain-of-custody **isolated** from moisture? Y N
- 16. Were coolers/shipping containers properly **labeled** and **sealed**? Y N
  - origin and destination clearly marked on each cooler
  - taped shut to prevent damage, contamination and/ or loss
  - tamper-proof seal affixed
- 17. Were Chain-of-custody **procedures** observed/followed throughout the project? Y N
- 18. Was any **supplemental information** included with the Chain-of-custody? Y N

List any deficiencies regarding sample custody activities:

---

**N. CONTINGENCIES**

Were problems encountered during the sampling event (equipment malfunction, inclement weather, etc.)? Was a change in sampling procedure required? Was it an approved procedure? How did the team react? Were they able to make the necessary changes?

---

Comments:

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**O. EXIT CONFERENCE**

Briefly describe the exit conference following field audit, if conducted.

---

Recommendations:

---

**PART II. LABORATORY AUDIT CHECKLIST**

**General Laboratory Procedures:**

**YES NO**

- |    |   |     |     |
|----|---|-----|-----|
| 1. | Have unique sequential laboratory numbers been assigned to each sample?             | ___ | ___ |
| 2. | Has the data from the Chemistry Field Data Log been input to the computer directly? | ___ | ___ |
| 3. | Have samples been stored in an appropriate secure area?                             | ___ | ___ |
| 4. | Has sample custody been maintained by the laboratory?                               | ___ | ___ |
| 5. | Has the proper bar code label been attached to each sample I.D. tag?                | ___ | ___ |
| 6. | Were the samples properly divided into aliquots?                                    | ___ | ___ |

Comments: \_\_\_\_\_

**Analytical Methods:**

- |  | <b><u>YES</u></b> | <b><u>NO</u></b> |
|--|-------------------|------------------|
| 1. Have approved analytical methods or procedures been followed?   | _____             | _____            |
| 2. Does the project plan include copies of any non-standard methods without appropriate quality assurance results for validation of the method?              | _____             | _____            |
| 3. Does use of the analytical methods specified result in data of adequate detection limit, accuracy, and precision to meet the requirements of the project? | _____             | _____            |

Comments: \_\_\_\_\_  
\_\_\_\_\_

**Laboratory Quality Control:**

- |   | <b><u>YES</u></b> | <b><u>NO</u></b> |
|---|-------------------|------------------|
| 1. Have approved sample holding times been observed?                                      | _____             | _____            |
| 2. Have replicate analyses been performed on at least one sample?                         | _____             | _____            |
| 3. Have spike analysis been performed on at least one sample?                             | _____             | _____            |
| 4. Have the quality control reporting forms been properly filled out?                     | _____             | _____            |
| 5. Are current instrument calibration curves used for all methods?                        | _____             | _____            |
| 6. Did the spiking procedures follow acceptable protocols for quantity and concentration? | _____             | _____            |

**Laboratory Quality Control (continued):**

- |  | <b><u>YES</u></b> | <b><u>NO</u></b> |
|--|-------------------|------------------|
| 7. Are quality control charts used to track QC precision and accuracy?                           | _____             | _____            |
| 8. Are QC charts kept up to date?  | _____             | _____            |
| 9. Is the precision of the data presented within acceptable limits?                              | _____             | _____            |
| 10. Is the accuracy of the data presented within acceptable limits?                              | _____             | _____            |
| 11. Are recent (one year or less) performance audit results available?                           | _____             | _____            |
| 12. Has the laboratory followed the preventative maintenance procedures outlined in the QA plan? | _____             | _____            |

Comments: \_\_\_\_\_

**Data Validation and Reporting:**

- |  | <b><u>YES</u></b> | <b><u>NO</u></b> |
|--|-------------------|------------------|
| 1. Were all the steps in the data validation procedure outlined in the QA plan followed? | _____             | _____            |
| 2. Was the data reported in the proper format with the proper units?                     | _____             | _____            |
| 3. Was the laboratory I.D. number included on each page of the data?                     | _____             | _____            |

Comments: \_\_\_\_\_  
\_\_\_\_\_

**NOTE: Use a detailed spreadsheet to tabulate QC data for parameters audited.**

## 15.0 Quality Assurance Reports

The Division Quality Assurance Officers are responsible for preparing a quarterly internal quality assurance report to management. These reports are for internal use and are not submitted to DEP. These reports to the Division Director include the following:

1. An assessment of data accuracy, precision, and method detection limits
2. Results of performance and systems audits
3. Significant quality assurance/quality control problems and the recommended solution
4. Outcome of any corrective action.

For bimonthly, quarterly or semiannual sampling schedules, the QA reports are generated annually (submitted to DEP only upon request). The reports to DEP are written by the Division Quality Assurance Officers, Laboratory Quality Assurance Officer and the Project Managers. The Project Manager is responsible for submitting the report to DEP.

Should DEP request the QA Report and no project audits were performed and no significant quality assurance/quality control problems occurred for a specific project, a letter stating these facts will be sent to DEP in lieu of the quality assurance report.

The quality assurance reports must include the following for performance audits:

1. Date of the audit
2. System tested
3. Persons performing/administering the audit
4. Parameters analyzed
5. Reported results
6. True values of the samples (if applicable)
7. If any deficiencies or failures occurred, a summary of the problem and the corrective action taken
8. Copies of documentation.

The quality assurance reports must include the following for systems audits:

1. Date of the audit
2. System tested
3. Who performed/administered the audit
4. Parameters analyzed
5. Results of tests
6. Parameters for which results were unacceptable
7. Explanation of the unacceptable results including probable reasons and the corrective action taken
8. Copies of documentation.

For significant quality assurance/quality control problems, the following information must be included in the report:

1. Identify the problem and the date it was found
2. Identify the individual who reported the problem
3. Identify the source of the problem
4. Discuss the solutions and corrective actions taken to eliminate the problem.

QA/QC reports are also sent quarterly to the Technical Oversight Committee for the following projects that are related to the Everglades Forever Act. The report contains an assessment of the performance of field and laboratory in relation to generation of data for the associated projects as well as significant QC problems encountered and resolution.

METHOD # 11001	METHOD NAME APPENDIX A COLOR	REVISION 1.2	REFERENCE SM 2120B	STATUS EFFECTIVE
PAGE 1 OF 9				DATE 03/15/99
APPROVALS/DATE				
DIVISION DIRECTOR <i>[Signature]</i> 7/8/99	LAB SUPERVISOR <i>[Signature]</i> 6/15/99	QUALITY ASSURANCE <i>[Signature]</i> 6/15/99	METHODS <i>[Signature]</i> 3/1/99	

## SECTION 1.0 - TABLE OF CONTENTS

<u>SECTION</u>	<u>PAGE</u>
2.0 - METHOD DESCRIPTION/HISTORY	1
3.0 - SAFETY PRACTICES	1
4.0 - LIST OF EQUIPMENT/INSTRUMENTATION	2
5.0 - REAGENTS	2
6.0 - STANDARDS	2
7.0 - QUALITY CONTROL	3
8.0 - STEP-BY-STEP PROCEDURE	3
9.0 - DATA HANDLING	6
10.0 - INSTRUMENT CLEANUP/SHUTDOWN/TROUBLESHOOTING	8
11.0 - REFERENCES	9

## SECTION 2.0 - METHOD DESCRIPTION/HISTORY

2.1 Color in water may result from the presence of metallic ions (iron and manganese), organic acids, humus and peat materials, plankton, weeds, and industrial waste.

2.2 In our laboratory, color analysis is performed on samples filtered through 0.45um membranes. Filtration removes large particulates and turbidity that may interfere with spectrophotometric measurements. It should be noted that the filtration procedure may remove some of the color from the sample.

2.3 The color of the sample is determined by spectroscopic comparison to platinum-cobalt color solutions at 465 nm in a 5 mm quartz flowcell. One unit of color corresponds to 1 mg/L of platinum in the form of the chloroplatinate ion. The MDL (Method Detection Limit) is 1.0 platinum-cobalt color unit.

2.4 This method version 1.2 was adopted on March 15, 1999 and is an internally developed (SFWMD) method and is based on Standard Methods SM 2120B. This revision reflects changes in the method of analysis due to complete automation of the procedure by using components from a Rapid Flow Analyzer.

## SECTION 3.0 - SAFETY PRACTICES

3.1 Wear safety glasses and a full-length, long-sleeved laboratory coat.

3.2 Latex or polyethylene gloves (non-powdered) may be worn when handling the samples.

METHOD # 1100.1	METHOD NAME <b>APPENDIX A</b>  COLOR	REVISION 1.2	REFERENCE SM 2120B	STATUS EFFECTIVE
PAGE 2 OF 9				DATE 03/15/99
<b>APPROVALS/DATE</b>				
DIVISION DIRECTOR <i>[Signature]</i> 2/8/99	LAB SUPERVISOR <i>[Signature]</i> 6/15/99	QUALITY ASSURANCE <i>[Signature]</i> 6/15/99	METHODS <i>[Signature]</i> 3/1/99	

### SECTION 3.0 - SAFETY PRACTICES (CONTD)

3.3 All personnel conducting this method should be familiar with the SFWMD Chemical Hygiene Plan and should have reviewed any pertinent Material Safety Data Sheets. Note: pay special attention to the MSDS for Platinum Cobalt Solution, as it is a suspected carcinogen (Note: Prolonged exposure to Platinum-Cobalt solutions causes degradation of tooth enamel).

3.4 No hazardous wastes are generated by this procedure; liquid waste may be disposed of in the sink.

### SECTION 4.0 - LIST OF EQUIPMENT/INSTRUMENTATION

4.1 Alpkem Rapid Flow Analyzer (with autosampler, peristaltic pump, and a colorimeter), equipped with a personal computer and software for automated data collection.

4.2 Sample cups

4.3 Miscellaneous volumetric flasks, graduated cylinders and beakers

### SECTION 5.0 - REAGENTS

5.1 Dowfax® (surfactant)

5.2 Dowfax Wash Solution - pipet 2 ml of Dowfax (5.1) into approximately 1 L of D.I. water.

### SECTION 6.0 - STANDARDS

6.1 Platinum Cobalt Color Stock Solution/Standard 500 c.u. - STD1 (500 mg/L) - (Fisher Scientific #SO-P-120).

6.2 Platinum Cobalt Color Standard 300 c.u. - STD2 (300 mg/L) - measure 30 mL of stock solution with a class A volumetric pipet and dilute with D.I. water to 50 mL in a class A volumetric flask.

6.3 Platinum Cobalt Color Standard 100 c.u. - STD3 (100 mg/L) - measure 10 mL of stock solution with a class A volumetric pipet and dilute with D.I. water to 50 ml in a class A volumetric flask.

6.4 Platinum Cobalt Color Standard 50 c.u. - STD4 (50 mg/L) - measure 5 mL of stock solution with a class A volumetric pipet and dilute with D.I. water to 50 mL in a class A volumetric flask.

METHOD # 1100.1	METHOD NAME APPENDIX A COLOR	REVISION 1.2	REFERENCE SM 2120B	STATUS EFFECTIVE
PAGE 3 OF 9				DATE 03/15/99
APPROVALS/DATE				
DIVISION DIRECTOR <i>[Signature]</i> 2/8/99	LAB SUPERVISOR 6/15/99 <i>[Signature]</i>	QUALITY ASSURANCE 6/16/99 <i>[Signature]</i>	METHODS <i>[Signature]</i> 3/1/99	

## SECTION 7.0- QUALITY CONTROL

7.1 The Platinum Cobalt Color standard recoveries are checked (see acceptance criterion in Section 8.0) by the analyst before conducting sample analyses. The results are recorded on the QA/QC logsheet.

7.2 The sample holding time is 48 hours. Notify the supervisor or team leader if any samples are out of the holding time.

7.3 QC1 and QC2 are prepared on request by the QA unit. QC1 and QC2 are analyzed at beginning of each run, and either QC1 or QC2 is reanalyzed at the end of the run. Select a true matrix sample for repeat analysis. If there is limited volume to use the same sample throughout the run, two or more samples may be used for the repeat and reported separately.

7.4 A repeat analysis (sample selected at random) should be conducted for every 20 samples analyzed. These results are recorded on the QC sheet and physical parameters log. The mean and coefficient of variation of the replicate set is determined (using the formula below) and noted on the QC sheet and physical parameters logsheet.

$$\%RSD = \frac{STD. DEV.}{MEAN CONC.} * 100$$

7.5 All quality control data must be within the current established limits before entering sample data into the LIMS system.

7.6 Samples must be at room temperature and should be shaken gently prior to analyses; excessive shaking will entrain air and result in erroneous readings.

## SECTION 8.0- STEP-BY-STEP PROCEDURE

8.1 Create a workgroup for the analyses to be conducted. Refer to the ACS LIMS users Guide for instructions on "Creation of a Workgroup". Remove the samples to be tested from the refrigerator and allow them to warm to room temperature (this may require several hours). Failure to do so will result in erratic readings.



METHOD # 1100.1	METHOD NAME <b>APPENDIX A</b>  <b>COLOR</b>	REVISION 1.2	REFERENCE SM 2120B	STATUS EFFECTIVE
PAGE 4 OF 9				DATE 03/15/99
APPROVALS/DATE				
DIVISION DIRECTOR <i>[Signature]</i> 7/8/99	LAB SUPERVISOR <i>[Signature]</i> 6/15/99	QUALITY ASSURANCE <i>[Signature]</i> 6/15/99	METHODS <i>[Signature]</i> 3/1/99	

## SECTION 8.0 - STEP-BY-STEP PROCEDURE (CONT'D)

### 8.2 Instrument Setup

8.2.1 Turn on instrument and allow to warm up for 15 to 30 minutes.

- A. Secure platens and compress pump tubes evenly
- B. Connect sample wash reservoir.
- C. Make sure all lines are in the Dowfax Wash Solution (5.2).
- D. Turn on the power to the autosampler, detector, and pump.
- E. Turn on the power to the computer and monitor.

8.2.2 With all lines in deionized water with Dowfax®, check for a stable detector reading. Ensure that the reagent flow is steady and that the debubbler is efficiently removing the bubbles. Check for leaks or clogged lines.

### 8.3 Computer/Tray Protocol

8.3.1 At the main menu press F4 (sample table). This will bring up the skeleton table. Fill in the sample & QC numbers according to the set format. You can select the channel that you want to enter the table for by pressing Alt and F1 for channel 1.

8.3.2 Hold down the Alt key and F (to access files), then hold down the Alt key and S (for save). When asked for a file name, enter the workgroup number (e.g. WG20536).

8.3.3 Hit Esc to exit back to the main menu.

8.3.4 At the main menu press F5 (Analog Display).

8.3.5 Set the wavelength on the colorimeter to 455 nm. Set the range to 0.1. Set the rise time to 3.0 seconds.

8.3.6 Hit the ZERO button on the colorimeter and wait for the instrument's absorbance to stabilize at 0.000.

8.3.5 Hold down the Alt key and hit 1. This will initialize the file on channel 1

8.3.6 Hit F3 to start the baseline display.

METHOD # 1100.1	METHOD NAME <b>APPENDIX A</b>  COLOR	REVISION  1.2	REFERENCE  SM 2120B	STATUS <b>EFFECTIVE</b>
PAGE 5 OF 9				DATE 03/15/99
APPROVALS/DATE				
DIVISION DIRECTOR <i>[Signature]</i> 7/8/99	LAB SUPERVISOR 6/15/99 <i>[Signature]</i>	QUALITY ASSURANCE 6/15/99 <i>[Signature]</i>	METHODS <i>[Signature]</i> 3/1/99	

## SECTION 8.0 - STEP-BY-STEP PROCEDURE (CONT'D)

### 8.4 Analysis

8.4.1 Set "Stop Count" to the number of cups in tray protocol.

8.4.2 Set "Sample Time" to **30** sec and "Wash Time" to **90** sec.

8.4.3 Begin filling sample cups with each sample according to the Tray Protocol (see Fig. 2 for sample tray protocol).

8.4.4 When you have 10 - 15 cups filled, continue as follows:

- A. Press "start" on the sampler.
- B. When the first peak appears verify that the peak height is approximately 90% of full scale.

8.4.5 Hit **Esc** until you return back to the Main Menu. **Do not allow the computer to remain on the Analog Display for extended periods of time during data collection.** Leaving the computer on the Analog Display may cause the software to "time-out". If this occurs, data received during the "time-out" may be lost.

8.4.6 Check for Quality Control

- A. Check millivoltage readings of Standards.
- B. Check values of QC and RPT Recovery.
- C. If the above is not within the acceptable ranges, see a supervisor or the QA section.

8.4.7 Stop Run

- A. Hit reset on the front panel of the sampler when the instrument "beeps".
- B. Hit **F5** (Analog Display). Set "Start Time Min" to a value approximately 10 minutes less than that of "Collection Time Min".
- C. Allow peaks to finish. (There is approximately a 4 peak delay). Allow at least 2 minutes to elapse after the last peak to establish a final baseline.
- D. On the computer, Press **Esc** to get to the timer.
- E. Hold down the **Alt** key and press **1** (for channel 1) to stop data collection for channel 1.
- F. Press **Esc** to obtain the main menu.

METHOD # 1100.1	METHOD NAME <b>APPENDIX A</b>  COLOR	REVISION 1.2	REFERENCE SM 2120B	STATUS EFFECTIVE
PAGE 6 OF 9				DATE 03/15/99
<b>APPROVALS/DATE</b>				
DIVISION DIRECTOR <i>[Signature]</i> 7/8/99	LAB SUPERVISOR <i>[Signature]</i> 6/15/99	QUALITY ASSURANCE <i>[Signature]</i> 6/15/99	METHODS <i>[Signature]</i> 3/1/99	

## SECTION 9.0 - DATA HANDLING

### 9.1 Computer Data Calculations

- 9.1.1 From the main menu, press **F8** (Calculate).
- 9.1.2 Press **F8** (Calculate).
- 9.1.3 Press **Enter** (From raw data).
- 9.1.4 Enter the file name (ex. WG20536) and press **Enter**.
- 9.1.5 After peaks are displayed press **F9** (continue) until the slope of the standards is displayed.
- 9.1.6 After the slope of the standards are displayed press **F9** (continue) again.
- 9.1.7 Once reaching the results screen, press **F2** (print report) then **Enter** to print the results.
- 9.1.8 Press **F9** (save and exit) and type in the file and the extension (.IN) in order to store the calculations which will be dumped into the LIMS system (ex. WG20536.IN).
- 9.1.9 Press **Esc** to Exit. Note: **F9** will also save the file in order for you to start the next run before you have done steps 8 and 9.
- 9.1.10 Press **Esc** to return to the main menu.

### 9.2 Transfer File to LIMS

- 9.2.1 At the main menu Press **F10** (exit/Quit). Type **S** (for shell). Hit **Enter**.
- 9.2.2 Select the **S2Send** icon.
- 9.2.3 Select the directory and the appropriate file which is to be sent into LIMS.
- 9.2.4 Click on **Send File**.
- 9.2.5 On the "S2Send - File Transfer" screen, verify that the correct file is being sent and select **OK**.

METHOD # 1100.1	METHOD NAME <b>APPENDIX A</b>  COLOR	REVISION  1.2	REFERENCE  SM 2120B	STATUS <b>EFFECTIVE</b>
PAGE 7 OF 9				DATE 03/15/99
<b>APPROVALS/DATE</b>				
DIVISION DIRECTOR <i>[Signature]</i> 7/8/99	LAB SUPERVISOR <i>[Signature]</i> 6/15/99	QUALITY ASSURANCE <i>[Signature]</i> 6/15/99	METHODS <i>[Signature]</i> 3/1/99	

**SECTION 9.0 - DATA HANDLING (CONT'D)**

**9.3 Paperwork**

9.3.1 Complete QC form/calculations.

**9.4 Software Settings**

9.4.1 Channel Setup (Main Menu: F4 (Sample Table) then Alt+C (Channel))

CHANNEL # = [1 OR 2]  
 CHANNEL NAME = COLOR  
 DATA TYPE = CF  
 METHOD NAME = COLOR  
 SAMPLE TIME = [120]  
 DELAY TIME = [0]  
 COLLECTION RATE = [2] POINTS/SEC

9.4.2 Calculations Setup Parameters (Main Menu: F8 (Calculate) then F3 (Edit Methods))

Method Name: Color  
 Invert Raw Data (Y/N): N  
 Do Corrections (Y/N): N  
 Peak Height/Area: Height  
 Decimal Places (0-7): 0  
 Full Scale (10-100): 90  
 Chart Speed (10-180): 30  
 Auto/Interactive: Inter  
 - Print Curve (Y/N): N  
 - Print Calibration (Y/N): N  
 - Print Report (Y/N): N  
 - Save Spreadsheet (Y/N): N  
 Curve Regeneration (Y/N): N  
 - B (deformation, 10-30): 30  
 First Sample # (1-359): 1  
 Start Ignore Time (0-3600): 0  
 Initial Baseline (0-3600): 100

METHOD # 1100.1	METHOD NAME <b>APPENDIX A</b>  COLOR	REVISION 1.2	REFERENCE SM 2120B	STATUS EFFECTIVE
PAGE 8 OF 9				DATE 03/15/99
<b>APPROVALS/DATE</b>				
DIVISION DIRECTOR <i>[Signature]</i> 7/1/99	LAB SUPERVISOR <i>[Signature]</i> 6/15/99	QUALITY ASSURANCE <i>[Signature]</i> 6/15/99	METHODS <i>[Signature]</i> 3/1/99	

## SECTION 9.0 – DATA HANDLING (CONT'D)

### 9.4.2 Calculations Setup Parameters (Cont'd)

Final Baseline (0-3600): 100  
 Threshold (1-300): 20  
 Ascending Slope (0-100): 1  
 Apex (1-100): 10  
 Descending Slope (0-100): 1  
 Plateau Points (0-100): 3  
 Integration Points (1-3600): 7  
 Smooth Factor (0-15): 0  
 Units: UNITS

### 9.4.3 Standards Table (Main Menu: **F4** (Sample Table) then **Alt+V** (View Standards))

Method Name:	COLOR
Calibration Code:	3
1	500
2	300
3	100
4	50
5	0
6..20	0

## SECTION 10.0 - INSTRUMENT CLEANUP/SHUTDOWN/TROUBLESHOOTING

- 10.3 Turn off the main power switch, computer and monitor.
- 10.4 Disengage all platens.
- 10.5 Wipe instrument (including the platens) after each use with moist paper towel and dry.
- 10.6 Inspect all tubing and fittings.
- 10.7 Empty waste containers.

METHOD # 1100.1	METHOD NAME <b>APPENDIX A</b>  <b>COLOR</b>	REVISION  1.2	REFERENCE  SM 2120B	STATUS <b>EFFECTIVE</b>
PAGE 9 OF 9				DATE 03/15/99
<b>APPROVALS/DATE</b>				
DIVISION DIRECTOR <i>[Signature]</i> 3/15/99	LAB SUPERVISOR 6/15/99 <i>[Signature]</i>	QUALITY ASSURANCE 6/15/99 <i>[Signature]</i>	METHODS <i>[Signature]</i> 3/1/99	

## SECTION 11.0 - REFERENCES

- 11.1 Standard Methods for the Examination of Water and Wastewater, 18<sup>th</sup> Edition, 1992.
- 11.2 ACS LIMS Users Guide, version 1.0, 1992.
- 11.3 SFWMD Comprehensive Quality Assurance Manual, current version.
- 11.3 Alpkem Flow Solution Operator's Manual.
- 11.4 Softpac Software Guide.

<b>METHOD</b> 3111	<b>METHOD NAME</b> APPENDIX B SILICA (SiO <sub>2</sub> )	<b>REVISION</b> 2.0	<b>REFERENCE</b> SM4500SiD (Modified)	<b>STATUS</b> EFFECTIVE
<b>PAGE</b> 9				<b>DATE</b> 1/13/99
<b>DIVISION</b> <i>me</i>	<b>LAB SUPERVISOR</b> <i>B. Dwanoff</i>	<b>QUALITY ASSURANCE</b> <i>DR. [Signature]</i>	<b>METHODS</b> <i>Christina [Signature]</i>	<b>DATE</b> 1/26/99 <i>J. Janson</i>

## SECTION 10 - TABLE OF CONTENTS

<u>SECTION</u>	<u>PAGE</u>
2.0 - <del>METHOD</del> DESCRIPTION/HISTORY	1 - 2
3.0 - <del>SAFETY</del> PRACTICES	2 - 3
4.0 - <del>LIST OF</del> EQUIPMENT/INSTRUMENTATION	3
5.0 - <del>REAGENTS</del>	3 - 4
6.0 - <del>STANDARDS</del>	4 - 5
7.0 - <del>QUALITY</del> CONTROL	6
8.0 - <del>STEP-BY-STEP</del> PROCEDURE	6 - 8
9.0 - <del>DATA</del> HANDLING	8 - 10
10.0 - <del>INSTRUMENT</del> CLEANUP/SHUTDOWN/TROUBLESHOOTING	10
11.0 - <del>REFERENCES</del>	11

## SECTION 20 - METHOD DESCRIPTION/HISTORY

21 ~~Silicon~~ ranks next to oxygen in abundance in the earth's crust. Degradation of silica-containing rocks or ~~minerals~~ results in the presence of silica in natural waters as suspended particles, in a colloidal or polymeric state, and as silicic acids or silicate ions. The silica content of natural water most commonly is in the 1 to 30 ~~mg/L~~ range, although concentrations as high as 100 mg/L are not unusual and concentrations exceeding 100 ~~mg/L~~ are found in some brackish waters and brines.

22 ~~The~~ reaction of silicate with molybdate forms B-molybdosilicic acid at a pH of 1.0-1.8. The B-molybdosilicic acid is reduced by tin (II) to form molybdenum blue, which is measured at 820 nm.

23 ~~Interference~~ from orthophosphate and tannin is eliminated by the use of tartaric acid. Colors absorbing at ~~the~~ analytical wavelength will interfere. Samples for analysis are filtered in the field through a 0.45  $\mu$ m filter.

24 ~~The~~ analyses are conducted in a highly automated instrument called a Rapid Flow Analyzer (RFA). The instrument is equipped with an autosampler for sample introduction, a peristaltic pump, a mixing manifold, and a photometer for calorimetric measurement. The analog output of the photometer is relayed to a personal computer equipped with NAP data collection software.

<b>METHOD</b> <b>3120.1</b>	<b>METHOD NAME</b> <b>APPENDIX B</b> <b>SILICA</b> <b>(SiO<sub>2</sub>)</b>	<b>REVISION</b>  2.0	<b>REFERENCE</b>  SM4500SiD (Modified)	<b>STATUS</b>  EFFECTIVE
<b>PAGE 2 OF 11</b>				<b>DATE</b>  1/13/99
<b>DIVISION DIRECTOR</b> <i>[Signature]</i> 2/8/99	<b>LAB SUPERVISOR</b> <i>[Signature]</i> 1/26/99	<b>QUALITY ASSURANCE</b> <i>[Signature]</i> 2/1/99	<b>METHODS</b> <i>[Signature]</i> 1/26/99	

**SECTION 2.0 – METHOD DESCRIPTION/HISTORY (CON'T)**

**2.5** This modified method version is based on APHA Standard Method 4500SiD. This revision, version **2.0**, was adopted on January 13, 1999 and reflects changes due to the use of quadratic regression (2<sup>nd</sup> order fit) for curve calibration, changes in the instrument setup, and data handling.

**SECTION 3.0 - SAFETY PRACTICES**

**3.1** Wear safety glasses and a full-length, long-sleeved laboratory coat.

**3.2** Latex or polyethylene gloves (non-powdered) may be worn when handling the samples.

**3.3** All personnel conducting this method should be familiar with the SFWMD Chemical Hygiene Plan and should have reviewed any pertinent Material Safety Data Sheets.

**3.4** The disposal of samples can be done in the sink, flushing with ample amounts of tap water.

**3.5** Preparation of reagents containing hydrochloric acid, chloroform and stannous chloride solutions should be conducted in a fume hood. The reagents should be prepared by slow addition of concentrated hydrochloric acid to D.I. water. Use an acid resistant bottle carrier when carrying glass containers of concentrated hydrochloric acid and chloroform.

**3.6** Before starting any run, all lines connecting the instrument to the reagents should be checked and tightened if necessary. In case of a leak onto an electrical system, the power should be disconnected before conducting any repairs.

**3.7** The electrical power should be disconnected before conducting any repairs inside the instrument on controllers, electrical wiring or any other components near sources of electricity.

**3.8** In case of spills of concentrated hydrochloric acid the spill should be first treated with an appropriate spill kit and the contaminated absorbent should be collected and placed into adequate storage containers for disposal.



METHOD # 3120.1	METHOD NAME <b>APPENDIX B</b>  <b>SILICA</b> (SiO <sub>2</sub> )	REVISION  2.0	REFERENCE  SM4500SiD (Modified)	STATUS <b>EFFECTIVE</b>
PAGE 3 OF 11				DATE 1/13/99
APPROVED				
DIVISION DIRECTOR <i>[Signature]</i> 2/8/99	LAB SUPERVISOR <i>[Signature]</i> 1/26/99	QUALITY ASSURANCE <i>[Signature]</i> 2/1/99	METHODS <i>[Signature]</i> 1/26/99	

## SECTION 3.0 - SAFETY PRACTICES (CON,T)

3.9 Follow the Personal Safety Protection Codes below during analysis:

- A = Lab coat, glasses
- B = Lab coat, acid resistant gloves, glasses
- C = Lab coat, glasses, apron, gloves
- 1X = Rubber acid carrier
- 2X = Lab coat, acid resistant gloves, goggles, face shield, apron
- 3X = Lab coat, apron, acid resistant gloves, face shield+goggles+respirator or full-face respirator
- G = Flush sink drain with ample amount of tap water

3.10 In case of spills be sure to utilize the appropriate material kit to absorb the spill, if you are not sure of the appropriate material or method for cleaning a spill contact your supervisor. **Notify a supervisor immediately in case of any large spill of hazardous materials.**

## SECTION 4.0 - LIST OF EQUIPMENT/INSTRUMENTATION

- 4.1 ALPKEM<sup>TM</sup> Rapid Flow Analyzer (RFA), Model 300 with XYZ autosampler
- 4.2 Personal Computer equipped with A/D converter, printer and NAP data collection software.
- 4.3 Class A volumetric glassware (pipettes and volumetric flasks)
- 4.4 Clean Nalgene plastic containers.

## SECTION 5.0 - REAGENTS

5.1 Sodium lauryl sulfate solution - Dissolve 5.0 grams of dodecyl sodium sulfate in about 90 mL of deionized water in a 250 mL Erlenmeyer flask. It may be necessary to warm the mixture to obtain a homogeneous solution. Transfer the solution to a 100 mL volumetric flask and dilute to mark with deionized water. Transfer to a small plastic dropping bottle for daily use. (Safety PP = A)

REVISION	METHOD NAME	APPENDIX B	REVISION	REFERENCE	STATUS
3811		SILICA (SiO <sub>2</sub> )	2.0	SM4500SiD (Modified)	EFFECTIVE
					DATE 1/13/99
PERSONNEL					
DIAGNOSTICIAN	LAB SUPERVISOR	QUALITY ASSURANCE	METHODS		
<i>MC</i> 2/8/99	<i>DB Juaneff</i> 1/26/99	<i>BBM</i> 2/1/99	<i>Christopher J. Janson</i> 4/24/99		

### SECTION 5.0 - REAGENTS (CON'T)

**12 Tartaric acid 10% w/v** - Dissolve 100 grams of tartaric acid in approximately 800 mL of deionized water in a 1 liter volumetric flask. Cap and shake to dissolve the salt; dilute the solution to 1 liter with D.I. water. Transfer the solution to a liter plastic container. Add 2 drops of chloroform and shake well. Store the reagent at 2-6 °C. (Safety PP = A)

**13 Hydrochloric acid 1.2 N** - In a fume hood, cautiously add (with stirring) 100 mL of concentrated (12N) hydrochloric acid to approximately 800 mL of deionized water contained in a 1 liter volumetric flask. When the solution has returned to room temperature, dilute to 1 liter with D.I. water and mix well. Store the reagent in a 1 liter plastic container. (Safety PP = 1X, 2X)

**14 Stock stannous chloride** - In a fume hood, cautiously add (with stirring) 10 mL of concentrated (12N) hydrochloric acid to 10 mL of deionized water in a 50 mL Pyrex beaker. Dissolve 10 grams of stannous chloride in the acidic solution. Heating may be required to obtain a homogeneous solution. Store the stock solution in a tightly closed plastic container and refrigerate at 2-6 °C. (Safety PP = 1X, 2X)

**15 Working stannous chloride reagent** - In a 60 mL plastic container, mix together 50 mL of 1.2 N hydrochloric acid and 0.5 mL stock stannous chloride. This reagent should be prepared fresh daily. (Safety PP = A)

**16 Ammonium molybdate reagent** - Dissolve 1.080 grams of ammonium molybdate in approximately 80 mL of deionized water in a 100 mL volumetric flask. Add 0.3 mL (9 drops) of 50% sulfuric acid. Add 1 mL of 5% sodium lauryl sulfate, dilute to 100 mL with deionized water, and mix well. Transfer the solution to a clean plastic 175 mL container. This reagent should be prepared fresh daily. (Safety PP = A)

### SECTION 6.0 - STANDARDS

**NOTE:** Immediately after mixing, the standards should be poured into labeled, clean 175 mL plastic containers.

**11 Silica stock standard** - NIST standard solution or traceable stock, 10,000 mg/L as Si (21,300 mg/L SiO<sub>2</sub>)

**12 Solution A (1065 mg/L)** - In a 100 mL class A volumetric flask, pipette 5 mL of stock solution and dilute to the mark with deionized water. Cap the flask and mix well.

METHOD # 3120.1	METHOD NAME <b>APPENDIX B</b>  SILICA (SiO <sub>2</sub> )	REVISION  2.0	REFERENCE  SM4500SiD (Modified)	STATUS <b>EFFECTIVE</b>
PAGE 5 OF 11				DATE 1/13/99
APPROVALS				
DIVISION DIRECTOR <i>[Signature]</i> 1/8/99	LAB SUPERVISOR <i>[Signature]</i> 1/26/99	QUALITY ASSURANCE <i>[Signature]</i> 2/1/99	METHODS <i>[Signature]</i> 1/26/99	

**SECTION 6.0 – STANDARDS (CON'T)**

6.3 **Standard 1 (21.30 mg/L)** - In a 100 mL class A volumetric flask, pipette 2 mL of solution A and dilute to the mark with deionized water. Cap the flask and mix well.

6.4 **Standard 2 (10.65 mg/L)** - In a 100 mL class A volumetric flask, pipette 1 mL of solution A and dilute to the mark with deionized water. Cap the flask and mix well.

6.5 **Standard 3 (5.32 mg/L)** - In a 200 mL class A volumetric flask, pipette 1 mL of solution A and dilute to the mark with deionized water. Cap the flask and mix well.

6.6 **Standard 4 (2.66 mg/L)** - In a 100 mL class A volumetric flask, pipette 50 mL of standard 3 and dilute to the mark with deionized water. Cap the flask and mix well.

6.7 **Standard 5 (1.06 mg/L)** - In a 100 mL class A volumetric flask, pipette 10 mL of standard 2 and dilute to the mark with deionized water. Cap the flask and mix well.

6.8 **Standard 6 (0.53 mg/L)** - In a 100 mL class A volumetric flask, pipette 10 mL of standard 3 and dilute to the mark with deionized water. Cap the flask and mix well.

6.9 **Standard 7 (0.27 mg/L)** - In a 100 mL class A volumetric flask, pipette 10 mL of standard 4 and dilute to the mark with deionized water. Cap the flask and mix well.

6.10 **Standard 8 (0.00 mg/L)** – Deionized water only.

STANDARD	CONCENTRATION	VOLUME SOLN.	FINAL VOLUME
SiO <sub>2</sub> STOCK	21,300 mg/L		
SOLUTION A	1065 mg/L	5.0 mL of Soln. A	100 mL
STANDARD 1	21.30 mg/L	2.0 mL of Soln. A	100 mL
STANDARD 2	10.65 mg/L	1.0 mL of Soln. A	100 mL
STANDARD 3	5.32 mg/L	1.0 mL of Soln. A	200 mL
STANDARD 4	2.66 mg/L	50.0 mL of Std. 3	100 mL
STANDARD 5	1.06 mg/L	10.0 mL of Std. 2	100 mL
STANDARD 6	0.53 mg/L	10.0 mL of Std. 3	100 mL
STANDARD 7	0.27 mg/L	10.0 mL of Std. 4	100 mL
STANDARD 8	0.00 mg/L	-	DEIONIZED WATER

METHOD # 3120.1	METHOD NAME APPENDIX B SILICA (SiO <sub>2</sub> )	REVISION 2.0	REFERENCE SM4500SiD (Modified)	STATUS EFFECTIVE
PAGE 6 OF 11				DATE 1/13/99
DIVISION DIRECTOR <i>[Signature]</i> 2/8/99	LAB SUPERVISOR <i>[Signature]</i> 1/26/99	QUALITY ASSURANCE <i>[Signature]</i> 2/1/99	METHODS <i>[Signature]</i> 1/24/99 anson	

## SECTION 7.0 - QUALITY CONTROL

7.1 QC1 and QC2 are prepared fresh monthly or as needed by the QA unit. QC1 and QC2 are analyzed at beginning of each set of analyses. QC2 is repeated at the end of the analytical run.

7.2 Spikes are prepared from samples selected at random (1 for every 20 samples analyzed), and are made by adding 0.1 mL of the solution A (with a 1.0 mL Tensette) to a 10 mL volumetric flask and diluting to the mark with the sample.

7.3 A repeat analysis ( of matrix sample chosen at random ) must be run for every 20 samples analyzed.

7.4 All quality control data must be within the current established limits, and the supervisor or the QA officer must check the run before sending the sample data into the LIMS system.

## SECTION 8.0 - STEP-BY-STEP PROCEDURE

8.1 Sign on to LIMS and create a workgroup for SiO<sub>2</sub> (see creating a Workgroup and Printing a Workgroup in the ACS Lims Users Guide).

8.2 Turn ALPKEM 304 regulated power ON.

8.3 Turn on light source.

8.4 Place all reagent lines in DI H<sub>2</sub>O containing 5 drops of sodium lauryl sulfate.

8.5 Latch platens and turn on 302 pump module.

8.6 After flow has stabilized, verify a smooth and consistent bubble pattern throughout the manifold.

8.7 Set photometer parameters as defined by flow diagram.

8.8 On photometer, set center knob to "sample" position.

8.9 Slowly turn the sample fine adjust knob to set the LCD display to 5.00 volts.

8.10 On the photometer, set the center knob to "reference" position.

METHOD# 3120.1	METHOD NAME APPENDIX B  SILICA (SiO <sub>2</sub> )	REVISION  2.0	REFERENCE  SM4500SiD (Modified)	STATUS EFFECTIVE
PAGE 7 OF 11				DATE 1/13/99
DIVISION DIRECTOR <i>[Signature]</i> 1/8/99	LAB SUPERVISOR <i>[Signature]</i> 1/26/99	QUALITY ASSURANCE <i>[Signature]</i> 2/1/99	METHODS <i>[Signature]</i> 1/26/99	

### SECTION 8.0 - STEP-BY-STEP PROCEDURE (CON'T)

8.11 Slowly turn the reference fine adjust knob to set the LCD display to 5.00 volts.

8.12 Place center knob in "absorbance" position. Using the reference fine adjust knob, set the LCD display to 0.20 ( $\pm 0.01$ ).

8.13 Place reagent lines in their respective containers. Allow 2 to 3 minutes before placing stannous chloride line in the reagent bottle. A blue precipitate will form if the stannous chloride is allowed to mix with the ammonium molybdate reagent.

8.14 After 15 minutes, reagent flow should be stabilized. Repeat steps 8.8 through 8.12.

8.15 While reagents are stabilizing, create the sample table. Open NAP (New Analyzer Program) on the computer by selecting its icon on the Windows desktop.

8.17 To create a SiO<sub>2</sub> sample table in NAP, load the SiO<sub>2</sub> sample template (SiO<sub>2</sub>.spl), and type in the sample ID's from the workgroup to be analyzed.

8.18 When sample table is completed, save it using the following format: use the parameter code (SiO<sub>2</sub>), the 3 digit Julian date, and a letter corresponding to the order of analysis; example: SIO2136A (1<sup>st</sup> run); SIO2136B (2<sup>nd</sup> run).

8.19 Print a hard copy of the table file.

8.20 Load the sample table in the "Sample Table" field (next to the SIO2 method) on the NAP main screen.

8.21 In the "Data" field, enter SI, followed by the Julian date, and a letter corresponding to the order of analysis; example: SI136A (1<sup>st</sup> run); SI136B (2<sup>nd</sup> run).

8.22 When the baseline is stable and smooth, click **Control ON** to start data collection. Click **View** to monitor data collection.

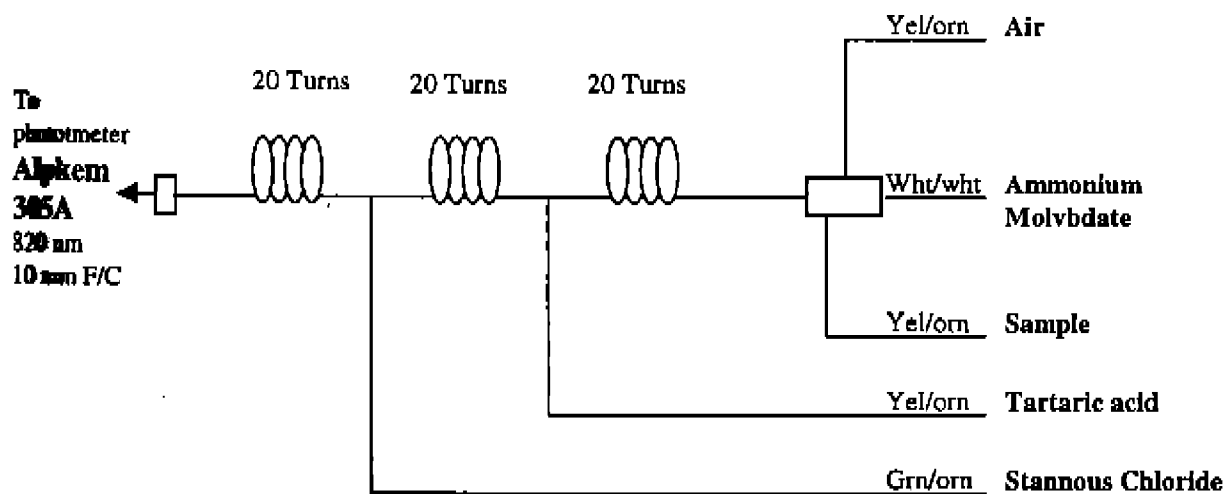
8.23 While baseline is being monitored, begin pouring the samples, and placing them into the autosampler according to the sample table.

<b>METHOD #</b> 320.1	<b>METHOD NAME</b> APPENDIX B  SILICA (SiO <sub>2</sub> )	<b>REVISION</b>  2.0	<b>REFERENCE</b> SM4500SiD (Modified)	<b>STATUS</b> EFFECTIVE
<b>PAGE</b> OF 11				<b>DATE</b> 1/13/99
<b>DIVISION DIRECTOR</b> <i>W. J. ...</i> 2/8/99	<b>LAB SUPERVISOR</b> 1/26/99 <i>D. ...</i>	<b>QUALITY ASSURANCE</b> <i>...</i> 2/1/99	<b>METHODS</b> <i>Christopher ...</i> 1/24/99	

**SECTION 8.0 – STEP-BY-PROCEDURE (CON'T)**

- 824 Manually activate the sampler and set the stop count to the cup number corresponding to the end of the sample table.
- 825 Observe that the standards appear linear and that peaks do not have spikes or any unusual shape to them.
- 826 Finish placing all the samples into the autosampler according to the sample table.
- 827 When the run is complete, click **Control Off** on the NAP main screen to stop the analytical run.

**Analytical Cartridge Diagram for Silica**



**SECTION 9.0 - DATA HANDLING**

- 9.1 After the analytical run is complete, check each quality control value to be sure it falls within acceptable limits.
- 9.2 If run is acceptable, print the analytical report from NAP.

METHOD # 3120.1	METHOD NAME <b>APPENDIX B</b>  SILICA (SiO <sub>2</sub> )	REVISION  2.0	REFERENCE  SM4500SiD (Modified)	STATUS  EFFECTIVE
PAGE 9 OF 11				DATE 1/13/99
DIVISION DIRECTOR <i>[Signature]</i> 2/8/99	LAB SUPERVISOR <i>[Signature]</i> 1/26/99	QUALITY ASSURANCE <i>[Signature]</i> 2/1/99	METHODS <i>[Signature]</i> 1/26/99	

## SECTION 9.0 - DATA HANDLING (CON'T)

9.3 To transfer the file to LIMS, place the cursor on the SIO2 data field, in the main screen of NAP. Click on **Reporting**; a window will appear. Click on **Output to ASCII file**. In the "file" field, enter the exact name for which the data was collected for the analytical run. Click on **Output**. Exit the NAP software. Click on the **S2Send** icon in the windows desktop. Double click on C:\ and then on NAP and find the ASCII file that was created for the analytical run. Once the file is located, select the file, and click the "send file" button. A window will appear confirming that the file will be sent to Lims.

9.4 After the file is sent, pick up the report at the printer.

9.5 Fill out all logbooks and QC sheets daily for each analytical run.

### 9.6 Software Settings

#### 9.6.1 Method Setup (NAP Software)

CHANNEL # = [ 3 ]	PLATEAU POINTS = [ 3 ]
METHOD NAME = [ SIO2 ]	INTEGRATION = [ 10 ]
START IGNORE TIME = [ 0 ]	FILTER LEVEL = [ 0 ]
INITIAL BASELINE = [ 82 ]	PEAKS PER SCREEN = [ 20 ]
FINAL BASELINE = [ 82 ]	PERCENT FULL SCALE = [ 100 ]
CORRECTIONS CODE = [ Y ]	CHART SPEED (cm/h) = [ 60 ]
CYCLE TIME = [ 55 ]	UNITS = [ mg/L ]
THRESHOLD = [ 5 ]	
ASCENDING SLOPE = [ 10 ]	
DESCENDING SLOPE = [ 10 ]	
APEX POINT = [ 10 ]	
REPORT NEGATIVE CONCENTRATIONS = [ Y ]	

METHOD # 3120.1	METHOD NAME <b>APPENDIX B</b>  SILICA (SiO <sub>2</sub> )	REVISION  2.0	REFERENCE  SM4500SiD (Modified)	STATUS  EFFECTIVE
PAGE 10 OF 11				DATE 1/13/99
DIVISION DIRECTOR <i>[Signature]</i> 1/8/99	LAB SUPERVISOR <i>[Signature]</i> 1/26/99	QUALITY ASSURANCE <i>[Signature]</i> 2/1/99	METHODS <i>[Signature]</i> 1/24/99 <i>[Signature]</i> Johnson	

## SECTION 9.0 - DATA HANDLING (CON'T)

### 9.6.2 Standards Table

Calibration Code:	2 (Quadratic Regression)
Name:	SIO2
S1	21.30
S2	10.65
S3	5.33
S4	2.67
S5	1.06
S6	0.53
S7	0.27
S8	0.00

## SECTION 10.0 - INSTRUMENT CLEANUP/SHUTDOWN/TROUBLESHOOTING

- 10.1 Remove stannous chloride reagent line 2 to 3 minutes before other reagent lines. Pre-rinse all lines in clean DI water.
- 10.2 Place all lines in clean DI water and flush instrument for 10 - 15 minutes.
- 10.3 Turn pump module off and unlatch platens.
- 10.4 Turn pump module off and unlatch platens.
- 10.5 Dispose of all sample cups, clean the work area, and rinse and store all glassware.
- 10.6 If troubleshooting is necessary, refer to the RFA manual - troubleshooting section. Document all troubleshooting and maintenance in the instrument maintenance notebook.
- 10.7 Consult the Shift Supervisor before making any major changes, adjustments or repairs to the instrument.



METHOD # 3120.1	METHOD NAME <b>APPENDIX B</b>  SILICA (SiO <sub>2</sub> )	REVISION  2.0	REFERENCE  SM4500SiD (Modified)	STATUS  EFFECTIVE
PAGE 11 OF 11				DATE 1/13/99
DIVISION DIRECTOR <i>[Signature]</i> 2/8/99	LAB SUPERVISOR <i>[Signature]</i> 1/26/99	QUALITY ASSURANCE <i>[Signature]</i> 2/1/99	METHODS <i>[Signature]</i> 1/26/99 <i>[Signature]</i> 1/26/99	

SECTION 11.0 - REFERENCES

- 11.1 EPA Methods for Analysis of Water and Wastes, EPA-600/4-79-020, March 1979.
- 11.2 Standard Method for the Examination of Water and Wastewater, 17<sup>th</sup> Edition.
- 11.3 ACS LIMS Users Guide, version 1.0, 1992
- 11.4 SFWMD Comprehensive Quality Assurance Manual, current version.
- 11.5 ALPKEM RFA 300 series Operator's Manual
- 11.6 NAP Software Manual

## Appendix C

June 17, 1998  
Page 1 of 2

### Soluble Reactive Phosphate

Reference: Stannous Chloride - APHA Standard Methods, 15th ed., p. 417. Method 424E (1980).

Equipment: Spectrophotometer, Hach 2000

Reagents: The reagents for use in this procedure are purchased as part of a test kit, K-8513, Phosphate (M-Blue), 0-4 ppm, from Chemetrics, Inc., Route 28, Calverton, Virginia, 22016-0214. The ammonium molybdate (R-8513) is supplied in evacuated 13mm diameter glass ampoules. The stannous chloride (A-8500) is supplied in a plastic dropper bottle. Each kit contains enough reagent for testing 30 samples.

Standards: Stock solution = 1000 mg/l  $\text{PO}_4\text{-P}$  = 4.394 grams potassium phosphate, monobasic ( $\text{KH}_2\text{PO}_4$ ) dissolved in 1 liter deionized (18 megohm) water. This solution is prepared monthly in West Palm Beach by the Lab QA Officer.

Working standard solutions are prepared from the stock and preserved with 10 drops of 50% sulfuric acid before dilution to 1000 ml.

4.0 mg/L = 40 ml stock diluted to 1000 ml with di  $\text{H}_2\text{O}$   
2.0 mg/L = 20 ml stock diluted to 1000 ml with di  $\text{H}_2\text{O}$   
1.5 mg/L = 15 ml stock diluted to 1000 ml with di  $\text{H}_2\text{O}$   
1.0 mg/L = 10 ml stock diluted to 1000 ml with di  $\text{H}_2\text{O}$   
0.5 mg/L = 5 ml stock diluted to 1000 ml with di  $\text{H}_2\text{O}$   
Blank = 1000 ml di  $\text{H}_2\text{O}$

Standard Additions (Spikes): 5.0 ml of the 2.0 mg/L working standard is added to 20 ml of sample. Standard addition concentration is equal to 0.80 times the samples concentration plus 0.5 mg/L.

QC Check Solutions (Known). Prepared monthly by the Laboratory Quality Assurance Officer in West Palm Beach.

Procedure: Sample and standard treatment: 25 mls of sample or standard is poured into a beaker. Two drops of stannous chloride (A-8500) is added and mixed well. The tip of the evacuated ampoule containing the ammonium molybdate solution is broken off under the surface of the sample. The ampoules then fill automatically. The ampoule is inverted several times to mix the sample and solution and the color is allowed to develop for at least 10 minutes but less than 30 minutes. The absorbance is measured by inserting the ampoule into the spectrophotometer.

Calibration: The spectrophotometer is calibrated by treating the working standards and deionized water blank by the procedure described above. The absorbance is measured at 690 nm and a calibration curve is generated.

Quality Control Procedures

1. Calibration standards are run every 20 samples.
2. A standard addition is run every 10 samples
3. A QC check samples is run every 10 samples.
4. A repeat (duplicate) is run every 10 samples

The results from all quality control samples must fall within the current acceptable limit ranges

General Description: This method measures reactive (ortho) phosphate on an unfiltered sample. Suspended sediment is not found to produce significant interference due to its settling out during the 10 - 30 minute color development time. Similarly, at this wavelength, sample color does not interfere. The sample values range between the laboratory values for total phosphorus and orthophosphate. The sensitivity of this procedure is 0.02 mg/L.

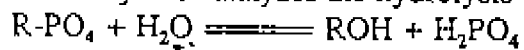
METHOD	METHOD NAME	REVISION	REFERENCE	STATUS
3160.1	ACID AND ALKALINE PHOSPHATASE ACTIVITY (APA)	00	Pettersson and Jansson, 1978	EFFECTIVE
PAGE 1 OF 8				DATE 10-01-94
APPROVALS/DATE				
DIVISION DIRECTOR <i>W. Lee</i> 11/12/94	LAB SUPERVISOR <i>J. [unclear]</i> 11-1-94	QUALITY ASSURANCE <i>M. [unclear]</i> 11-1-94	METHODS <i>D. B. [unclear]</i>	

## SECTION 1.0 - TABLE OF CONTENTS

<u>SECTION</u>	<u>PAGE</u>
2.0 - METHOD DESCRIPTION/HISTORY	1
3.0 - SAFETY PRACTICES	2
4.0 - LIST OF EQUIPMENT/INSTRUMENTATION	2
5.0 - REAGENTS	2
6.0 - STANDARDS	2
7.0 - QUALITY CONTROL	2
8.0 - STEP-BY-STEP PROCEDURE	3
9.0 - DATA HANDLING	5-7
10.0 - INSTRUMENT CLEANUP/SHUTDOWN/TROUBLESHOOTING	7
11.0 - REFERENCES	7

## SECTION 2.0 - METHOD DESCRIPTION/HISTORY

2.1 Phosphatases can be associated with algal and bacterial cell wall and released into water by disintegration of algal cells. These enzymes catalyze the hydrolysis of phosphomonoesters to orthophosphate and an alcohol:



2.2 Phosphatases are classified as either acid or alkaline, depending on the pH of the environment in which they exist. The determination of acid phosphatase activity (APA) and alkaline phosphatase activity is conducted at this native pH by adjusting the pH of the buffer solution.

2.3 The substrate used in this assay is methylumbelliferyl phosphate (MUP), which has a low background fluorescence, thus allowing assay of wide variety of concentration with very high sensitivity. The amount of substrate added is determined by preparing increasing amount of substrate solution.  $V_{max}$  is calculated as the optimum amount of substrate for enzymatic hydrolysis.

2.4 Basically, MUP is prepared in a pH adjusted buffer and added into the sample. The phosphatase enzyme that maybe present in the sample will hydrolyze MUP into methylumbelliferone and phosphate. Methylumbelliferone fluoresces at a specific wavelength when excited with UV light and can be quantified by a spectrophotometer or a fluorometer. A computer aided Cytofluor, a fluorescence plate scanner, is used in our laboratory to perform the analysis.

METHOD 3160.1	METHOD NAME ACID AND ALKALINE PHOSPHATASE ACTIVITY (APA)	REVISION 00	REFERENCE Pettersson and Jansson, 1978	STATUS EFFECTIVE
PAGE 2 OF 8				DATE 10-01-94
APPROVALS/DATE				
DIVISION DIRECTOR <i>Mill</i> 11/1/94	LAB SUPERVISOR <i>J...</i> 10-11-94	QUALITY ASSURANCE <i>M...</i> 11-1-94	METHODS <i>DB Swanson</i>	

## SECTION 3.0 - SAFETY PRACTICES

3.1 All personnel conducting this method should be familiar with the SFWMD Chemical Hygiene Plan and should have reviewed any pertinent Material Safety Data Sheets.

3.2 No hazardous wastes are generated by this procedure; liquid waste may be disposed of in the sink.

3.3 Follow the Personal Safety Protection Codes below during analysis:

A = Lab coat, glasses, gloves

B = Lab coat, apron, acid resistant gloves, face shield + goggles + respirator or full-face respirator

C = Lab coat, acid resistant gloves, goggles, face shield, apron

D = Lab coat, acid resistant gloves, glasses

E = Lab coat, glasses, apron, gloves

F = Rubber acid carrier

G = Flush sink drain with ample amount of tap water

## SECTION 4.0 - LIST OF EQUIPMENT/INSTRUMENTATION

4.1 Millipore CytoFluor 2350 Multiwell Fluorescence Plate Reader

4.2 IBM-compatible PC, with Windows 3.1 and Excel 3.0, and a printer

4.3 Cytofluor computer interface

4.4 Multiwell Low fluorescence plates (24 wells), opaqued

4.5 Multiwell pipetter, 0-150  $\mu$ L capacity

4.6 Eppendorf Micropipettor, adjustable 250  $\mu$ L-1000  $\mu$ L

4.7 Analytical balance, 0.1 mg sensitivity

4.8 Volumetric flasks, 10 and 1000 mL capacity

4.9 Graduated pipets, 1, 2, 5, 10 mL capacity

4.10 Freezer

4.11 Incubator, ambient to 40°C

METHOD	METHOD NAME	REVISION	REFERENCE	STATUS
250.1	ACID AND ALKALINE PHOSPHATASE ACTIVITY (APA)	00	Pettersson and Jansson, 1978	EFFECTIVE
PAGE 1 OF 1				DATE 10-01-94
APPROVALS/DATE				
DIVISION DIRECTOR <i>[Signature]</i> 11/12/94	LAB SUPERVISOR <i>[Signature]</i> 10-11-94	QUALITY ASSURANCE 11-1-94 <i>[Signature]</i>	METHODS <i>[Signature]</i>	

## SECTION 5.0 - REAGENTS

**5.1 Tris stock buffer:** Prepare a 0.1M solution of Tris (base) buffer. Add 12.11 g Tris to 1000 mL volumetric flask and add enough Millipore water to bring it into solution. Add 0.2037 g of anhydrous  $MgSO_4$ , to get final concentration of 0.01M. (Safety PP = A)

**5.2 Working buffer A:** Measure 100 mL of Tris stock buffer into 1L volumetric flask. Bring to volume using sterile Millipore water. Adjust the pH to pH 8.00 for alkaline phosphatase, by slowly adding 1N HCl while stirring. The final concentration of this solution is 0.01M Tris/0.001M  $MgSO_4$ . (Safety PP = A)

**5.3 Working buffer B:** Measure 100 mL of Tris stock buffer into 1L volumetric flask. Bring to volume using sterile Millipore water. Adjust the pH 6.5 to for acid phosphatase, by slowly adding 1N HCl while stirring. The final concentration of this solution is 0.01M Tris/0.001M  $MgSO_4$ . (Safety PP = A)

**5.4 Substrate :** Methylumbelliferyl phosphate (MUP) (FW=256.2). Weigh 0.128 g of MUP and bring to 250 mL volume using the TRIS stock buffer. (Safety PP = A)

## SECTION 6.0 - STANDARDS

**6.1 Stock standard (1000  $\mu$ M MU):** Dry approximately 1g of methylumbelliferone (MU) overnight at 105 °C. Weigh out 0.1982 g of oven-dried MU into a 1L volumetric flask and dilute to volume with working Tris buffer A or B. Keep at room temperature, in a dark container.

**6.2 Secondary stock standard (10  $\mu$ M MU):** Pipet 100  $\mu$ L of stock MU solution into a 10 mL volumetric flask and add working Tris buffer A or B to volume.

## 6.3 Working Standards

Std.	Methylumbelliferone conc.,		Vol. of Stock MU, mL	Final Volume, mL (Add Tris Buffer C to volume)
	$\mu$ M	nM		
S1	0.1	100	0.1	10
S2	0.3	300	0.3	10
S3	0.5	500	0.5	10
S4	1.0	1000	1.0	10
S5	2.0	2000	2.0	10

METHOD	METHOD NAME	REVISION	REFERENCE	STATUS
3160.1	ACID AND ALKALINE PHOSPHATASE ACTIVITY (APA)	00	Pettersson and Jansson, 1978	EFFECTIVE
PAGE 4 OF 8				DATE 10-01-94
APPROVALS/DATE				
DIVISION DIRECTOR <i>[Signature]</i> 11/12/94	LAB SUPERVISOR <i>[Signature]</i> 10-11-94	QUALITY ASSURANCE <i>[Signature]</i> 1-11-94	METHODS <i>[Signature]</i>	

## SECTION 7.0 - QUALITY CONTROL

7.1 Run a duplicate set of each working standard for each analysis. Record the fluorescence value on the instrument log.

7.2 Run a QC solution after a set of working standard and at the end of each analysis.

7.3 A repeat analysis should be conducted for every 20 samples analyzed. These results are recorded on QC sheet and instrument log. The mean and coefficient of variation of the replicate set is determined and noted on the QC sheet and physical parameters log.

7.4 All quality control data must be within the current established limits before entering sample data into the LIMS system. Consult the supervisor or QA officer if unable to obtain acceptable QC result.

7.5 Samples should be mixed thoroughly each time when taking an aliquot.

## SECTION 8.0 - STEP-BY-STEP PROCEDURE

8.1 Create a workgroup for APA (Product). Refer to the ACS LIMS users Guide for instructions on "Creation of a Workgroup" and to Section 9.2.1 and Section 9.2.1. Remove the samples to be tested from the refrigerator and allow them to warm to room temperature (this may require several hours).

8.2 Turn on the Cytofluor and allow it to warm up for at least 15 minutes. Select the CYTOCALC Program (double click with the mouse).

8.3 Determine the pH of the water samples by referring to the hydrolab data or by laboratory measurement with a pH meter. Prepare a fresh set of working Tris buffer A or B, based on the pH range of the samples to analyze, and by following the procedure in Section 5.0. (Therefore, TRIS buffer A should be prepared and used if sample pH is greater than 7, and TRIS buffer B should be used when the sample pH is less than 7).

8.4 Prepare a fresh set of working standards, as described in Section 6.0.

8.5 The well plate template is displayed automatically when entering CYTOCALC program. If the 24-well plate template is not displayed, open the file 24well.CFL (file, open, 24 well.CFL), or the most recent run file with 24 well. Edit the plate protocol by entering the last four digits of the sample number. Use one plate for every 10 samples. It is important to have a duplicate of each standard for the CYTOCALC to function

METHOD	METHOD NAME	REVISION	REFERENCE	STATUS
3160.1	ACID AND ALKALINE PHOSPHATASE ACTIVITY (APA)	00	Pettersson and Jansson, 1978	EFFECTIVE
PAGE 5 OF 8				DATE 10-01-94
APPROVALS/DATE				
DIVISION DIRECTOR <i>[Signature]</i> 11/2/94	LAB SUPERVISOR <i>[Signature]</i> 10-11-94	QUALITY ASSURANCE <i>[Signature]</i> 1-11-94	METHODS <i>[Signature]</i>	

## SECTION 8.0 (CON'T)

8.6 Alternatively, a new protocol can be created by following these steps:

- On the well displayed on the screen, click the well you want to use.
- On the upper right hand corner of the screen, click the well assignment you need (Bl=Blank, Un=Sample, St=Standard, Co=Control, Em=Empty)
- On the edit bar located at the upper portion of the screen, edit the correct I.D. You will need to enter the concentration values of each standard and control.

8.7 Measure 2 mL of blank, standard and QC into each assigned well.

8.8 Pipet 1.8 mL of samples according to the tray protocol. Add 200  $\mu$ L of MUP into each sample well. **DO NOT ADD MUP SUBSTRATE TO STANDARD, BLANK AND QC WELLS.**

8.9 Immediately place the well plate in the door transport, ensure proper seating of the plate and that the first well is on the top right position. Scan within 10 seconds (Click RUN, COLLECT DATA, then enter WORKGROUP number under file name). Record the exact time of the start of the incubation. The system will automatically scan for time 0 reading, then a message "50 % completed will be displayed" on the scan window (This means that a second scan will resume after 1800 seconds or 30 minutes).

8.10 At the end of the second scan, the system will prompt a message, "100 % completed", and will give you an option to CLOSE DOOR or IGNORE DOOR. Choose IGNORE DOOR if another plate is to be scanned and CLOSE DOOR if no more plate is to be scanned.

8.11 At this stage, a message may appear "Cytofluor setting has been changed". Hit OK to display the plate layout. Note that the fluorescence data will be displayed on the plate layout.

8.12 On the top right corner of the screen, depress the LINK button. Note that any associated well (standard, blanks, QC and sample well) is highlighted (black background). Double click each well that is not highlighted. **IMPORTANT:** Only highlighted well (blackened background) will be calculated with the standard curve.

8.13 After highlighting each well, depress the DATA button on the right hand corner of the screen. The system will prompt "ACCEPT CURRENT LINK?". If this is your final link, select YES to proceed. Otherwise, depress the plate button on the upper right hand corner of the screen and make any ID corrections. (At this stage, any outlier standard or sample can be hidden to exclude from calculations. Press the HI button).



METHOD 3160.1	METHOD NAME ACID AND ALKALINE PHOSPHATASE ACTIVITY (APA)	REVISION 00	REFERENCE Pettersson and Jansson, 1978	STATUS EFFECTIVE
PAGE 6 OF 8				DATE 10-01-94
APPROVALS/DATE				
DIVISION DIRECTOR <i>[Signature]</i> 11/12/94	LAB SUPERVISOR <i>[Signature]</i> 11-08-94	QUALITY ASSURANCE <i>[Signature]</i> 11-08-94	METHODS <i>[Signature]</i>	

## SECTION 9.0 - DATA HANDLING

## 9.1 Cytofluor PC-Data Handling

8.14 (After LINK command from Steps 8.12 and 8.13) On the menu bar, select DATA, FORMAT. Specify SCAN 1, then press CALCULATE (Ensure that Calculate and Statistics are marked with X on the screen).

8.15 The computer will automatically go to Excel Program, and display the worksheet with the calculated values. Enter the complete LIMS ID for each sample and QC.

8.16 Select FILE, PRINT to print the time 0 worksheet. Select FILE, SAVE AS, and give file name (.csv) to save file

8.17 Select FILE, END DATA DISPLAY to return to Calculate window. Specify Scan 2. Repeat steps 8.14 to 8.16 to calculate, print and save results of SCAN 2. Save as Filename.csv.

## 9.2 APA Calculation (PC Windows-Excel)

9.2.1 To calculate final APA values in nM/min-mL, the equation below is used:

$$\text{APA (nM/min-mL)} = \frac{\text{MU conc. at time 0 } (\mu\text{M}) - \text{MU conc. after 30 minutes } (\mu\text{M})}{(30 \text{ minutes} \times 1.8 \text{ mL})} \times 1000$$

This equation is entered into Excel worksheet, with filename APA.XLM. Calculation can be done in these worksheet by opening this file, then the time 0 and time 30 minutes files. Copy and paste the time 0 values into APA.XLM worksheet. Repeat to copy time 30 values into the calculation worksheet. Calculation will be automatic. Review the QC and blank values to ensure accurate calculations.

9.2.2 The calculated APA values can be sent to LIMS following Step 9.2.2.

METHOD 3160.1	METHOD NAME ACID AND ALKALINE PHOSPHATASE ACTIVITY (APA)	REVISION 00	REFERENCE Pettersson and Jansson, 1978	STATUS EFFECTIVE
PAGE 7 OF 8				DATE 10-01-94
APPROVALS/DATE				
DIVISION DIRECTOR <i>[Signature]</i> 11/12/94	LAB SUPERVISOR <i>[Signature]</i> 10-11-94	QUALITY ASSURANCE <i>[Signature]</i> 1-11-94	METHODS <i>[Signature]</i>	

## SECTION 9.0 - DATA HANDLING (CON'T)

## 9.2 LIMS Database

9.2.1 Prior to running samples: Go into the ACS LIMS via the command `sl` and create a workgroup for the test APA and exit the SEEDPAK1 Main Menu (see Creating a Workgroup and Printing a Workgroup in the ACS LIMS Users Guide).

9.2.2 After running the samples: Examine the results for acceptability of QC samples and repeats either by manual entry or by transfer from disk through the LIMS Database Analyst. To enter manually go the WORKSTAT, MANUAL ENTRY, APA. Enter the workgroup number. This will prompt the sample numbers one by one. Enter the concentration results.

9.2.2 Pick up the LIMS data entry report for the samples you have just entered from the system printer and examine against the raw data report. Submit any necessary corrections to the DATA UNIT by filling a LIMS Database Correction form.

## SECTION 10.0 - INSTRUMENT CLEANUP/SHUTDOWN/TROUBLESHOOTING

10.1 Wipe dry the surfaces of the plate incubator, the Cytofluor and the work areas. Use D.I. water to clean any spill on the instrument.

10.2 Rinse the plate thoroughly with dilute Liquinox™ and D. I. water. Place the plate upside down on paper towel, to dry. Discard the plate if any visible crack or scratches is observed.

## SECTION 11.0 - REFERENCES

11.1 Pettersson, K. and M. Jansson. 1978. Determination of phosphatase activity in lake water-a study methods. Verh. Internat. Verein. Limnol. 20:1226-1230.

11.2 Prof. Robert G. Wetzel. 1994. Personal Communication. Department of Biological Sciences, The University of Alabama, Tuscaloosa, Alabama 35487-0344, USA.

11.3 Cytofluor 2300 Manual. 1992. Millipore Corporation, Bedford, MA.

Appendix D

METHOD 3160.1	METHOD NAME ACID AND ALKALINE PHOSPHATASE ACTIVITY (APA)	REVISION 00	REFERENCE Pettersson and Jansson, 1978	STATUS EFFECTIVE
PAGE 8 OF 8				DATE 10-01-94
<b>APPROVALS/DATE</b>				
DIVISION DIRECTOR <i>[Signature]</i> 4/12/94	LAB SUPERVISOR <i>[Signature]</i> 10-1-94	QUALITY ASSURANCE <i>[Signature]</i> 11-94	METHODS <i>[Signature]</i>	

FIGURE 1.0 SAMPLE MULTIWELL PROTOCOL (24-well plate)

(A1)  S1 (2000 nM)	(A2)  S2 (1000 nM)	(A3)  S3 (500 nM)	(A4)  S4 (300 nM)	(A5)  S5 (100 nM)	(A6)  BLANK
(B1)  S1 (2000 nM)	(B2)  S2 (1000 nM)	(B3)  S3 (500 nM)	(B4)  S4 (300 nM)	(B5)  S5 (100 nM)	(B6)  BLANK
(C1)  QC1	(C2)  QC2	(C3)  Sample	(C4)  Sample	(C5)  Sample	(C6)  Sample
(D1)  Sample	(D2)  Sample	(D3)  Sample	(D4)  Sample	(D5)  Sample	(D6)  RPT

June 17, 1998  
Page 1 of 18

DER Biology Section

v. 1-7/6/93

SOP #BA-7  
Benthic Macroinvertebrate  
Dip Net Sample Collection

(based on Plafcin, et al, 1989, *Rapid bioassessment protocols for use in streams and rivers: benthic macroinvertebrates and fish*, EPA/444/4-89-001)

## STEPS

## COMMENTS

## Materials

1. *Field Physical/Chemical Characterization Data Sheet*
2. *Habitat Assessment Sheet*
3. Dip Net with No. 30 mesh
4. 4-liter wide-mouth plastic jugs
5. 100% formalin

Prepare per SOP #BA-2.1

## Methods

1. Visually examine the area or reach to be sampled. You must either walk or boat throughout the aquatic system, paying close attention to its physical and habitat characteristics.
2. Fill out *Field Physical/Chemical Characterization Data Sheet* and *Habitat Assessment Sheet*. The percent coverage of substrate type refers to how much of each habitat type is actually present at the sampling site.
3. Determine the number of sweeps to perform in each habitat type out of the 20 total sweeps per station. This requires a two step process. First, select the "major" or "most productive" habitats for the stream type. Use the following formula to calculate the number of sweeps in each habitat type:

$$\frac{\text{Number of sweeps per Major Habitat}}{20} = \frac{\text{Number of Major Habitats} + 1}{20}$$

The result is rounded to the nearest integer. The remaining number of sweeps (to make a total of 20) is evenly divided among the minor habitats (such as sand, mud, or muck in most cases).

In fairly small (1st to 4th order) streams, the length of a discrete station should consist of a 100 m stretch of stream, and the width should be from bank to bank. In very large systems it may be necessary to establish more than one station to adequately characterize the biota.

See SOP's #BA-17 and BA-18 for instructions on filling out these forms.

It is important to accurately determine the spatial extent of each substrate type (in a 3 dimensional context) for habitat scoring procedures.

Generally, the most (to least) productive habitat types are as follows: snags, aquatic vegetation, leaf packs, roots, undercut banks, rocky outcrops, muck, and sand. All but the last two can be considered "major" or "productive".

Example: If 3 major habitat types are present, perform 5 sweeps in each of these habitats and divide the remaining 5 sweeps up among the other non-major habitats, so that a total of 20 sweeps are performed. If 4 major habitats are present, perform 4 sweeps in each of these, then 4 divided up among the remaining types. For 5 major habitats do 3 in each major habitat and divide the remaining 5 sweeps up among the other non-major types.

Proper interpretation of benthic collections requires that samples be collected from multiple habitats that are representative of the site. If possible, the same habitats should be sampled at reference and test sites the same number of times to isolate the effects of water quality on the benthic community.

DER Biology Section

## STEPS

4. Perform 20 discrete 0.5 meter sweeps with the dip net. Sample the available substrates as determined by the above procedures.
  - a. In streams with sufficient water velocity, the most effective way to capture invertebrates is to place the bottom rim of the dip net downstream of the area to be sampled. Disturb, agitate, or dislodge organisms (with hands and/or feet) from substrates (snags, etc.) at a distance of 0.5 m upstream of the net.
  - b. For areas without flow, disturb an area of substrate that is one dip net width wide and approximately 0.5 m long, and sweep the net over the area a few times to ensure the capture of organisms which were living there.
  - c. For heavily vegetated areas (some streams, lake margins, or wetlands) jab the net into the base of the vegetation, digging down to the substrate, and dislodge organisms using a one-half meter sweeping motion with the net.
  - d. Sample leaf packs (if present) by disturbing leaf pack areas with hands or feet before scooping one-half meter worth of material into the net.
  - e. Sand, muck, mud, and silt (non-major habitats) can be sampled by taking 0.5 meter sweeps with the net while digging into the bottom approximately 1 cm.
5. Record the number of sweeps for each habitat on the *Field Physical/Chemical Characterization Data Sheet*.
6. Reduce the sample volume after each discrete sample by dislodging organisms from larger debris (but retaining invertebrates in the net or sieve) and discarding the debris. Save finer debris plus organism mixture in large wide mouth jugs. Try to reduce enough of the sample volume in the field so that no more than 2 gallons of material are collected. If this is not possible, put the material into additional jugs. Sample reduction is easier in the laboratory.

v. 1-7/693

## COMMENTS

When performing an upstream/downstream type of study, sample the downstream station first to prevent upstream invertebrates from drifting into a location they were not originally inhabiting.

Catch organisms by allowing them to flow into the net and also by sweeping the net towards disturbed material.

Several sweeps over the same 0.5 meter area are recommended to make sure all organisms are captured. This sampling effort in a discrete 0.5 meter spot is considered as 1 sweep.

Where a continuous half meter sweep is impossible, take 2 quarter meter sweeps in the same area to attain a full 0.5 meter sweep.

If the net is pushed too deep in coarse sand, very little of the sand will be washed through the net resulting in a sample that contains few organisms and is hard to process.

Ideally, control and test sites will be sampled the same number of times in the same habitats.

The relative proportions of the organisms collected must be maintained intact to calculate many community metrics. Some field picking of delicate organisms is acceptable as long as community composition is not altered.

Indicate on the label how many jugs the entire sample is contained in, e.g., "1 of 2", "2 of 2".

DER Biology Section

STEPS

7. If laboratory sorting can be performed within 24 hours, place samples immediately on ice. Cold temperatures should slow organisms enough to prevent predation (and subsequent alteration of community structure). If sorting will be delayed, preserve with 10% formalin (do this by adding one part of 100% formalin to the jug with 9 parts ambient water). After organisms have been removed from detritus, they should be placed into 70% ethanol.

v. 1--7/6/93

COMMENTS

If organisms are too active during sorting, pour some carbonated water, clove oil, or other relaxing agent into the sample.

Samples that will not be sorted within 2 days should be preserved in formalin. Ethanol alone will not prevent the vegetative debris from decomposing, resulting in a sample that is very unpleasant to sort.

DER Biology Section

v. 1-7/693

SOP #BA-8  
Benthic Macroinvertebrate Qualitative (Dip Net)  
Sample Handling

STEPS	COMMENTS
<b>Materials</b>	
1. Waterproof paper and permanent marker	For making labels
2. U.S. 30 mesh sieve	
3. U.S. 10 mesh sieve	
4. Ethanol filled squeeze bottle (80%)	
5. White enamel pan, marked with a grid of 5 cm squares	
6. List of random numbers	
7. 250-mL glass jar	
8. Dissecting microscope	
9. 100 x 15 mm petri dish	
10. Forceps	
11. Vials for picked organisms (1 or 2 dram)	
12. Laboratory counter	
13. <i>Benthic Macroinvertebrate Bench Sheet</i>	
<b>Methods</b>	
1. Check labels so you know which sample you are dealing with (control site, test site, etc.). Make a very clear label to go into the bottle of picked bugs with station identification, date sampled, replicate number, and your initials.	Make sure that you know how many containers in which the particular sample is stored (there may be several jugs). The entire sample must be included in this reduction and homogenization process.
2. Place a portion of the contents of the sample (first sized) into a U.S. 10 mesh sieve with a U.S. 30 mesh sieve underneath.	
3. Rinse with tap water (a small hose attached to the faucet works best), spraying organisms and small detritus down into the U.S. 30 mesh sieve. Visually inspect large debris (leaves, plants, twigs) held in the U.S. 10 mesh sieve for animals before discarding. Wash fine debris (silt, mud) through the bottom (U.S. 30 mesh) sieve. Repeat procedures #2 and #3 until all the sample from all the jugs has been processed.	This inspection is best accomplished by placing the debris in a white pan and observing it with the Luxo <sup>®</sup> lighted magnifier. Organisms found (generally the ones too large to pass through the U.S. 10 mesh sieve) should be placed into the U.S. 30 mesh sieve with the rest of the unpicked sample.
4. Place sample in gridded pan. Each 5 cm grid should have a pre-assigned number. Liquid present in the sample should be sufficiently reduced to prevent material from shifting among grids during the sorting process.	There are 24 total 5 cm grids in a standard white enamel pan.

Mar 17, 1998

Page 3 of 18

## DETRITUS Section

## STEPS

COMMENTS <sup>v. 1--7/16/93</sup>

5. ~~Thoroughly~~ mix the sample so that a homogeneous distribution of organisms is achieved in the detrital matrix.
6. ~~Select~~ a grid using the random number table. Remove the contents of the entire grid and place in a glass jar.
 

Use a ruler to delineate the edges of a grid while removing the sample.
7. ~~Take~~ a small amount of this detritus plus organism mixture and place it in the bottom portion of a petri dish. Add enough liquid (usually ethanol) so that the material is wet enough to move around easily with forceps.
 

The top portion of the petri dish may later be placed over the sample to prevent desiccation if you must leave the sample overnight.
8. ~~Place~~ the petri dish under a dissecting scope set at low power (approximately 7x or 10x). In a deliberate, systematic manner scan back and forth or up and down picking each and every organism from the aliquot and placing it into an alcohol-filled vial (clearly identified as per step #1).
 

Using a pair of forceps in each hand enables you to better tease organisms out of fibrous detritus. Forceps should be sharp and properly aligned.

Use the laboratory counter to keep a running total of the number of organisms picked.
9. ~~After~~ scanning dish in one pattern (e.g., up and down), go back through using a different pattern (back and forth) to assure that all organisms have been removed from the aliquot.
 

Picking accuracy should be checked by a co-worker in 10 % of the samples.
10. Continue steps 6, 7, 8, and 9, until you obtain a minimum of 100 organisms. Once a grid is selected, its entire contents must be sorted.
 

If an obvious organism is observed but its grid number was not selected and no examples of that organism were present in grids which were selected, that organism may be noted as qualitatively observed. The organism should NOT be included in the analysis.
11. Record the information requested on the *Macroinvertebrate Lab Bench Sheet* which includes site, laboratory sample number, STORET station number, sample type, replicate number, and date collected. Include the initials of the persons who collected and sorted the sample. Record the number of grids selected (e.g., "4 of 24") to enable conversion to total abundance present in the original sample.
 

Failure to record the number of grids selected (out of the total grids possible) seriously compromises the usefulness of the data.



DER Biology Section

v. 1--7/6/93

SOP #BA-8.1  
Preparation of 80% Ethanol

STEPS	COMMENTS
<b>Materials</b>	
<ol style="list-style-type: none"><li>1. 100% Ethanol (HPLC grade)</li><li>2. D.I. water</li><li>3. 4000-mL graduated cylinder</li><li>4. 4-L glass amber jug</li><li>5. Plastic funnel to fit into 4-L jug</li></ol>	
<b>Methods</b>	
1. Fill graduated cylinder with 3200 mL of 100 % ethanol.	This operation is easier with two people as the ethanol is purchased in 5-gallon cans. One person holds the cylinder while the other pours the ethanol.
2. Add D.I. water to the graduated cylinder until the total volume is 4000 mL.	
3. Using the funnel, transfer the dilute ethanol to the 4-L jug which should be properly labeled as 80% ethanol.	
4. Rinse graduated cylinder and funnel with D.I. water and return them to the shelf above the sink.	

DER Biology Section

v. 1-71693

**SOP #BA-9**  
**Benthic Macroinvertebrate**  
**Grab Sample Collection**  
*(Modified from Standard Methods 10500B.3)*

**STEPS****COMMENTS****Materials**

1. Ekman or Petite Ponar dredge
2. U.S. 30 mesh box sieve
3. White enamel pan
4. Plastic squeeze bulb ("turkey baster")
5. Small bucket
6. Wide mouth plastic sample containers
7. Tape and permanent markers

For making labels

**Methods**

- |   |   |
|---|---|
| <p>1. Use of the Ekman dredge is restricted to sampling soft substrates (silt, muck) in areas with little current. The Ponar dredge may be used for sampling under these conditions and also in areas with a harder substrate (rocks, shells, sand).</p>  | <p>The number of replicates collected is dependent upon several factors including the area sampled by the device, the purpose of the study, and the degree of patchiness in the distribution of the organisms at the site. Routinely, take 3 dredges. All replicates are placed in separate sample containers (for statistical analyses). If it has been determined that you are sampling in an exceptionally depauperate area, additional replicates may be required (pilot study needed). In that case the number of replicates sampled at the group of stations you wish to compare should be equal.</p> |
| <p>2. When sampling from a boat, dredge samples are collected from the rear and downstream of the vessel to avoid contamination of other types of samples with disturbed sediments. Rinse the box sieve with ambient water and tie it to the side of the boat where samples will be collected.</p>  | <p>The box sieve is constructed of fiberglass-coated wood and U.S. 30 mesh screen. When placed in the water, it will float at the surface. If a box sieve is unavailable, the dredged material may be washed in the dip net providing it is fitted with a U.S. #30 mesh sieve material. The disadvantage of using the dip net is that it requires 2 people: 1 to hold the net, 1 to manipulate the dredge.</p>  |
| <p>3. Ekman: Open the spring-loaded jaws and attach the chains to the pegs at the top of the sampler. Lower the dredge to the bottom, making sure it settles flat. Holding the line taut, send down the messenger to close the jaws of the Ekman dredge. Pull the sampler to the surface and place it immediately into the box sieve. Carefully open the jaws and discharge the contents into the sieve, rinsing to assure complete sample purging.</p> | <p>The spring-loaded Ekman is dangerous. Hold the dredge firmly above the hinges, and be very careful that no body parts get pinched by the snapping jaws, which could produce serious injury.</p> <p>Check to make sure the jaws are fully closed and that no sample was lost while lifting the dredge.</p>  |

DER Biology Section

v. 1--7/693

## STEPS

## COMMENTS

- |   |  |
|---|--|
| <p>3. Ponar: Open the jaws and place the cross bar into the proper notch. Lower the dredge to the bottom, making sure it settles flat. When tension is removed from the line, the cross bar will drop, enabling the dredge to close as the line is pulled upward during retrieval of the dredge. Pull the Ponar to the surface and place it immediately into the box sieve. Carefully open the jaws and discharge the contents into the sieve, rinsing to assure complete sample purging.</p> <p>4. Swirl the box sieve in the water with a back and forth motion to wash the fine sediments through. Concentrate the remaining sample into one corner of the sieve.</p> <p>5. Fill the small bucket with ambient water and use this water to fill the squeeze bulb. Using the squeeze bulb, rinse the sample from the sieve to the enamel pan.</p> <p>6. Transfer the sample from the enamel pan into the pre-marked wide mouth jug (again, using the squeeze bulb), making sure the location, date, and replicate number is accurate.</p> <p>7. Preserve the sample with 10% formalin by adding a 10 to 1 ratio of water to 100% formalin. If laboratory processing is possible within 8 hours, the samples may be stored on ice, without addition of formalin.</p> | <p>Check to make sure the jaws are fully closed and that no sample was lost while lifting the dredge.</p> <p>If a sediment type is especially clayey or mucky, it may be necessary to use a hand to break up clumps and agitate the sample to reduce it. Make sure you rinse any detritus from your hand back into the sieve.</p> <p>Take care to rinse the entire contents of the sample into the pan. Some organisms may stick to the screen.</p> <p>Rose bengal dye may be added to the sample, as a picking aid, if desired.</p> |
|---|--|

June 17, 1998  
Page 9 of 18

DER Biology Section

v. 1-7/693

**SOP #BA-10**  
**Benthic Macroinvertebrate Grab**  
**Sample Handling**  
(Modified from *Standard Methods 10500C*)

STEPS	COMMENTS
<b>Materials</b>	
1. Waterproof paper and permanent marker	For making labels
2. U.S. 30 mesh sieve	
3. Ethanol filled squeeze bottle (80%)	Prepare per SOP #BA-8.1
4. Glass jars	
5. Dissecting microscope	
6. 100 x 15 mm petri dish	
7. Forceps	
8. Vials for picked organisms (1 or 2 dram)	
9. <i>Benthic Macroinvertebrate Bench Sheet</i>	
<b>Methods</b>	
1. Check labels so you know which sample you are dealing with (control site, test site, etc.) Make a very clear label to go into the bottle of picked bugs with station identification, date sampled, replicate number, and your initials.	It is critical that no errors be made during this step. If samples are mixed up, the entire study could be rendered invalid.
2. Pour the contents of the wide mouth jug over a U.S. 30 mesh sieve. Rinse the jug with tap water to make sure all organisms are put into the sieve.	
3. Rinse with tap water (a small hose attached to the faucet works best). Wash fine debris (silt, mud) through the sieve. Any large debris (leaves, shells, etc.) present should be brushed clean of organisms and discarded. Rinse the organism plus detritus mixture to one small area of the sieve.	
4. Using an ethanol-filled (80%) squeeze bottle, rinse the organism plus detritus matrix into the smallest practical container (usually a 100 mL to 250 mL glass jar). Put the label inside the jar.	Place jars on the sample shelf so that samples for a given study are organized together and clearly marked.
5. Record the information requested on the <i>Macroinvertebrate Lab Bench Sheet</i> , which includes site, laboratory sample number, <del>STATION</del> station number, sample type, replicate number, and date collected. Include the initials of the persons who collected and sorted the sample.	

DER Biology Section

v. 1-7/693

## STEPS

## COMMENTS

- |   |  |
|---|--|
| <p>6. Take a small amount of detritus plus organism mixture and place it in the bottom half of a petri dish. Add enough liquid (usually ethanol) so that the material is wet enough to move around easily with forceps.</p>   | <p>The top portion of the petri dish may later be placed over the sample to prevent desiccation if you must leave the sample overnight.</p> <p>Do not overload the petri dish with too much sample. This results in sloppy work.</p> |
| <p>7. Place the petri dish under a dissecting scope set at low power (approximately 7x or 10x). In a deliberate, systematic manner scan back and forth or up and down, picking each and every organism from the aliquot and placing it into an alcohol-filled vial (clearly marked as per step #1).</p> | <p>Using a pair of forceps in each hand enables you to better tease organisms out of fibrous detritus. Forceps should be sharp and properly aligned.</p>   |
| <p>8. After scanning dish in one pattern (e.g., up and down), go back through using a different pattern (back and forth) to assure that all organisms have been removed from the aliquot.</p>   |  |
| <p>9. Continue steps 6, 7, and 8 until the sample is finished.</p>  | <p>Picking accuracy should be checked by a co-worker in 10% of the samples.</p>  |

June 17, 1998  
Page 11 of 18

DER Biology Section

v. 1—7/6/93

**SOP #BA-11**  
**Benthic Macroinvertebrate Core**  
**Sample Collection**  
(Modified from *Standard Methods 10500B.3*)

**STEPS****COMMENTS****Materials**

1. Coring Device
2. U.S. 30 mesh box sieve
3. White enamel pan
4. Plastic squeeze bulb
5. Small bucket
6. Wide mouth plastic sample containers
7. Tape and permanent markers

For making labels

**Methods**

1. Use of coring devices is restricted to sampling fairly soft substrates (silt, muck, with only small amounts of sand or shell) usually in marine systems. The Biology Section uses two sizes of coring devices.

The number of replicates collected is dependent upon several factors, including the area sampled by the device, the purpose of the study, and the degree of patchiness in the distribution of the organisms at the site. Routinely, take enough cores so that an area equivalent to 3 Ponar dredges is collected (approximately 675 cm<sup>2</sup>). With our large (4 inch diameter) coring device, collect 8 replicates to achieve this. All replicates are routinely placed in separate sample containers (for statistical analyses). Depending on the study objectives, replicates may also be composited, as long as the number of replicates is equal for each station and clearly recorded so that the number of organism per square meter can be calculated.

2. When sampling from a boat, use the 4 inch diameter coring device that is attached to a long pole, and has a valve near the top. Core samples are collected from the rear and downstream of the vessel to avoid contamination of other types of samples with disturbed sediments. Rinse the box sieve with ambient water and tie it to the side of the boat where samples will be collected.

The box sieve is constructed of fiberglass-coated wood and U.S. 30 mesh screen. When placed in the water, it will float at the surface. If a box sieve is unavailable, the dredged material may be washed in a dip net, providing it is fitted with a U.S. #30 mesh sieve material. The disadvantage of using the dip net is that it requires two people (one to hold the net, and one to manipulate the coring device).

3. Lower the coring device to the bottom with the valve open. After quickly pushing the device into the sediments, close the valve. The resulting vacuum will keep the material in the tube as it is raised up to the boat.

Many clean water organisms are somewhat motile and may elude capture if you are not quick during sampling.

4. When collecting samples in wadable waters, a smaller coring device (2 inch diameter) can be used. This corer utilizes a flapper-valve equipped stopper which is inserted into the top of the pipe. Vacuum inside the pipe holds the material until the stopper is removed.

This small corer should be used primarily for non-biological sediment sampling (grain size, metals, etc.), as it is thought to be too small to effectively capture many organisms (e.g., crustaceans or tubicolous worms which are generally large in size) considered useful in impact determination.

DER Biology Section

## STEPS

v. 1-7/6/93  
COMMENTS

5. Pull the sampler to the surface, open the valve or remove the stopper, and place it immediately into the box sieve. Disgorge the contents into the sieve, rinsing to assure complete sample purging.
6. Swirl the box sieve in the water with a back and forth motion to wash the fine sediments through. Concentrate the remaining sample into one corner of the sieve.
7. Fill the small bucket with ambient water and use this water to fill the squeeze bulb. Using the squeeze bulb, rinse the sample from the sieve to the enamel pan.
8. Transfer the sample from the enamel pan into the pre-marked wide mouth jug (again, using the squeeze bulb), making sure the location, date, and replicate number is accurate.
9. Preserve the sample with 10% formalin by adding a 10 to 1 ratio of water to 100% formalin. If laboratory processing is possible within 8 hours, the samples may be stored on ice, without addition of formalin.

If a sediment type is especially clayey or mucky, it may be necessary to use a hand to break up clumps and agitate the sample to reduce it. Make sure you rinse any detritus from your hand back into the sieve.

Take care to rinse the entire contents of the sample into the pan. Some organisms may stick to the screen.

Rose bengal dye (use a very small amount) may be added to the sample, as a picking aid, if desired.





DER Biology Section

## STEPS

6. Take a small amount of detritus plus organism mixture and place it in the bottom half of a petri dish. Add enough liquid (usually ethanol) so that the material is wet enough to move around easily with forceps.
7. Place the petri dish under a dissecting scope set at low power (approximately 7x or 10x). In a deliberate, systematic manner, scan back and forth or up and down, picking each and every organism from the aliquot and placing it into an alcohol-filled vial (clearly marked as per step #1).
8. After scanning dish in one pattern (e.g., up and down), go back through using a different pattern (back and forth) to assure that all organisms have been removed from the aliquot.
9. Continue steps 6, 7, and 8 until the sample is finished.

v. 1-7/693

## COMMENTS

The top portion of the petri dish may later be placed over the sample to prevent desiccation if you must leave the sample overnight.

Do not overload the petri dish with too much sample. This results in sloppy work.

Using a pair of forceps in each hand enables you to better tease organisms out of fibrous detritus. Forceps should be sharp and properly aligned.

Picking accuracy should be checked by a co-worker in 10% of the samples.

June 17, 1998  
Page 15 of 18

DER Biology Section

v. 1—7/693

SOP #BA-13  
Benthic Macroinvertebrate Hester-Dendy  
Sample Collection

*(Modified from Standard Methods 10500B.5)*

## STEPS

## COMMENTS

## Materials

1. 3 or 4 Hester-Dendy artificial substrates
2. Customized Hester-Dendy block, with coupling nuts for attachment of HD samplers and eye bolts for attachment of cable
3. Stainless steel cable
4. Nico-press<sup>®</sup> tool with fasteners
5. Whirl-pak<sup>®</sup> bags
6. Permanent marker

For labeling bags

## Methods

1. Attach three HD's to the HD block, and place the block at a depth of one meter (or the deepest spot available if shallower than one meter). Take care to place control and test site blocks in areas of similar flow and habitat type. Space for 4 H-D's has been provided on the block, for use in studies requiring additional replication.
2. Attach cable to a point on the bank sufficiently high to enable recovery even if the water level increases.
3. After a 28 day incubation period, recover the HD samplers. Approach the block carefully, without disturbance, from the downstream position. In a deliberate, gentle manner lift the block straight up from the bottom and immediately place on a flat surface.
4. Quickly place the Whirl-pak bags over all the HD's, and unscrew them from the block. If an organism is observed crawling off a HD, capture it and put it in the appropriate Whirl-pak. Fill the Whirl-paks with ambient water (so that all the plates are wet), secure them (twirl three times and twist the ends), and place on ice.

Knowledge of the system's hydrologic regime is important to make sure samplers will not go dry during the 28 day incubation period. For example, if it is flood stage and you expect the water to drop 2 meters in the next few weeks, place sampler so that it will be 1 meter deep at the end of incubation.

In shifting sand substrates place the block so that existing rags will deflect sand from being deposited on the samplers. This can be determined by close examination of the bottom topography.

Wrap the cable around the base of a tree on the bank and use the Nico-press<sup>®</sup> tool and fasteners to secure the block. If vandalism is a potential problem, attempt to conceal the cable so that no one but you can find it. If the Nico-press<sup>®</sup> tool is unavailable, the fasteners may be crimped by hammering (two hammers are needed).

Wade or use a boat. DO NOT pull the block up from the shore.

Whirl-paks should be pre-labeled with the station, sample date, and replicate number, using the permanent marker.

Samples should NEVER be preserved until after organisms are scraped from the Hester-Dendy plates. Preservatives will poison the plates, preventing them from being used again.

DER Biology Section

v. 1-7/6/93

**SOP #BA-14**  
**Benthic Macroinvertebrate Hester-Dendy**  
**Sample Handling**  
 (Modified from *Standard Methods 10500C*)

STEPS	COMMENTS
<b>Materials</b>	
1. Waterproof paper and permanent marker	For making labels
2. U.S. 30 mesh sieve	
3. Wrench for dismantling HD	
4. Ethanol filled squeeze bottle (80%)	Prepare per SOP #BA-8.1
5. Glass jars	
6. Dissecting microscope	
7. 100 x 15 mm petri dish	
8. Forceps	
9. Vials for picked organisms (1 or 2 dram)	
10. <i>Benthic Macroinvertebrate Bench Sheet</i>	
<b>Methods</b>	
1. Check labels so you know which sample you are dealing with (control site, test site, etc.). Make a very clear label to go into the bottle of picked bugs with station identification, date sampled, replicate number, and your initials.	It is critical that no errors be made during this step. If samples are mixed up, the entire study could be rendered invalid.
2. Pour the contents of the Whirl-pak bag (an assembled Hester-Dendy and associated detritus) over a U.S. 30 mesh sieve. Using a wrench to remove the bottom nut, dismantle the Hester-Dendy.	Rinse the Whirl-pak bag with tap water to make sure all organisms are put into the sieve.
3. Rinse with tap water (a small hose attached to the faucet works best). Scrape and simultaneously rinse organisms off HD plates with fingers (or a soft brush), using care not to damage the organisms. Wash fine debris (silt, mud) through the sieve. Any large debris (leaves, twigs) present should be brushed clean of organisms and discarded. Rinse the organism plus detritus mixture to one small area of the sieve.	Save the HD plates and hardware, and place them into the drying oven.
4. Using an ethanol-filled (80%) squeeze bottle, rinse the organism plus detritus matrix into the smallest practical container (usually a 100 mL to 250 mL glass jar). Put the label inside the jar.	Place jars on the sample shelf so that samples for a given study are organized together and clearly marked.

June 17, 1998

Page 17 of 18

## DER Biology Section

## STEPS

5. Record the information requested on the *Macroinvertebrate Lab Bench Sheet*, which includes site, laboratory sample number, STORET station number, sample type, replicate number, and date collected. Include the initials of the persons who collected and sorted the sample.
6. Take a small amount of detritus plus organism mixture and place it in the bottom half of a petri dish. Add enough liquid (usually ethanol) so that the material is wet enough to move around easily with forceps.
7. Place the petri dish under a dissecting scope set at low power (approximately 7x or 10x). In a deliberate, systematic manner, scan back and forth or up and down, picking each and every organism from the aliquot and placing it into an alcohol-filled vial (clearly marked as per step #1).
8. After scanning dish in one pattern (e.g., up and down), go back through using a different pattern (back and forth) to assure that all organisms have been removed from the aliquot.
9. Continue steps 6, 7, and 8 until the sample is finished.

v. 1--7/6/93

## COMMENTS

The top portion of the petri dish may later be placed over the sample to prevent desiccation if you must leave the sample overnight.

Do not overload the petri dish with too much sample, as this results in sloppy work.

Using a pair of forceps in each hand enables you to better tease organisms out of fibrous detritus. Forceps should be sharp and properly aligned.

Picking accuracy should be checked by a co-worker in 10% of the samples.

Macrobenthic Invertebrate Keys

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- Berner, L. and M.L. Pescador. 1988. The Mayflies of Florida (Revised edition). Univ. of Fla. Press, Gainesville, FL. 267 pp.
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METHOD #	METHOD NAME	REVISION	REFERENCE	STATUS
3150.2	TOTAL INORGANIC CARBON (TIC) DISSOLVED INORGANIC CARBON (DIC)	2.0	EPA 415.1	EFFECTIVE
PAGE 1 OF 6				DATE 04/27/98
APPROVALS/DATE				
DIVISION DIRECTOR <i>[Signature]</i> 5/14/98	LAB SUPERVISOR <i>[Signature]</i> 5/11/98	QUALITY ASSURANCE <i>[Signature]</i> 5/14/98	METHODS <i>[Signature]</i> 5/14/98	

## SECTION 1.0 - TABLE OF CONTENTS

<u>SECTION</u>	<u>PAGE</u>
2.0 - METHOD DESCRIPTION/HISTORY	1
3.0 - SAFETY PRACTICES	2
4.0 - LIST OF EQUIPMENT/INSTRUMENTATION	2
5.0 - REAGENTS	3
6.0 - STANDARDS	3
7.0 - QUALITY CONTROL	4
8.0 - STEP-BY-STEP PROCEDURE	4
9.0 - DATA HANDLING	5
10.0 - INSTRUMENT CLEANUP/SHUTDOWN/TROUBLESHOOTING	6
11.0 - REFERENCES	6

## SECTION 2.0 - METHOD DESCRIPTION/HISTORY

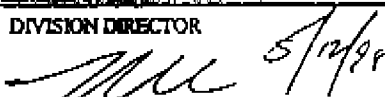
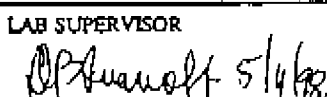

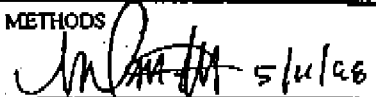
2.1 Inorganic carbon species in natural waters include gaseous and dissolved  $\text{CO}_2$ , carbonic acid ( $\text{H}_2\text{CO}_3$ ), bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ), occurring in either free forms or as conjugate base (example  $\text{CaCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{MgCO}_3$ ,  $\text{NaHCO}_3$ , etc). The nature and abundance of individual species depends on the source of water and the underlying soil/sediment material.

2.2 The carbonate species determine the capacity of water to neutralize acid or base (alkalinity or acidity, respectively). Carbon dioxide is a participant in the biological processes of respiration ( $\text{CO}_2$  produced), and biosynthesis of autotrophs or photosynthetic organisms ( $\text{CO}_2$  consumed).

2.3 Inorganic carbon is determined directly using a high temperature combustion-infrared detection system. Analysis is done on a non-acidified sample, **unfiltered for TIC and filtered** through a 0.45  $\mu\text{m}$  filter for DIC. In the absence of a set holding time for inorganic carbon, the **holding time for alkalinity (14 days)** is followed.

2.4 Calibration is done using standards ranging from 0-200  $\text{mg/L C}$  (in the form of  $\text{Na}_2\text{CO}_3$ ) and the concentration of the samples are expressed as  $\text{mg/L C}$ .

2.5 This method (Version 2.0) was revised 27-APR-98 to reflect changes due to new instrumentation and changes in the LIMS programming. The method is the same in principle as Version 1.0.

METHOD # 3150.2	METHOD NAME TOTAL INORGANIC CARBON (TIC) DISSOLVED INORGANIC CARBON (DIC)	REVISION 2.0	REFERENCE EPA 415.1	STATUS EFFECTIVE
PAGE 2 OF 6				DATE 04/27/98
APPROVALS/DATE				
DIVISION DIRECTOR  5/12/98	LAB SUPERVISOR  5/14/98	QUALITY ASSURANCE  5/11/98	METHODS  5/14/98	

## SECTION 3.0 - SAFETY PRACTICES (CONTD)

- 3.1 Wear safety glasses and a full-length, long-sleeved laboratory coat.
- 3.2 Use acid resistant gloves when handling concentrated phosphoric acid.
- 3.3 All personnel conducting this method should be familiar with the SFWMD Chemical Hygiene Plan and should have reviewed Material Safety Data Sheet for phosphoric acid.
- 3.4 The electrical power should be disconnected before conducting any repairs inside the instrument on controllers, electrical wiring or any other components near sources of electricity.
- 3.5 In case of spills of concentrated  $H_3PO_4$ , treat first with an appropriate spill kit and collect the contaminated absorbent and place into adequate storage containers for disposal.
- 3.6 When changing compressed air bottles, take extra precaution in transporting the bottle to and from the room. It is advisable to request delivery by the vendor to the desired location. After closing the main tank valve, release the pressure slowly in the old tank until the pressure gauge displays 0 psi. Disconnect the regulator from the bottle and cap the bottle tightly with the provided cap. If transporting is required, carefully load the bottle on the hand truck bottle carrier and secure tightly with the strap. Use the same carrier to transport a new compressed air bottle. Secure the new bottle with the strap and connect the regulator. Use teflon tape to avoid any leak. After the regulator is secured and the main tank valve opened, use the SNOOP™ to check for any leaks.

## SECTION 4.0 - LIST OF EQUIPMENT/INSTRUMENTATION

- 4.1 Shimadzu 5050A TIC Analyzer with autosampler
- 4.2 Volumetric Flasks (Class A): 1000 mL, 100 mL capacity
- 4.3 Volumetric pipets (Class A): 20, 10, and 2 mL
- 4.4 Amber Bottle, 1L
- 4.5 Tensette pipet, 0.1-1.0 mL capacity
- 4.6 8 mL Disposable Test Tubes

## Appendix F

METHOD # 3150.2	METHOD NAME TOTAL INORGANIC CARBON (TIC) DISSOLVED INORGANIC CARBON (DIC)	REVISION 2.0	REFERENCE EPA 415.1	STATUS EFFECTIVE
PAGE 3 OF 6				DATE 04/27/98
<b>APPROVALS/DATE</b>				
DIVISION DIRECTOR <i>[Signature]</i> 5/11/98	LAB SUPERVISOR <i>[Signature]</i> 5/11/98	QUALITY ASSURANCE <i>[Signature]</i> 5/11/98	METHODS <i>[Signature]</i> 5/11/98	

## SECTION 5.0 - REAGENTS

- 5.1 Phosphoric acid, concentrated, reagent grade
- 5.2 Carbon-free water (distilled water, preferably double distilled)
- 5.3 Working Phosphoric acid solution (20%): Add 75 mL of concentrated phosphoric acid to 175 mL of DI water in the HDPE reagent bottle. Transfer to the solution to the acid reservoir (located in side of the analyzer).
- 5.4 Sodium Carbonate, anhydrous.
- 5.5 Zero (synthetic) air (<1 ppm CO<sub>2</sub> or hydrocarbons)

## SECTION 6.0 - STANDARDS

- 6.1 Stock Inorganic Carbon (IC) standard solution (1000 mg C/L) - Dissolve 1.7660 g of Sodium Carbonate in ~70 mL of DI water contained in a 200 mL class A volumetric flask. Swirl to dissolve the salt, and dilute to the mark with DI water. (Do not add sulfuric acid to this reagent).
- 6.2 Standard 1 (Blank) - Deionized water
- 6.3 Standard 2 (20 mg C/L) - Dilute 2 mL of stock IC solution and dilute to 100 mL with DI water using a Class A volumetric flask.
- 6.4 Standard 3 (100 mg C/L) - Dilute 10 mL of stock IC solution and dilute to 100 mL with DI water using a Class A volumetric flask.
- 6.3 Standard 4 (200 mg C/L) - Dilute 20 mL of stock IC solution and dilute to 100 mL with DI water using a Class A volumetric flask.



## Appendix F

METHOD #	METHOD NAME	REVISION	REFERENCE	STATUS
3150.2	TOTAL INORGANIC CARBON (TIC) DISSOLVED INORGANIC CARBON (DIC)	2.0	EPA 415.1	EFFECTIVE
PAGE 4 OF 6				DATE 04/27/98
APPROVALS/DATE				
DIVISION DIRECTOR <i>[Signature]</i> 5/12/98	LAB SUPERVISOR <i>[Signature]</i> 5/11/98	QUALITY ASSURANCE <i>[Signature]</i> 5/11/98	METHODS <i>[Signature]</i> 5/11/98	

## SECTION 7.0 - QUALITY CONTROL

7.1 A check standard (Standard 3) is run every 20 samples to verify the calibration. The recovery of this standard must be within  $\pm 5\%$  of the true value (47.5 – 52.5 mg C/L).

7.2 QC1 and QC2 will be prepared by the QA unit. QC1 and QC2 are analyzed at beginning and end of each set of analyses. Results must be within current QA acceptance limits. In case of unacceptable recoveries, see your supervisor or QA unit staff.

7.3 A repeat sample, selected at random should be analyzed for every 20 samples analyzed. These results are recorded on the QC sheet. The mean and coefficient of variation of the replicate set is determined and noted on the QC sheet. If recoveries are not within the current QA acceptance limits, see your supervisor or QA unit staff.

7.4 A spiked sample must be analyzed for every 20 samples. Add 0.5 mL of stock IC solution, using a tensette pipette, into a 10 mL volumetric flask. Bring to volume with the sample being spiked and mix well. This results in an addition of 50 mg/L C.

7.5 All quality control data must be within the current established limits before entering sample data into the LIMS system. Complete and submit the QC result form.

## SECTION 8.0 STEP-BY-STEP PROCEDURE

## 8.1 Daily Start-up


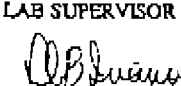

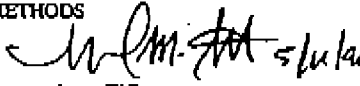
8.1.1 Check the gas supply. Ensure that there is enough gas for a day's operation. Change the air tank when pressure goes below 100 psi.

8.1.2 Check the acid reservoir level (located on the inside of the analyzer). Make sure that the reservoir is at least  $\frac{1}{2}$  full before beginning the analyses.

8.1.3 Check the humidifier level (located on the inside of the analyzer). Make sure the water level is between the marks on the container, if not add DI water.

8.1.4 If the instrument power is not on, refer to section 10.3 and follow the procedure to power up the instrument.

## Appendix F

METHOD # 3150.2	METHOD NAME TOTAL INORGANIC CARBON (TIC) DISSOLVED INORGANIC CARBON (DIC)	REVISION 2.0	REFERENCE EPA 415.1	STATUS EFFECTIVE
PAGE 5 OF 6				DATE 04/27/98
<b>APPROVALS/DATE</b>				
DIVISION DIRECTOR 	LAB SUPERVISOR  5/11/98	QUALITY ASSURANCE  5/11/98	METHODS  5/11/98	

## SECTION 8.0 STEP-BY-STEP PROCEDURE (CONT)

8.2 Placing samples into the autosampler.

8.2.1 Create a workgroup for the samples to be analyzed (see section 9.1) and complete a sample ID worksheet. The worksheet is preformatted with the proper location of standards, check standards and QC samples. Enter the sample ID, and type for each sample in the workgroup. This worksheet will be used as guide to place the samples in the autosampler.

8.2.2 Remove the samples from the refrigerator, and using the worksheet as a guide, pour the standards, QC solutions and samples into disposable test tubes and place them into the autosampler in the location indicated on the worksheet.

8.3 Starting the analytical run.

8.3.1 From the main menu on the analyzer select "Autosampler". The screen will display the initial and final sampler positions to be analyzed. Make sure that the initial sample is set to 1 and the final sample position is set to the number of the last tube in the autosampler tray.

8.3.2 Press the "Next" key twice and Press "Start/Stop" on the analyzer keypad to begin the analyses. A tray of 74 samples will take ~14 hours to complete. Because of the susceptibility of the sample to exchange CO<sub>2</sub> with the atmosphere, do not pour more than 20 samples at a time.

8.4 Completion of the run

8.4.1 When the run is completed, remove the printed results from the analyzer and write the individual results on the sample ID worksheet. Check to make sure that all of the QA/QC samples are within limits.

8.4.2 Complete an instrument log form for the run and place it into the instrument logbook.

8.4.3 Enter the results to LIMS (see Section 9.3).

## SECTION 9.0 DATA HANDLING

9.1 Follow the instructions given in the LIMS manual to create a workgroup for TIC or DIC.

9.2 Review the data printout and complete the INSTRUMENT LOG, QC RESULT and MAINTENANCE

METHOD # 3150.2	METHOD NAME TOTAL INORGANIC CARBON (TIC) DISSOLVED INORGANIC CARBON (DIC)	REVISION 2.0	REFERENCE EPA 415.1	STATUS EFFECTIVE
PAGE 6 OF 6				DATE 04/27/98
<b>APPROVALS/DATE</b>				
DIVISION DIRECTOR <i>[Signature]</i> 5/12/98	LAB SUPERVISOR <i>[Signature]</i> 5/11/98	QUALITY ASSURANCE <i>[Signature]</i>	METHODS <i>[Signature]</i> 5/11/98	

## SECTION 9.0 DATA HANDLING (CONT'D)

9.3 Log into the LIMS, and at ISOTOPE%, type lims. At the main menu select "Workstat", "Dataentry", and "Manual". Enter TIC or DIC under parameter, then enter the Workgroup #. Type the each sample concentration corresponding to the sample number from the sample ID worksheet and hit ENTER, after each entry. Press ENTER again after confirming that the correct result has been entered.

## SECTION 10.0 - INSTRUMENT CLEANUP/SHUTDOWN/TROUBLESHOOTING

10.1 Leave the furnace, gas and the instrument on, unless the unit will not be used for a prolonged period.

10.2 Remove used test tubes, empty the contents on the sink, and dispose of glass test tubes in designated glass disposal receptacle. Wipe up any spill around the work area and on the instrument.

## 10.3 Instrument Startup

10.3.1 If the instrument has been powered off, make sure that the gas flow is turned on, and switch the power on by pressing the switch on the left side of the analyzer. It will take a few seconds for the initialization screen to appear.

10.3.2 When the initialization screen appears, press the "Initialize Autosampler" key to initialize the autosampler. This will take about one minute.

10.3.3 After the autosampler has initialized, the furnace will begin to heat. Again, check the gas flow and make sure it is set to 150 mL/min; adjust, if necessary, by turning the carrier gas knob inside the analyzer front panel. Allow the instrument to stabilize for 2-3 hours before beginning any analyses.

## SECTION 11.0 - REFERENCES

11.1 U. S. Environmental Protection Agency. March 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020.

11.2 American Public Health Assoc., 1989. Standard Method for the Examination of Water and Wastewater, 17<sup>th</sup> Edition.

11.3 Shimadzu 5050A Operators Manual.

**APPENDIX G**  
**Procedures for Collecting Sediment and Porewater Samples**  
**and Monitoring Sediment Deposition Rates in Wetlands**

**1.0 SEDIMENT CORE COLLECTION**

**1.1 Field Sampling Procedures**

1. To avoid disturbing the sediments, soil cores are collected from the airboat. Sediment cores will be obtained by driving a stainless steel coring device, fitted with a clear butyryte sleeve, to a depth of approximately 30 cm into the peat.
2. Before the cores are pulled, the water depth is measured. The core sleeve is marked to indicate the water depth plus 30 cm. A rubber band is placed on the sleeve to indicate how deep to insert the corer into the sediments.
3. The corer device is inserted into the sediments, up to the level indicated by the rubber band. Then, the sediment core, with the overlying water, is pulled out of the sediment. If the core is not intact, the core is discarded and another one collected.
4. Intact cores are measured to determine if there was any compaction of the sediments. If no compaction occurred, the amount of sediment collected will be about 30 cm deep. If the amount of sediment collected is significantly less than 30 cm (i.e., if the amount of sediments is < 25 cm), this suggests that compaction has occurred and the core is discarded and another one collected. Compaction ratios, which is the amount of sediment collected divided by the expected amount, is recorded on the chain-of-custody sheets.
5. Once compaction has been measured, the butyryte sleeve is labeled, capped at both ends using rubber stoppers, stored out of direct sunlight, and transported to the laboratory for analysis. Each sample label will contain the following information:
  - a. Station designation,
  - b. Sample replicate information if appropriate
  - c. Date,
  - d. Time, and
  - e. Initials of field personnel collecting sample.
6. Triplicate cores, for replication, are collected at each site.
7. Field personnel will complete all appropriate sections of the sample chain-of-custody form (see Appendix) immediately after collecting a sediment core sample at each station.
8. Both crew members will verify that all necessary samples have been collected and the information recorded on the sample label and chain-of-custody form is correct before leaving a station.
9. All samples should be delivered to laboratory and placed in the walk-in refrigerator. Arrangements for sample pick-up should be made with the contract lab prior to sampling.

**1.2 Sediment Core Field Equipment**

Butyryte Sleeves (3") with spares  
PVC coring attachment  
rubber stoppers  
hammer  
pipe pounder  
wooden pounding block  
knife

- sample labels and rubber bands
- compass
- metric measuring tape
- clipboard
- pencils/pens
- water-proof marking pens
- deionized water
- Chain-of-custody and field data sheets
- field notebook
- ENR Sediment/Porewater Monitoring Plan SOP

## **2.0 POREWATER COLLECTION**

Porewater will be collected using porewater wells. Each porewater well is composed of a PVC pipe with a well screen. The size and position of the screen on each well will depend on the desired sampling depth (e.g., 0-5 cm, 5-10 cm, or 10-30 cm depth increments). The end of the well that enters the soil is capped with a pointed PVC fitting while the sampling end is closed off with a rubber stopper. A clear acrylic (or similar inert plastic) tube extends through the rubber stopper to the base of the well. The acrylic tube is closed to the atmosphere by the attachment of a small length of impermeable hose which is closed with an inert stopper. This hose is also used to attach the well to a peristaltic pump. The wells are inserted into the soil and left to equilibrate for two weeks.

### **2.1 Porewater Sampling Procedure**

1. Each well is evacuated using a peristaltic pump. The pump is run at low speed. The well is then allowed to recharge for approximately 15 minutes or overnight until there is enough volume to meet sample needs.
2. After the well has been evacuated and before samples are collected, the pH of the porewater is measured using a compact pH meter.
3. Plastic gloves will be worn when collecting and processing the sample. Because the analytes of highest priority come from filtered samples, the filtered samples will be collected first. Samples will be collected with a peristaltic pump and will be deposited directly into labeled sample bottles. In-line 0.45 micron filters will be used for filtered samples.
4. Each sample is processed immediately (i.e., filtered and preserved, if necessary), labeled, and stored on ice in a light-tight cooler. The sample preparation, filtering, and handling protocols used for this study will follow procedures listed in the SFWMD's Laboratory Comprehensive Quality Assurance Plan and the contract laboratory's sampling instruction sheet. Samples will be transported back to the laboratory within 24 hrs from the time of field collection. Each sample label will contain the following information:
  - a. Station designation,
  - b. Sample replicate information if appropriate
  - c. Date
5. Field personnel will complete all appropriate sections of the chain-of-custody and field data form (see Appendix) immediately after collecting a porewater well sample at each station.
6. Both crew members will verify that all necessary samples have been collected and the information recorded on the sample label and chain-of-custody form is correct before leaving a station.
7. Samples analyzed for Alkaline Phosphatase Activity (APA) should be delivered to the laboratory as soon as possible. Samples going to the contract laboratory are placed in a cooler and completely iced. Copies of the chain-of-custody and field data form are sealed in a zip-lock plastic bag and placed in the cooler. The cooler is then securely taped, addressed and put in the proper location for over-night pickup.

## **2.2 Porewater Field Equipment**

### **2.2.1 Item Checklist**

Peristaltic pump  
marine battery  
sample labels for APA analysis and rubber bands  
60 mL SFWMD bottles  
Contract lab bottles  
0.45µm groundwater filters, 25 mm plain  
light-tight ice chests w/ice  
preservation chemicals (H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, NaOH, Zn Acetate)  
deionized water in 5 gallon carboy  
drinking water  
latex disposable gloves  
pH test strips (<2, >9)  
spare parts for wells  
clip board  
pencils/pens/water-proof marking pens  
waders  
Chain-of-custody and field data sheets  
field log book  
ENR Sediment/Porewater Monitoring Plan SOP  
Band Saw

## **2.3 pH METER CALIBRATION**

1. Two pH buffers which bracket the analytical range of interest (e.g., 4 and 7) should be used to calibrate the pH meter following the manufacturer's instructions. Calibrate the meter in the prior to taking any readings.
2. All calibration records must be kept in the field notebook.

## **3.0 SEDIMENT AND FOREWATER SUBMISSION PROCEDURES**

Sediment and porewater samples will be collected by field personnel and subsequently delivered to the contract laboratory for analysis. The sample transfer mechanism will be coordinated with the collection crew and the contract laboratory. The chain-of-custody sheets will accompany the samples at all times. These sheets will document the transfer of samples between departments within the District and between the District and the contract laboratory.

## **4.0 QUALITY ASSURANCE/QUALITY CONTROL**

The Project Manager will issue all field and laboratory personnel a copy of the Standard operating Procedures (SOP) and will verify that each staff member has read the SOP. A Quality Control program will be established for the analyses of sediment and porewater. Results of the QC analyses will be reported along with the regular data by the contract laboratory to the Project Manager. Sample chain-of-custody forms will document the transfer of samples between departments within the District and between the District and the contract laboratory. The Quality Control Program will follow the approved QA/QC procedures, as outlined in the project SOP.

## **5.0 Sediment Deposition Rate**

The long-term TP removal mechanism is generally regarded to be through peat accumulation which can be documented using sediment deposition markers called Feldspar Clay Markers. Feldspar is a white clay material not found in this region and clearly visible against the dark peat soils. To prepare the site, deposit a layer of feldspar in an even layer over the sediments. Sediment cores will be collected at yearly intervals and will be used to measure the amount of sediment deposited over the feldspar layer.

### **5.1 Field Procedures**

#### **5.1.1 Site Preparation**

1. Locate sites adjacent to existing sediment/porewater sites.
2. Place a round fiberglass mesocosm enclosure, 4 feet diameter and 4 feet tall into the wetland and press it about 5-10 cm into the sediment. The enclosure serves to contain the feldspar material as it settles through the water column on to the sediment.
3. Insert four PVC poles around the mesocosm enclosure. These poles support the mesocosm and will mark the location of the feldspar site once the feldspar material has settled and the ring is removed.
4. Using a colander, shift the feldspar equally within the ring to form a 1-2 cm uniform layer on the sediment. The enclosure remains undisturbed and in place in the wetland for at least 24 hours, to ensure that all the feldspar has settled out of the water column.
5. After the feldspar has settled, remove the enclosure, leaving the PVC poles in place to mark the site location.

#### **5.1.2 Sampling Procedures**

1. Sediment cores will be collected annually.
2. To avoid disturbing the sediments, soil cores are collected from the airboat. Collect 3-6 replicate cores at each feldspar marker location using a 5 cm diameter corer fitted with a clear butyryte sleeve. Each core will be taken at a 20 - 30 cm depth. The core sleeve will be pre-labeled with the station name, replicate number, and date collected.
3. Cores will be retrieved, capped, and transported back to the laboratory in a vertical position. At the laboratory, the cores are placed in the freezer.

### **5.2 Laboratory Procedures**

1. Melting ruins the cores. To ensure that the cores remain frozen, they are stored in coolers or in the freezer during processing.
2. Cut frozen cores lengthwise using a band saw.
3. Immediately after the cores have been cut, place a piece of wax paper between the two core halves. The wax paper prevents the two halves from re-freezing together. The halves are put back together, secured with a rubber band, and placed back into the freezer and stored there until the measurements are made.
4. Measurements of the newly deposited peat layer, located above the feldspar line, will be made on one-half of each of the cores. Starting at the top of the white feldspar layer to the top of the newly deposited sediment and working left to right, the new peat layer will be measured every 5 mm, to the nearest mm, using calipers. Measurements were made to the nearest mm. Record areas without feldspar is missing. All measurements will be recorded on pre-printed datasheets.
5. The thickness of the newly deposited peat layer is recorded as the average of all the measurements for that core.

## APPENDIX H

### STANDARD OPERATING PROCEDURES FOR FIELD DOCUMENTATION

- I. Field Logbook Entries - General
- II. Field Logbook Entries - Specific
- III. Chemistry Field Data Log Entries

This section contains guidelines that are general in nature, and therefore apply to all field logbooks. It is the minimum information required. Section II of this SOP delineates guidelines specific to different types of projects. Section III covers proper entries onto the Chemistry Field Data Log (CFDL) or "Header" sheets.

**Purpose:** This SOP is written for the purposes of standardizing the field reportable data and dialogue so that the intermediate and end-users can more readily access, comprehend and utilize it. All SFWMD field units responsible for submitting data to the SFWMD laboratory or database shall follow these Standard Operating Procedures. Accuracy, consistency and legibility are key factors that will be enhanced by the utilization of these SOP's. Printing instead of using cursive writing enhances legibility. In the likely event that field notes are electronically scanned into a computer, inaccuracies and messy logging will be frozen, thereby rendering some of the difficult work of the field crews virtually useless.

1. Relevant field observations are noted in a bound waterproof notebook, hereafter referred to as a field logbook or field book, that is specific to each field project.
2. Entries shall be made into the field logbook with a waterproof ink pen.
3. To avoid any confusion, entries for the number 0 will have a diagonal slash "Ø" to differentiate them from the letter O, particularly in alphanumeric fields.
4. Each field logbook must be clearly labeled on its cover and spine with the project name.
5. The first few pages of the field book should contain information such as: full project name, project start date, logbook start date, sites/ stations covered by the project, SOP revision date, contact person (usually the field supervisor), and abbreviations commonly used within the field book, etc. Maps, directions and a condensed version of the project SOP are examples of additional information that could appropriately be added to this section.
6. Each field logbook entry for a given project day will adhere to the following guidelines:
  - a) Each trip of the project will cover, at a minimum, one page of the logbook. In other words, at no time will more than one trip be included on the same page of a field logbook.
  - b) At the top of the first page for a given project day, the following information will be noted:
    - 1) Project name (i.e. STA6)
    - 2) Trip frequency (i.e. quarterly)
    - 3) Trip type (i.e. SW grabs)
    - 4) Full date, including year
    - 5) Collectors' initials. Spell out the entire name for first time entries of collectors.
    - 6) Corresponding responsibilities for each collector (i.e. AB - grabs, processing; CD - Hydrolab, books). Note if an individual is new to the project or learning.
    - 7) Weather - at the first sample site, or beginning of the project day. Aim for objectivity here. For instance, "low 90's" instead of "HOT". Items to include here are temperature, wind, sky conditions and any prevailing weather phenomena such as "Tropical Storm Warning today", or "apparent heavy rain recently". Any changes in weather conditions throughout the course of that project day shall be logged accordingly at the site and time that those changes become apparent, i.e. "G606 1300 Wind has shifted from the South". Remember that wind direction is that direction FROM which the wind is blowing.
    - 8) Acid - the acid(s) used for sample preservation on that project day.
    - 9) Labs - if any laboratory other than SFWMD is to be used for sample analysis, it must be annotated here (i.e. "organics to DEP, inorganics to SFWMD").
    - 10) Notes - any general notes that could apply to that project day, or that could affect the chemistry of the sample, but may not be site specific, should be noted. For example, "Construction ongoing at South end of the project, with heavy trucks traversing along the



## APPENDIX H (CON'T)

interior levee roads". If applicable, metering equipment ID and calibration information should be noted here as well.

- c) For subsequent pages of a project day, the following minimum items must be included at the top of those additional pages: the project name, date, collectors' initials and "continued from page \_\_\_" block.
- d) Entries shall be made into the logbook chronologically and sequentially by sample number, unless noted with explanation otherwise. For example, "Note: sampling out of numerical sequence due to unforeseen adverse weather conditions at G600 at 0900."
- e) Information may be entered in a four-column format in the following manner, from left to right:
  - 1) Sample ID #, 2) Sample Site/Station, 3) Time Collected, 4) Comments/Observations. Alternatively, loggers may wish to arrange the above items 1-3, vertically, on the left third of the page and leave the right two-thirds for the Comments/ Observations. To lessen redundancy and improve clarity, loggers may also add columns for items such as bottle, acid, flow, and vegetation cover. Maintain consistency of format and keep it clean and neat, remembering the intermediate and end-users who will access this information. (NOTE: The following guidelines apply to the current field "black" books. In the future, a more specific type of book may be implemented. These guidelines will be updated at that time.)
    - 1) The sample number is the same ID # that is noted on the sample tag and on the Chemistry Field Data Log (CFDL) sheet.
    - 2) The Site/ Station name is the same as noted on the CFDL sheet. A note should be placed in parenthesis here if, for example, it is an autosampler sample at the same site where a grab sample was also taken.
    - 3) Time is logged in 24-hour format (i.e. 1430) and corresponds to the same time labeled on the sample tags and CFDL sheet. Writing "hrs" after the time is not required in this format.
    - 4) Comments and observations shall be comprehensive yet concise, and as objective as possible. They shall include information about sample description and surrounding conditions including such things as flow and stage conditions, sample color, amount of suspended particulates, odor, ambient conditions such as "station is choked with water hyacinth" or "ash fallout from crop burning to NE", abnormal animal activity such as "lots of birds flew off as we arrived", type and amount of acid added to each bottle, equipment ID #'s (if applicable to that site), and visitors or persons other than sampling personnel at that site. Generally, the information noted here should accurately describe the sample, sampling activities and surrounding sampling conditions so that a future reader would clearly understand them as if he/she were actually there. An example of such an entry would be "All gates open 1.0', with light flow South. Sparse clumps of water lettuce in vicinity. Airboat passed area within 30 yards just prior to sampling. Two fishermen on West side of structure. Sampled from East side. Water column clear. Some litter along banks. Sample is light golden yellow with very light amount of fine suspended solids. Negligible odor. H2SO4: 8 drops Magenta, 4 drops Grey."
- f) At the bottom of a logbook page, logger will sign and date the page in the appropriate spaces.
- g) Should additional pages be required, the "Continued on page \_\_\_" and "Continued from page \_\_\_" blocks shall be filled accordingly, with each page signed and dated by the logger.
- h) At a later time, another collector from the same field unit shall read the logbook entries, checking for both accuracy and comprehension.
- i) If any corrections or deletions are necessary, a single line shall be drawn through the undesired material and the correcting person will place their initials, date and, if appropriate, comments adjacent to it.
- j) Upon fully reading, agreeing and understanding the entries for that project day, the collector will sign and date the appropriate "Read and Understood By" spaces of each page.
- k) Any portion of an unused logbook page shall be struck through, signed or initialed, and noted "No further entries this page" or words similar.
- l) Arrows may be drawn down for repetitive items, such as QC sampling at the same site, but at all times shall be clear and accurate.

## APPENDIX H (CON'T)

- m) Standard abbreviations such as "EB" and "FB" generally follow a station name when that QC sampling is performed for that sample number. However, comments should still be recorded here. For instance, "SITExyz (EB) TIME Equipment includes Niskin, bucket, syringe and filter. H2SO4: 7 drops Magenta, 3 drops Grey." The QC samples and codes must correspond to the entries on the CFDL sheet.
7. When the field scientific collector returns to the laboratory, he/she will make photocopies of **all** field logbook pages that correspond to the CFDL sheet(s) being submitted. In some cases, such as the RAIN project, there may be two or more field logbooks that contain information pertinent to one CFDL sheet. In order to fully encompass the logbook page, it is recommended that the copier setting be reduced to copy near the 80-85% range. It is the field scientific collector's responsibility to ensure that the copies are legible, all-inclusive and attached appropriately to their corresponding CFDL sheet(s). Paper clips are adequate for attachment since disassembly will be necessary shortly thereafter.
8. Time stamp both the CFDL sheet(s) and the field logbook copies prior to relinquishing them to the "To be Logged In" clipboard.
9. When a field logbook becomes full, both the beginning and ending dates are noted on the cover.