(WRE #343)

Standard Operating Procedures

STANDARD OPERATING PROCEDURES FOR WATER QUALITY COLLECTION IN SUPPORT OF THE BIG CYPRESS SEMINOLE INDIAN RESERVATION WATER QUALITY AGREEMENT

by

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STANDARD OPERATING PROCEDURE FOR	PROJECT	STATUS	REVISION DATE
SURFACE WATER QUALITY SAMPLING	BIG CYPRESS SEMINOLE INDIAN RESERVATION WATER QUALITY AGREEMENT	FINAL	
	DIVISION WATER QUALITY MONITORING	DATE 05/22/96	REVISION NUMBER 0

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1.0 INTRODUCTION

This document contains standard operating procedures for surface water quality collection which will provide data to determine the water quality at inflow points into the Big Cypress Seminole Indian Reservation. A separate document contains standard operating procedures for hydrologic data collection. The documentation of these procedures will assist in maintaining consistency in data collection and sampling and will also be used for training purposes for SFWMD field personnel.

1.1 Purpose and Scope

The sites described in this document are those monitored to satisfy the requirements of the agreement between the South Florida Water Management District and the Seminole Tribe of Florida providing for water quality, water supply, and flood control plans for the Big Cypress Seminole Indian Reservation and the Brighton Seminole Indian Reservation, implementing section C of Part V and section D of Part VI of the Water Rights Compact. The District, with the cooperation of the Tribe, shall initiate the following studies to determine:

- the quality of water delivered to the Big Cypress Indian Reservation through the L-28 Borrow canal before diversion of all or a portion of the C-139 Basin and C-139 Annex.
- the quality of water delivered to the Big Cypress Indian Reservation through the L-28 Borrow after diversion of all or a portion of the C-139 Basin and the C-139 Annex.
- the quality of water to be delivered to the Big Cypress Indian Reservation through the North and West Feeder Canals.

1.2 Sampling Locations

The four water quality monitoring locations discussed in this document are: the North Feeder Canal downstream of G108; the West Feeder Canal terminus (BCWeir); the downstream side of the U.S. Sugar Unit #1 gravity flow stucture, and in the L-3 Canal approximately 100 yards upstream of Oil

Well Bridge. These sites are denoted in the SFWMD database as: NFEED; WFEED; USSO, and USL3BRS, respectively. Autosamplers will be placed on specially constructed platforms that also house hydrologic instrumentation. The location of these four sites is depicted in Figure 1.1. Table 1.1 summarizes the sample sites and GPS coordinates.

Table 1.1 Summary of Sample Sites and GPS Coordinates

Site	GPS Latitude	GPS Longitude
NFEED	26 20' 19.217"N	80 58' 46.836"W
WFEED	26 18' 07.171"N	81 04' 29.209"W
USL3BRS	26 19' 57.423"N	80 52' 58.938"W
USSO	26 19" 47.006"N	80 52' 56.207"W

1.3 Sampling Frequency

The sampling frequency for the four monitoring sites is depicted in Table 1.2. Water quality samples are collected from all four sites weekly from the autosampler during periods of flow. Grab samples are collected from USSO and USL3BRS biweekly during flow conditions or monthly during periods of no flow. These grab samples will be analyzed for the parameters shown in Appendix A to meet monitoring criteria established by Chapter 40E-63.

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Figure 1.1 Monitoring Sites Used in the Big Cypress Seminole Indian Reservation Agreement

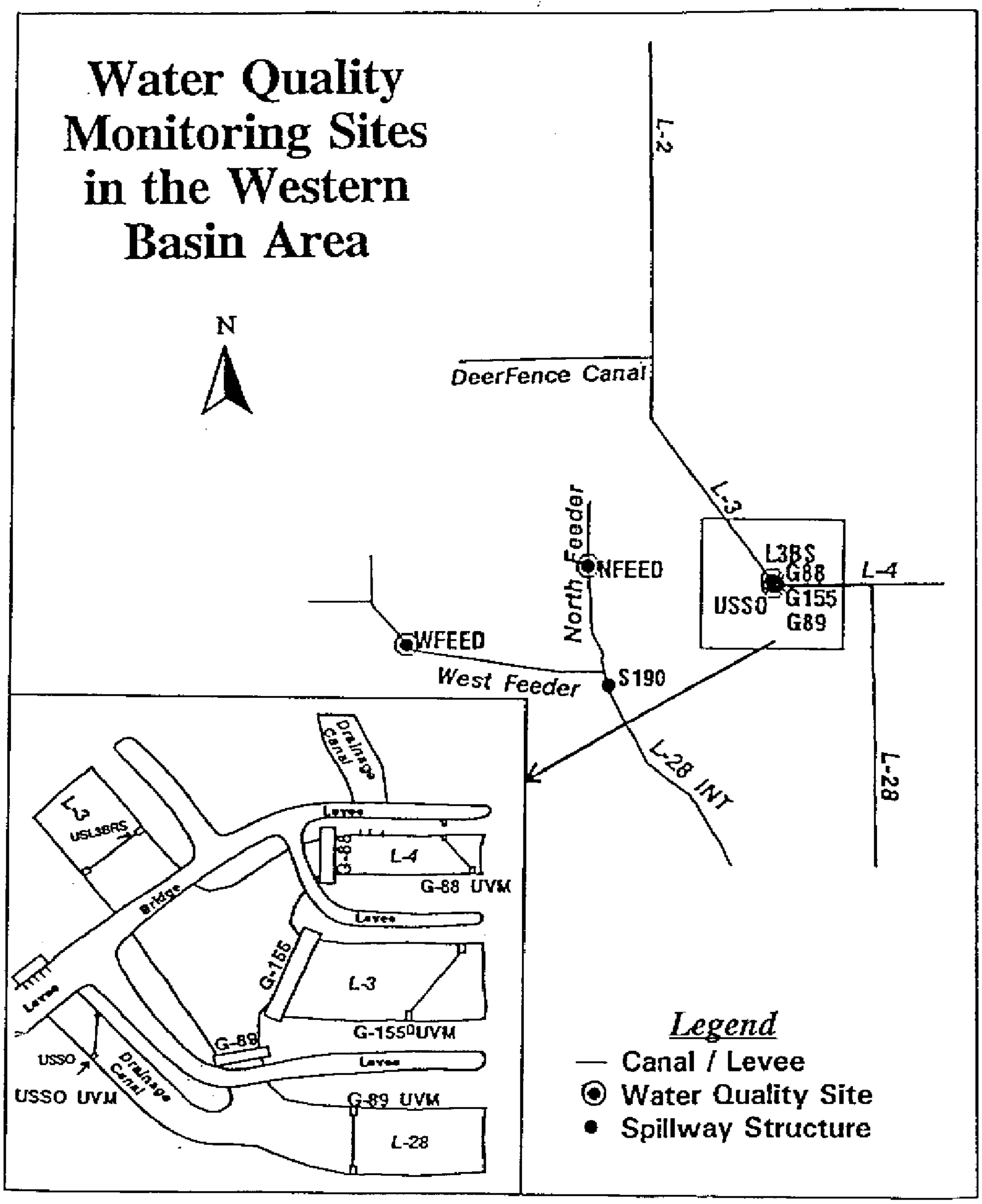


Table 1.2 Summary of Site Location, Sample Method and Frequency, and Parameter Selection for Monitoring Sites Used in the Big Cyrpress Seminole Indian Reservation Agreement

Sites	Method	Frequency	Parameters
NFEED	FPC	W	TPO_4, TKN, NOX, NH_4
WFEED	FPC	W	TPO_4, TKN, NOX, NH_4
USSO	FPC	W	TPO_4, TKN, NOX, NH_4
	Grab	BWF/M	Physicals, Nutrients
		QTR	Ions
		BA	Metals
USL3BRS	FPC	W	TPO_4, TKN, NOX, NH_4
	Grab	BWF/M	Physicals, Nutrients
		QTR	Ions
		BA	Metals

Notes: 1. W = weekly, BWF = bi-weekly during flow conditions, M = monthly, QTR = quarterly, BA= bi-annual, FPC=flow proportional composite. 2. Physical parameters measured with a Hydrolab.

1.4 Sample Identification

Each water sample is assigned an unique identification number in the field at the time of collection. This number (up to five digits), is written on the tag with waterproof ink and affixed to the sample bottle by a rubber band. The same number also identifies the sample on the water chemistry field data log and in the field notebook. Individual sampling programs are identified by a one to four character alphabetic code that is termed a "project code" which is also used as an identifier on the sample tag. Water samples collected at NFEED, WFEED USSO, and USL3BRS are collected under the District's CAMB (Conservation Area Material Budget/WCA inflow outflow network) project code.

The water-proof (Tyvek paper) color striped tags printed by the SFWMD print shop are used to identify water quality samples which will be analyzed at the District laboratory. Listed below are the tag colors associated with the various chemical analyses (refer to the Sample Submission Diagrams, Figures 4.1 and 4.2).

a. Magenta/White Tags - Used to identify unfiltered preserved samples in 175 ml bottles to be analyzed for TKN and TPO_4.

b. Orange/White Tags - Filtered, unpreserved samples to be analyzed for Color, OPO_4, NO_2, Cl, SO_4 and SiO_2.

c. Gray/White Tags - Filtered, preserved samples to be analyzed for NOX and NH_4. **Note:** Autosampler (pre-preserved) samples will not be filtered.

d. White Tags - Unfiltered, unpreserved samples to be analyzed for Turbidity.

e. Beige/White Tags - Unfiltered, unpreserved samples to be analyzed for Alkalinity.

f. Green/White Tags - Filtered, preserved samples to be analyzed for Ca, Mg, Na and K.

g. Dark Blue/White Tags - Unfiltered, preserved samples to be analyzed for TotAs, TotCd, TotCu, TotFe, TotPb and TotZn.

2.0 FIELD EQUIPMENT

2.1 Sample Collection Equipment

The following is a list of the equipment used for the collection of surface water samples at the four sites documented in the Big Cypress Seminole Indian Reservation Water Quality Agreement.

Sample collection devices:

1. Wildco 2.2 liter Van Dorn PVC horizontal sampling bottle
2. Wildco 3.2 liter Van Dorn PVC horizontal sampling bottle
3. American Sigma model 800SL automatic sampler

Multi-parameter field instrumentation:

1. Hydrolab Surveyor III

2.2 Sample Processing Equipment

The following is a list of the equipment used for the processing of surface water samples at the four sites documented in the Seminole Indian Agreement.

Sample Bottles

1. 5 gallon polypropylene jug with spigot (DI water for QA/QC and cleaning)
2. 1000 ml Nalgene polyethylene sample bottles
3. 175 ml Nalgene polyethylene sample bottles
4. 60 ml Nalgene polyethylene sample bottles
5. 250 ml Nalgene polyethylene trace metal sample bottles
6. 1000 ml polyethylene autosampler bottles

Filtration Supplies

1. Millipore reusable Swinnex 47 mm filter holder
2. Millipore reusable 50 ml syringe
3. Poretics 0.45 micron polycarbonate membrane filters
4. Poretics fiber glass prefilters

Preservation Supplies

1. H_2SO_4(50%) in 60 ml dropping bottle (fresh weekly, ACS reagent grade)
2. HNO_3 (50%) in 60 ml dropping bottle (fresh weekly, trace metal grade)
3. pH strips, 0 - 3 range
4. Safety goggles and gloves
5. Sodium bicarbonate or "Spill-X" for acid neutralization
6. Wet ice (in 48, 60, 80 or 96 quart coolers)

Hydrolab Field Calibration Supplies

1. Certified pH buffers - 4, 7 and 10
2. Certified conductivity buffers - 200, 720, or 2000 μmhos/cm
3. Calibration cup with hard and soft end caps

Miscellaneous Supplies

1. Five liter polyethylene bucket
2. Disposable powder free PVC or latex (for inorganics) gloves
3. Polyethylene tray (provides clean surface for processing)
4. Sample tags
5. Rubber bands (size #16)
6. Black waterproof pens (Sharpies)
7. Clipboard
8. Field notebook (waterproof and bound)
9. Chemistry field data log sheets
10. Watch

Navigational Aids

1. Project location maps
2. Site photographs
3. Global Positioning System (Pathfinder Basic Plus)

Communication / Safety Equipment

1. SFWMD low band FM radio
2. Cellular telephone
3. First aid kit

2.3 Field Trip Preparation

Routine procedures are currently employed by the Water Quality Monitoring Division (WQMD) to prepare equipment and supplies for field trips. An equipment checklist (Table 2.1) has been developed that technicians examine prior to each trip to make certain that the necessary equipment and supplies have been prepared.

District laboratory sample bottles - All sample bottles (except trace metal bottles) are washed by the SFWMD laboratory with liquinox soap, rinsed with tap water, 10% hydrochloric acid, tap water, deionized water, and air dried. Dry bottles are capped and stored in bottle bins in a storage area.

Table 2.1 WPB Data Collection Unit Equipment Checklist

FIELD TRIP PREPARATION AND CHECK-OFF LIST

PROGRAM: CAMB/Seminole   DATE:_________   PROGRAM CODE:________
(Routine / Quarterly / Bi-annual)

_____* Travel Request(per diem only)
_____* Sign Out Board
_____* SOP Manual & Maps
_____* Vehicle Packet/Credit Cards

_____* Sign Out Vehicle
_____* Gas Vehicle
_____* Maintenance Check
_____* Cellular Phone

_____* Field Notebook (CAMB)
_____* Sharpies (water proof markers)
_____* Header Sheets/Clipboard
_____* Pre Cleaned Sampling Bottle
_____* Tags/Rubber Bands
_____* Calibrated Hydrolab/Battery
_____* Calibration Cup & Buffers
_____* Gate Keys:_____________

_____* QC Trip Spikes
_____* DI Water for QA/QC
_____* Syringes
_____* Loaded Filters____
_____* pH Test Strips
_____* Clean Buckets
_____* Coolers, Ice
_____* Goggles, Gloves

_____* Acid Dispenser (Auto-pipetter with 50% H2SO4)
_____* Acid Dropper Bottles: 50% H2SO4 & 50% HNO3
_____* Bottles: 250ml-___, 175 ml-___, 60ml-___, 1 Liter___
_____* Autosampler Bottles (four sets of 24 1 liter bottles)
_____* For Trace Metals ONLY- 250ml TM Bottles-___, Spill-X
Special TM Sampling Bottle, 2 Liters 10% HCl,

Stations: WFEED, NFEED, USSO., USL3BRS

PERSONAL ITEMS

_____* Watch
_____* Hat
_____* Raingear

_____* Sunglasses
_____* Sunscreen
_____* Mosquito Repellent

_____* Drinking Water

POST TRIP PROCEDURES

_____* Sort Samples by Number & Color, Place in Refrigerator
_____* Sign Chain of Custody on Header Sheet, Get Time Stamp
_____* Return Clean Bottles to Bins in Lab
_____* Separate Filter Holders and Place in Soak Solution
_____* Return Dirty Bottles to Lab for Washing
_____* Clean Sampling Bottle per Comp QAP and Bag
_____* Clean Hydrolab Datasonde and Console per Comp QAP
_____* Replace Water in Hydrolab Stand (Tap Water Only!)
_____* Clean & Park Vehicle/Fill Out Trip Ticket/Return Keys
_____* Examine and Sign Field Notebook

INITIALS-__________

Sample bottles are transported to the field collection sites in sealed plastic bags. Trace metal bottles are washed with liquinox, rinsed with tap water, soaked in 20% HNO_3 overnight and rinsed with deionized water. The bottles are then filled with 10% HNO_3 until sample collection. The SFWMD may also purchase pre-cleaned and acidified bottles for sample collection.

Filter Loading - Reusable Millipore Swinnex 47 mm filter holders utilized in filtering water samples are washed by the SFWMD staff using the same procedure described above for the washing of District supplied sample bottles. The filter holders are loaded prior (up to five days) to leaving for the field using the following method:

Filter loading procedure:

a. The bottom of the filter holder is checked to see that it is properly fitted with a rubber O-ring and then moistened with deionized water.

b. Using a gloved hand, a Poretics 0.45 μM polycarbonate membrane is centered on the bottom portion of the filter holder with the shiny side up.

c. Using a gloved hand, a Poretics 47 mm prefilter is centered on top of the filter membrane with the rough surface up.

d. The rubber 0-ring is inspected for "fit" in the top portion of the filter holder.

e. The top and bottom portions are firmly screwed together by hand.

f. The loaded filter holders are rinsed by pushing approximately 25 ml of deionized water through the top of the filter holder using a clean 50 ml Millipore syringe.

g. The loaded filter holders are tested for leaks with an empty 50 ml Millipore syringe. Air is drawn into the syringe and then pushed into the top of the filter holder. If the filter holder has been properly loaded, air will not pass through it and pressure can be felt when depressing the syringe plunger. If the filter holder has not been properly prepared, air will pass through it completely and the filter holder must be reloaded and tested again.

h. The tested filter holders are sealed in a clean plastic bag and refrigerated at 4^0 C until they are used, to prevent the filter membrane and prefilter from drying.

Following usage in the field, the filter holders are disassembled and the dirty membranes and prefilters are properly discarded. The empty filter holders are returned to the laboratory.

Syringes - Reusable Millipore 50 ml syringes are precleaned before each trip with liquinox, tap water and deionized water.

Sampling Collection Bottles - The 2.3 or 3.2 liter Van Dorn type sampling bottles are precleaned before each trip with liquinox soap, tap water and deionized water. If trace metals are to be collected in addition to nutrients and physical parameters, the bottle is also rinsed with 10% HCl before the deionized water rinse.

Hydrolab Calibration - Calibration of the Hydrolab should be performed prior to each daily field trip. Most units will require calibration of conductivity, turbidity, pH and dissolved oxygen. See section 5.0 Physical Data Collection for calibration procedures.

3.0 WATER QUALITY SAMPLING PROCEDURES

3.1 Grab Sample Collection

The following procedures are performed when collecting surface water grab samples:

a. Grab samples are collected from the desired depth (generally 0.5 meters) with either a 2.2 or 3.2 liter Van Dorn type sampling bottle.

b. While wearing powder free latex or PVC gloves, the precleaned Van Dorn bottle is lowered into and raised from the water three times as a rinsing method.

c. After the third rinse, lower the Van Dorn bottle into the water column to the desired depth (generally 0.5 meters). Closure of the bottle is activated by a stainless steel messenger.

d. Use a small portion of the sample to triple rinse the pre-cleaned five liter polyethylene processing bucket prior to pouring in all of the collected water sample.

e. Once the remainder of the sample has been deposited into the bucket, the bucket is placed on a clean surface (i.e., pre-cleaned plastic tray) for processing.

Figure 3.1 depicts a flowchart that illustrates sampling procedures for inorganic surface water samples which are submitted to the District laboratory. This flowchart follows approved methods as established in the District's Comprehensive Quality Assurance Plan (CompQAP).

3.2 Autosampler Water Collection

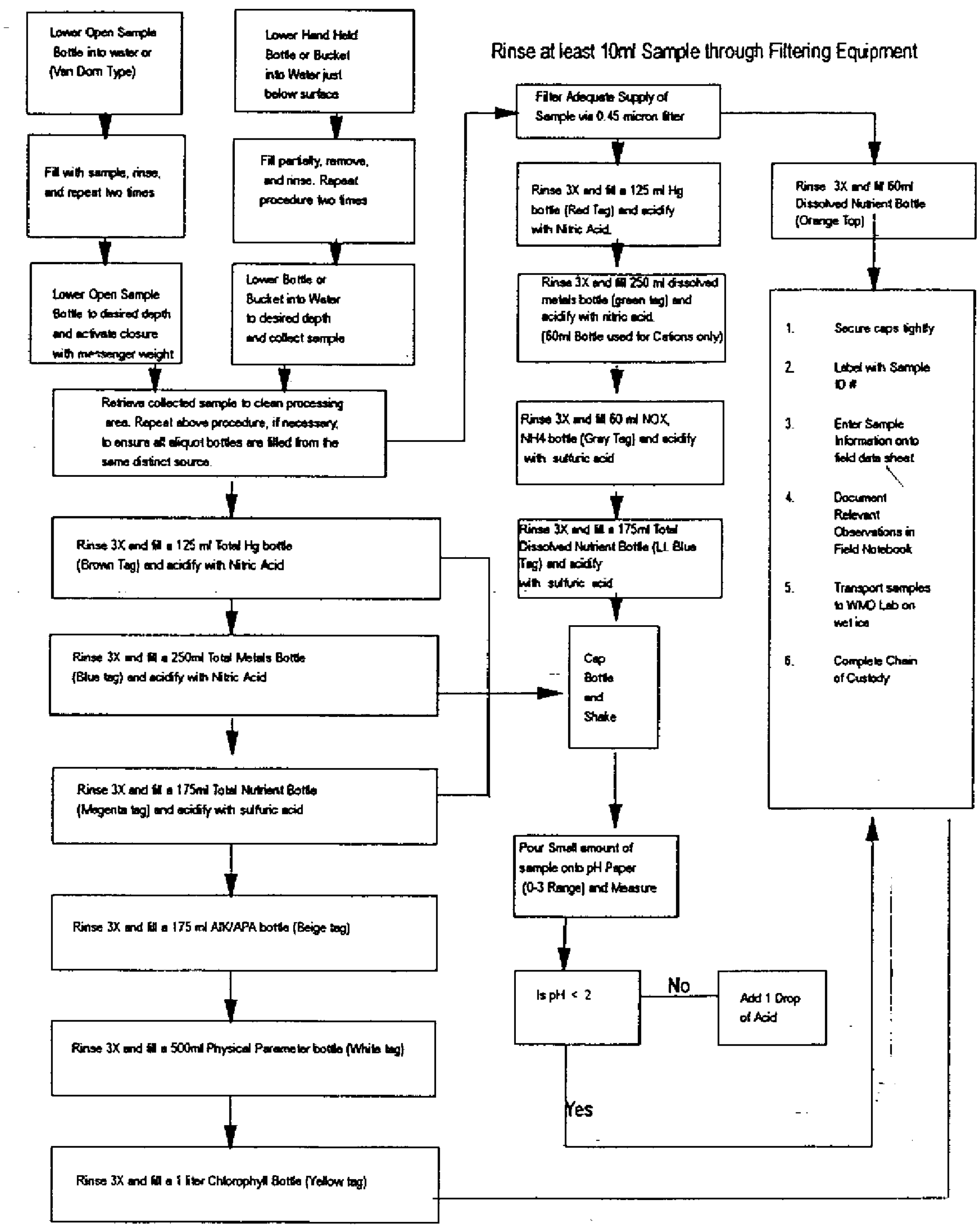
The autosamplers at the four monitoring locations operate on a flow proportional basis. Collection frequency (and therefore sample volume) is regulated by the amount of flow through the canal. This is accomplished by an electronic signal conveyed from an ultrasonic flow measurement structure to the autosampler. This electronic pulse is sent to the autosampler when the flow totalizer calculates a specified volume of water has passed through the canal at that location. The volume to be collected per electronic signal is programmed at 200 mls. The specifications for the autosamplers are contained in Table 3.1

The autosampler model utilizes a high speed peristaltic pump for the collection of the sample water. The intake lines are air purged before and after each sample is collected. The sampler case is constructed of impact-resistant polyethylene. The mechanical components and electronics are contained within a watertight and dust-tight polyethylene housing.

The sample intakes for the autosamplers are positioned based on mixing zones and minimum stage levels. The intakes are positioned in the center one-third of the canal, at a depth that will not allow the autosampler intake to be out of the water during the dry seasons. Therefore, the autosampler intakes are positioned at 0.5 meters below historic low water levels in order to prevent the autosampler from collecting air. The vinyl sample intake tubing (3/8" ID) and silicone peristaltic pump tubing (3/8" ID) are replaced on a quarterly basis as stipulated in the SFWMD CompQAP.

Samples are collected in 24 discreet one-liter bottles within the autosampler, collecting four samples per bottle. Two milliliters of 1:1 H_2SO_4 are placed in each autosampler bottles when they are positioned in the autosampler.

Figure 3.1 Inorganic Surface Water Sampling Procedure



*Preservation/filtration occurs within 15 minutes of colletcion

Table 3.1 Autosampler Specification Chart

LOCATION	DATE OF FIRST AUTOSAMPLER COLLECTION	AUTOSAMPLER MODEL	AUTOSAMPLER ACTIVATION FREQUENCY*
USL3BRS	6/95	American Sigma Streamline 800	1,800,000
USSO	10/95	American Sigma Streamline 800	1,800,000
NFEED	Within 10 days of QAPP approval	American Sigma Streamline 800	To be determined
WFEED	Within 10 days of QAPP approval	American Sigma Streamline 800	To be determined

* FLOW (CUBIC FEET) REQUIRED TO ACTIVATE AUTOSAMPLER

The following procedures are performed when collecting water samples from an autosampler:

a. Unlock the autosampler housing, and open the top and door.
b. Pull the autosampler out of the housing.
c. Remove the top cover from the bottom two sections of the autosampler.
d. Observe the autosampler display.
e. If display reads **"Program Running"**, continue with the following steps;
   1. Press the 'Change/Halt' key (the number 2 on the numerical keypad) to pause the program. Confirm that the program is paused by reading "Program Halted" in the display window.
   2. Remove the Control Head of the autosampler from the bottom portion which contains the sample bottles. Gently place the Control Head on the platform so that it will not be damaged. Remove the retaining ring from the center of the sample bottles.
   3. Make general observations on the samples before removing any of the bottles (such as: the number of bottles containing sample water, approximate volume of water in each bottle, skipped bottles, or other noticeable items).
   4. Estimate the total amount of sample contained in the sample bottles.

5. With gloved hands (the appropriate PVC lab gloves), pick up the first bottle containing sample water, cap the bottle, and swirl the contents (or invert the bottle several times), to mix the water and any suspended material that may have settled. Pour the entire sample into the sample bucket. Repeat this procedure until all sample bottles have been emptied in the sample bucket. Cover the bucket with its lid and restart the autosampler.
6. Collect the used sample bottles (now empty), and place them in a large plastic bag, to return to the lab for proper cleaning.
7. Move the bottles that remain into the first sampling positions in the autosampler.
8. Place clean bottles into the empty spaces in the autosampler. Add 25 to 35 drops of 50% H_2SO_4 into each of the clean bottles.
9. Replace the retaining ring in the center of the sample bottle area.
10. Before replacing the control head, restart the program by pressing the 'Start Program' key. The display will ask "Start or Resume?". Respond by pressing the 'Start Program' key again. This will reset the distributor arm back to the number one bottle position. Listen, or tilt the control head and watch to be sure the reset occurs. If there are no problems, the display will now read "Program Running". If there is a problem, the control head will beep and read "Dist Arm Failure". If this occurs, try restarting the program again, and push the distributor arm in the direction of the restart position. If the arm is difficult to move, do not force it, but replace the distributor arm and restart the program.
11. Replace the control head portion of the autosampler onto the bottom portion, and secure with the built-in clips that hold the sections together. There is only one way that the sections fit together, so care must be taken in lining up the clips.
12. Confirm that the display reads "Program Running", and place the cover on top of the control head. These sections also fit together in only one way.
13. Place the autosampler back into the shelter. Care must also be used here, as the unit must be rotated as it is pushed back into the shelter, in order to wrap the power cable and intake tubing around the unit. The intake tubing is wrapped around the unit in order to control the slope of the tubing. The slope should be a gradual downward slope from the intake of the autosampler to the penetration of the shelter. This is done to prevent low points, where water would collect and stagnate.
14. Close the door to the autosampler shelter and lock it.

f. If the display reads **"Program Complete"**, collect the samples as described in sections 1 through 14 above. Prior to leaving the site, refer to the operator's manual to reprogram the autosampler to ensure that the program is not completed prior to the next scheduled trip to the site. To do this, the sample size must be decreased, and the number of samples per bottle must be increased. Be careful to program the sampler so that the amount of sample collected in each bottle is less than 1000 ml.

g. If the display reads **"Program Halted"**, it is indicating that someone has paused the program, and failed to restart it. After collecting the samples (sections 1 through 14), restart the program by pressing the 'Start Program' key. The display will now read "Start or Resume?", respond by pressing the 'Start Program' key again.
h. If the display reads **"Dist Arm Failure"**, there may be a problem with the distributor arm, and it should be replaced to prevent further problems. Refer to the operator's manual for troubleshooting assistance. Collect the samples that are available, according to sections 1 through 14.

Automatic water samples are processed on site in the same manner as grab samples except for preservation and filtration (since the automatic water samples are pre-acidified). Powder-free latex or PVC gloves are worn at all times during the collection and processing of automatic water samples.

Complete documentation, including but not limited to the sampling, processing, autosampler restart information and identity of technicians, must be recorded in the project fieldbook.

3.3 Quality Control Procedures

Quality control procedures are those steps taken by the laboratory and field staff to ensure that the required precision, accuracy, and reliability levels are maintained. The steps taken to establish quality control for field sample collection are provided to ensure the quality, validity and representativeness of the collected sample. Quality control procedures are followed as described in the SFWMD CompQAP.

For each sample collection trip, a trip spike sample, equipment blank, split sample, field blank and replicate sample must be collected. These quality control terms are defined as follows:

1. **Trip Spike Sample (TS)** - A spiked sample of a known concentration prepared by SFWMD laboratory QC staff that is transported on a field trip as an actual sample. Only one TS per quarter is required per trip. Trip spike samples are requested via the Field QA/QC Sample Request Form (Figure 3.2)

2. **Equipment Blank (EB)** - A sample composed of deionized water (one liter) that is used to rinse all sampling equipment at the first field site before a field sample is taken. One EB is required per trip. The autosampler EB will be prepared by preserving one liter of de-ionized water at the time of deployment and allowing the EB to remain in the autosampler until the time of collection.

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Figure 3.2 Field QA/QC Sample Request Form

Field QA/QC Sample Request Form

This form must be completed by the project manager and returned to the Water Quality Monitoring Division at least two days prior to the trip date. Check only the parameters that apply to your sampling trip.

Project	Trip Date	Departure Time	Project Manager	Submitted By	Date Submitted

Label Color	Bottle Size (ml)	✓	Analysis	Solution Lot #
White	250		F 0.5	
Magenta	175		TKN 3.00	
			TPO4 0.163	
			TOC 50	
Orange	60		OPO4 0.129	
			CL 119	
			SO4 59.5	
			SIO2 7.4	
Light Blue	175		TDKN 3.00	
			TDPO4 0.163	
			DOC 50	
Gray	60		NOX 0.180	
			NH4 0.40	
Beige	175		ALKA 120	
Bright Blue	250		TOTAG 5	
			TOTAL 20	
			TOTAS 20	
			TOTBA 40	
			TOTBE 2.5	
			TOTCD 2.5	
			TOTCR 10	
			TOTCU 10	
			TOTFE 400	
			TOTMN 10	
			TOTNI 10	
			TOTPB 10	
			TOTSB 20	
			TOTSE 20	
			TOTTL 10	
			TOTZN 160	

Label Color	Bottle Size (ml)	✓	Analysis	Solution Lot #
Green	250		TDSAG 5	
			TDSAL 20	
			TDSAS 20	
			TDSBA 40	
			TDSBE 2.5	
			TDSCD 2.5	
			TDSCR 10	
			TDSCU 10	
			TDSFE 400	
			TDSMN 10	
			TDSNI 10	
			TDSPB 10	
			TDSSB 20	
			TDSSE 20	
			TDSSR 2.0	
			TDSTL 10	
			TDSZN 160	
			CA 30	
			K 6.0	
			MG 6.0	
			NA 30	
Brown	125		TOTHG 5.0	
Red	125		TDSHG 5.0	

QA/QC Solutions Prepared By (Signature) ____________ Date ____________

Form WQM-5 Revised 7/95

3. **Split Sample (SS)** - One sample which has been divided to make two duplicate samples. One SS is required per trip.

4. **Replicate Sample (RS)** - Two distinct samples collected nearly simultaneously from the same sampling site. One RS will be collected per trip. **Note:** *RS collected for grab samples only.*

5. **Field Blank (FB)** - Deionized water which has been preserved and iced in the same manner as the samples. One FB is required per trip.

4.0 SAMPLE SUBMISSION PROCEDURES

Sample custody adhered to is described in Section 7.0 of the SFWMD CompQAP.

Samples are taken to the SFWMD laboratory for analysis. The samples are sorted by tag color and numerical sequence and placed in the receiving refrigerator.

Samples are submitted as described on the Sample Submission diagrams (Figures 4.1 and 4.2).

The Chemistry Field Data Log (Figure 4.3) is signed, "time stamped", and is attached to the incoming samples clipboard in the laboratory.

5.0 PHYSICAL DATA COLLECTION

Simultaneous to the collection of water quality grab samples, in-situ physical parameters are measured using a Hydrolab Surveyor III. The following section describes Hydrolab Surveyor III operational procedures that includes a description of the calibration and operation procedures.

For samples collected by an autosampler, the Hydrolab is not used because the measurement of temperature, dissolved oxygen and pH are affected by the acidification of the sample and the age of the sample (up to seven days).

To obtain the physical parameters of the water, the Hydrolab sonde (probe) should be placed in the body of water in close proximity to where the grab sample is taken. The probe should be at a depth of 0.5 meters. Turn on the Surveyor III, and allow approximately three minutes for the readings to stabilize. The physical parameters are read directly from the Hydrolab console and are recorded on the SFWMD Water Chemistry Field Data Sheet (Figure 4.3).

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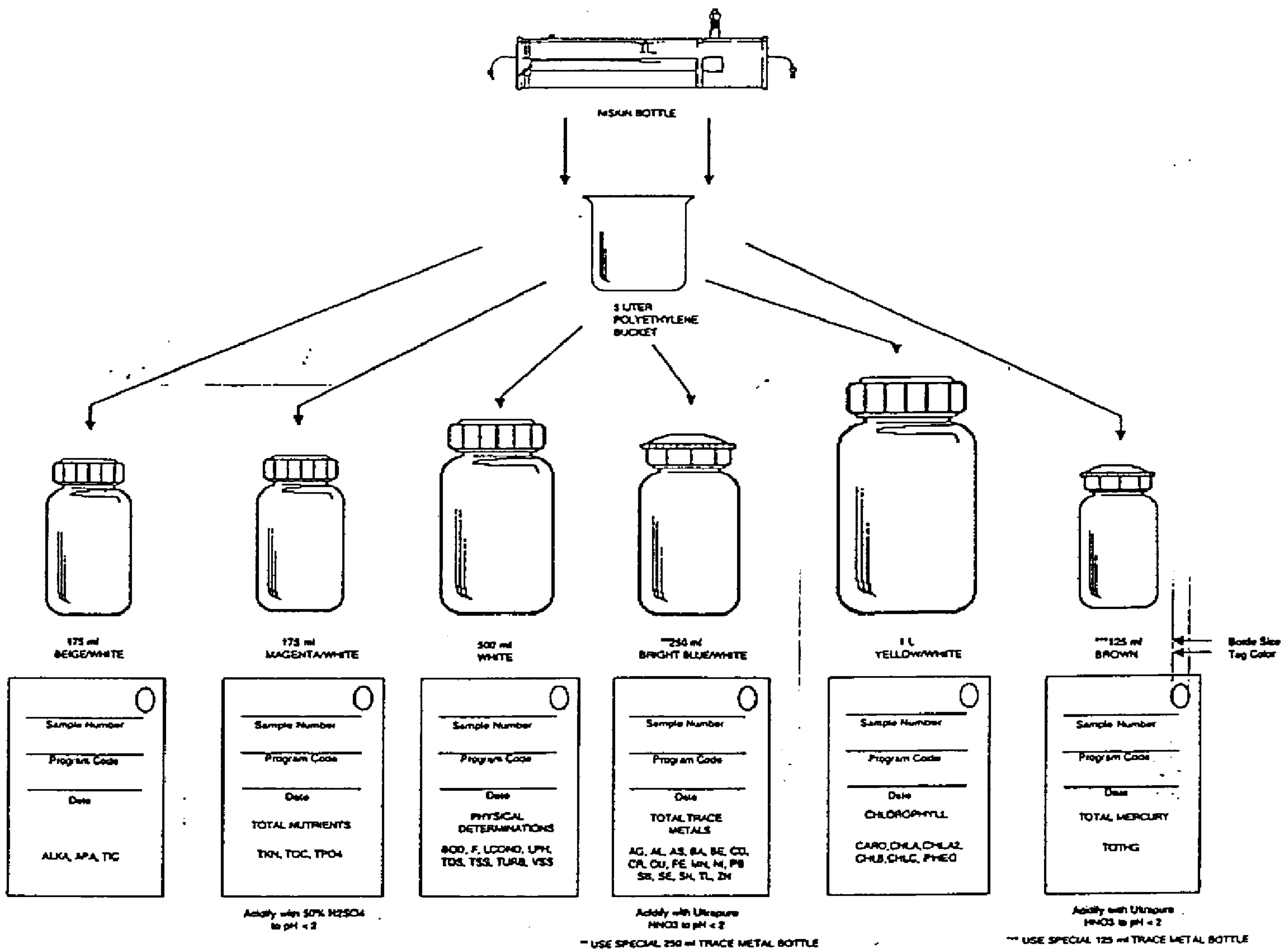
	WATER QUALITY MONITORING	05/22/96	0

APPROVALS/DATE		
DIVISION DIRECTOR [signature]	UNIT SUPERVISOR Sherry B. Scott	QUALITY ASSURANCE [signature]

Figure 4.1 Sample Submission Diagram for Unfiltered Water and Associated Color Tags



STANDARD OPERATING PROCEDURE FOR	PROJECT	STATUS	REVISION DATE
SURFACE WATER QUALITY SAMPLING	BIG CYPRESS SEMINOLE INDIAN RESERVATION WATER QUALITY AGREEMENT	FINAL	
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Figure 4.2 Sample Submission Diagram for Filtered Water and Associated Color Tags

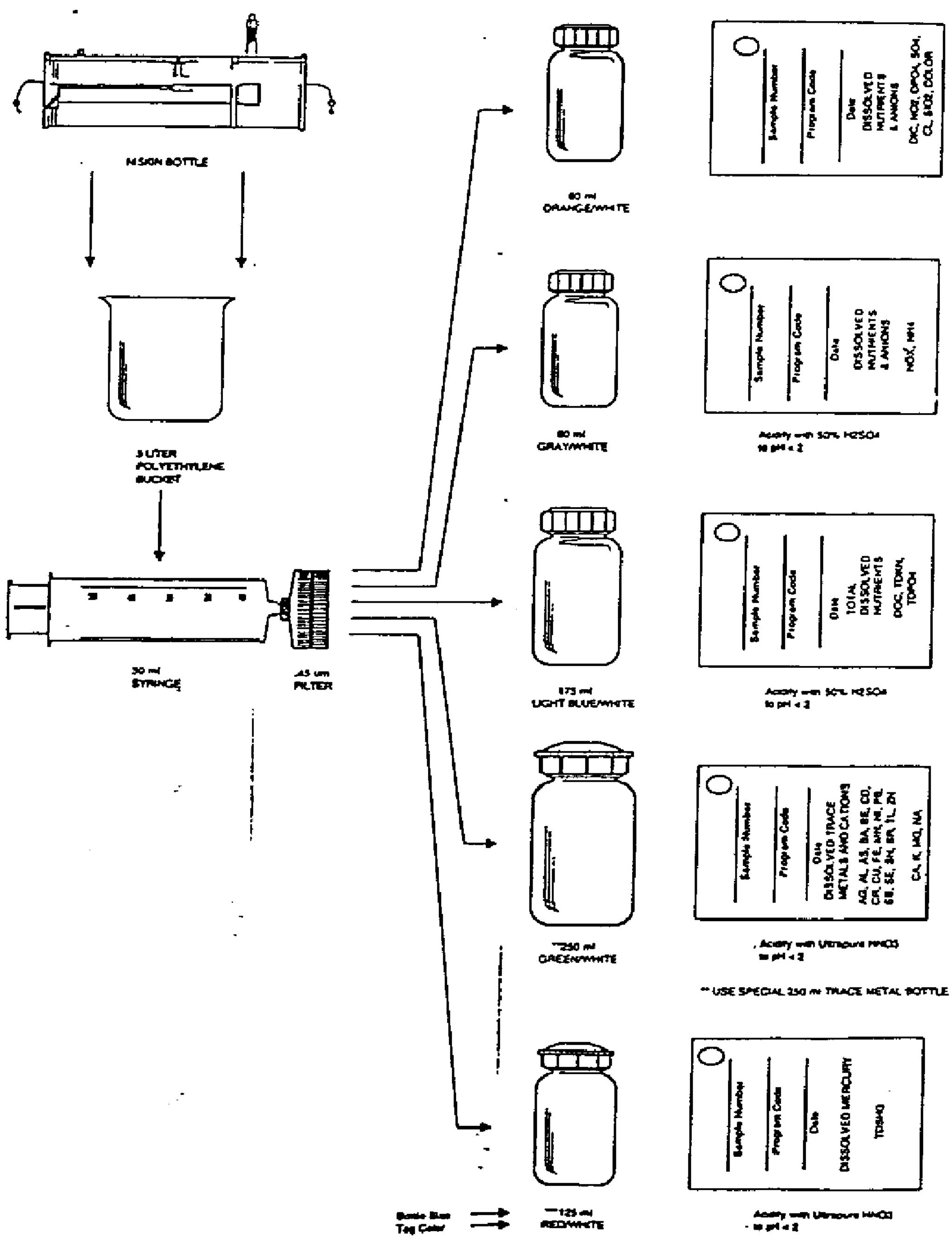
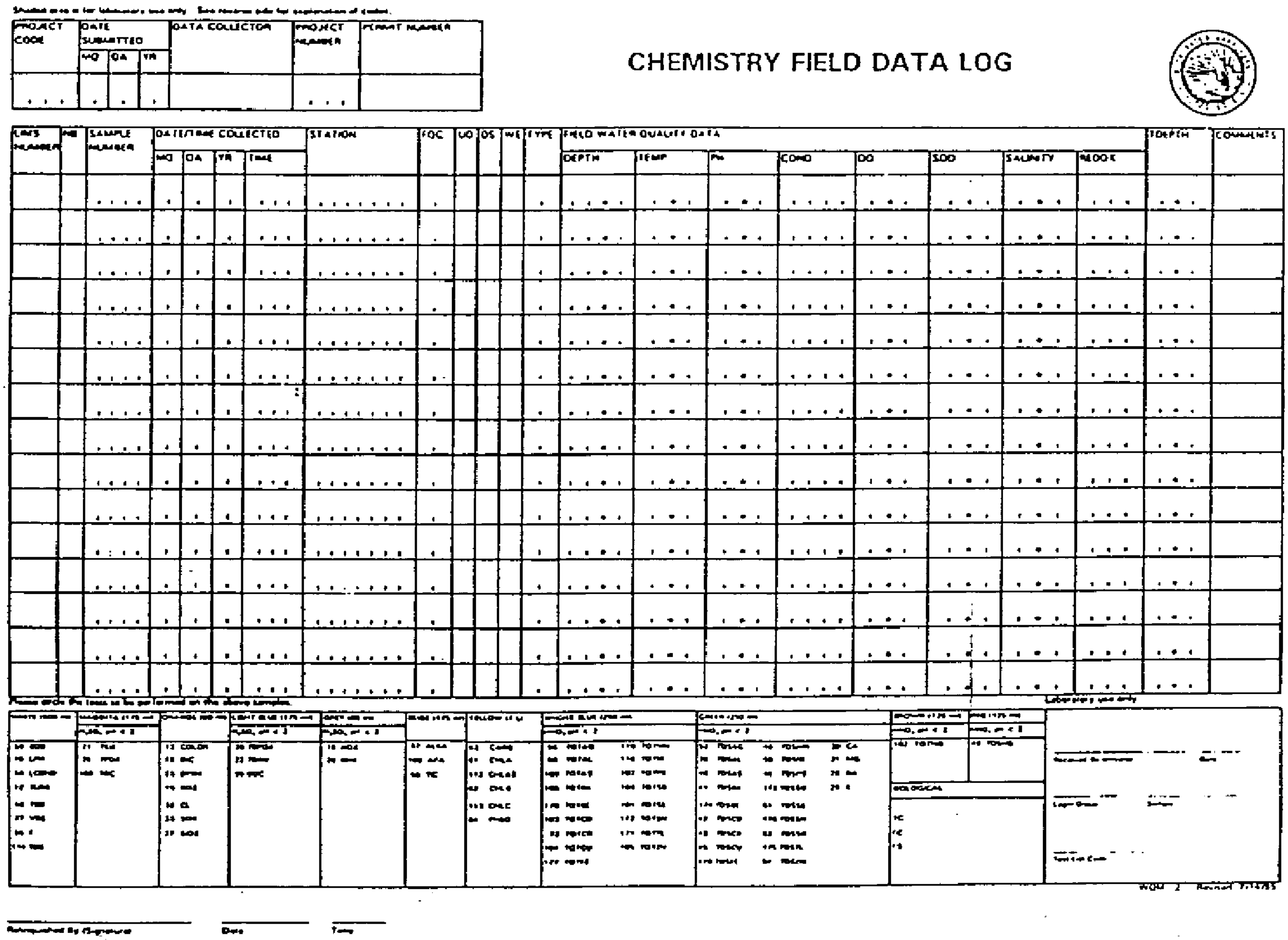


Figure 4.3 Chemistry Field Data Log



5.1 Hydrolab Operating Procedures - Temperature

5.1.1. Introduction

5.1.1.1. Theory

Temperature is perhaps the most commonly measured water quality parameter. The temperature of an object or a solution is a property which signifies the existence of a condition of thermal equilibrium. In limnological studies, water temperature as a function of depth is often required. Temperature directly and indirectly exerts many fundamental effects on limnological phenomena such as lake stability, gas solubility and biotic metabolism. It is also used to correct conductivity, pH, and dissolved oxygen measurements in multiparameter field instrumentation.

5.1.1.2. Instrument Siting and Exposure

Water quality instrumentation (Hydrolabs) are generally not installed at a specific site, therefore the following guidelines refer to portable operations only.

- Never operate the unit during electrical storms.
- Keep the display unit as dry as possible.
- Avoid swift moving currents near culvert openings or pump stations.
- Always make sure the sensors are protected.
- Keep unit clear of boat traffic when sampling from a bridge.
- Avoid kinks or sharp bends in the cable.
    - After each field trip, clean the datasonde with analyte free water.
    - Always store the datasonde in tap water.

5.1.1.3. Measurement Standards

The thermistor thermometer is accepted for field use by FDEP (Florida Department of Environmental Protection) provided that the thermometer's accuracy is verified daily against a calibrated laboratory thermometer (see Section 5.1.2.4.).

The standard unit of measurement of temperature is degrees Celsius.

The accuracy of the Hydrolab thermistor is 0.15^0 C . The accepted tolerance as stipulated in the SFWMD Comprehensive Quality Assurance Plan is 2% of the measured value. A Hydrolab whose temperature value that falls outside of the tolerance range is returned to the factory for calibration.

5.1.2. Instrumentation--Manual Measurements

5.1.2.1. Principle of Operation

In the field, water temperature is measured with a metallic composite whose electrical resistance varies predictably with temperature. An array of these sensors (thermistors) can be employed to produce a linear response. These thermistors are protected by a stainless steel tube on the Hydrolab datasonde.

5.1.2.2. Maintenance

Maintenance of the temperature sensor can only be performed at the Hydrolab factory, however, methyl alcohol can be used to clean any oil film or dirt buildup on the thermistor probe.

5.1.2.3. Sensors Used

5.1.2.3.1. Hydrolab Surveyor III / H2O Datasonde Temperature Specifications

RANGE:	-5^0 to 50^0 C
ACCURACY:	.15 ^{0}C
SENSOR:	thermistor
COMPENSATIONS:	none required
RESOLUTION:	0.01^0 C
CALIBRATION:	none required
RESPONSE TIME:	< one minute
STABILITY:	three years

5.1.2.4. Calibration Procedures

Because of the unvarying nature of the temperature sensor and its conditioning circuitry, the temperature calibration is factory-set and requires no field calibration. However, the SFWMD Comprehensive Quality Assurance Plan requires the verification of the Hydrolabs temperature reading against a laboratory thermometer that has been calibrated with a NIST thermometer. If the Hydrolab value is outside of a 2% range, then the data transmitter must be returned to the factory for recalibration.

5.2. Hydrolab Operating Procedures - pH

5.2.1. Introduction

5.2.1.1. Theory

The pH of a solution is a measure of its hydrogen ion activity and is the logarithm of the reciprocal of the hydrogen ion concentration.

5.2.1.2. Instrument Siting and Exposure (see Section 5.1.1.2.)

5.2.1.3. Measurement Standards

The glass pH electrode and reference electrode are accepted for field use by FDEP (Florida Department of Environmental Protection) provided that the pH is calibrated daily prior to use using certified buffer solutions (see Section 5.2.2.4.).

The standard unit of measurement of pH is a pH unit.
The accuracy of the Hydrolab pH system is 0.2 pH units. The accepted tolerance as stipulated in the SFWMD Comprehensive Quality Assurance Plan is 0.1 pH units. A Hydrolab whose pH value falls outside of the tolerance range requires recalibration. All calibrations must be logged in a bound waterproof notebook.

5.2.2. Instrumentation--Manual Measurements

5.2.2.1. Principle of Operation

The basic principle of electrometric pH measurement is determination of the activity of the hydrogen ions by potentiometric measurements using a standard hydrogen electrode and a reference electrode.

5.2.2.2. Maintenance

The pH glass electrode and reference electrode are cleaned on a quarterly basis as stipulated in the SFWMD Comprehensive Quality Assurance Plan (November, 1994). Additional maintenance is required only when the electrodes are obviously coated with oil, sediment, or biological growth. The glass electrode is cleaned with a clean, soft, non scratching cloth (cotton swab) wet with methyl alcohol.
Frequently during calibration, the pH display indicates that the pH measurement is "out if range". Usually this is because the pH reference solution has escaped from the porous reference sleeve. Servicing the reference electrode involves the replacement of the electrolyte solution (three-molar KCl saturated with silver chloride). Step by

step directions for this procedure are detailed in the Hydrolab H20 Operating Manual (March, 1991).
The pH and reference electrodes must never be allowed to dry out and should be stored in tap water.

5.2.2.3. Sensors Used

5.2.2.3.1. Hydrolab Surveyor III / H2O Datasonde pH Specifications

RANGE:	0 to 14 units
ACCURACY:	0.2 units
SENSOR:	glass pH; rebuildable reference electrode
COMPENSATIONS:	automatic for temperature
RESOLUTION:	0.01 unit
CALIBRATION:	pH 7 buffer, plus one slope buffer
RESPONSE TIME:	< one minute
STABILITY:	one month

5.2.2.4. Calibration Procedures

pH calibration is accomplished by filling the calibration cup with the "zero' buffer (7.00). Typing a "C" (for calibrate) while in the basic menu will access the "calibrate" function which will result in the message: **PCS%ORDLTIM:**

Then, typing "P" (for pH) will result in the message: **Std:**

This stands for Standard. When the reading for the 7.00 buffer has stabilized, the value of the buffer (7.00) is typed on the keyboard display to automatically calibrate the pH system zero. At this point, the display returns to the SOM (standard operating mode) to permit the calibration of the "slope" buffer. This buffer (4.00 or 10.00) should have a pH near that of the anticipated range of the samples to be measured (but not between 6.8 and 7.2).
After filling the calibration cup with the slope buffer and allowing the reading to stabilize, access the pH menu by typing "P" to get: **Std:**

The value of the slope buffer (4.00 or 10.00) is then typed in and the return key is hit. The slope will be set and the screen will be returned to the SOM.

5.3. Hydrolab Operating Procedure - Conductivity

5.3.1. Introduction

5.3.1.1. Theory

Conductivity is a numerical expression of the ability of an aqueous solution to carry an electric current. It is the reciprocal of resistance for which the standard unit is an ohm. Since conductance is the inverse of resistance, the unit on conductance is the mho, or in low-conductivity natural waters, the micromho. Because the measurement is made using two electrodes placed one centimeter apart, specific conductance is generally reported as micromhos per centimeter.

5.3.1.2. Instrument Siting and Exposure (see Section 5.1.1.2.)

5.3.1.3. Measurement Standards

The six electrode conductivity cell is accepted for field use by FDEP (Florida Department of Environmental Protection) provided that the specific conductance is calibrated daily prior to use using a certified buffer solution that is near the anticipated sampling range (see 5.3.2.2.).

The standard unit of measurement of specific conductance is a micromho/cm (or microSiemens/cm).

The accuracy of the Hydrolab conductivity system is 1% of the range. The accepted tolerance as stipulated in the SFWMD Comprehensive Quality Assurance Plan is 5% of the known value. A Hydrolab whose conductivity value falls outside of the tolerance range requires recalibration. All calibrations must be recorded in a bound waterproof notebook.

5.3.2. Instrumentation--Manual Measurements

5.3.2.1. Principle of Operation

The Hydrolab datasonde has a fresh water cell block that provides ranges of 0 to 0.15, 0.15 to 1.5, and 1.5 to 10 milliSiemens/cm. The measurement of specific conductance is made by the use of six electrodes that are housed in the conductivity cell on the H20 data transmitter. Four of the electrodes are used to establish a certain potential (voltage) in the conductivity cell, and the remaining two electrodes are used to measure the electrical current that a particular sample of water will pass at the set potential. The higher the conductivity of the sample, the higher the measured current in the cell.

5.3.2.2. Maintenance

The conductivity cell block should be stored in tap water when not in use.

The conductivity sensor is cleaned on a quarterly basis as stipulated in the SFWMD Comprehensive Quality Assurance Plan (November,1994). Additional maintenance is required when the six conductivity electrodes become fouled which is indicated by the inability to calibrate the conductivity function because the standard is "out of range".

To maintain the sensor, remove the white cell block covering the six pin-shaped nickel electrodes of the specific conductance sensor. Remove the six small o-rings that are slipped over the electrodes and polish all of the exposed surface of the electrodes (including the ends) with emery cloth or #400 wet/dry sandpaper. Avoid touching the nearby pH glass electrode with the abrasive. Once sanded, the electrodes and cell block are cleaned with a methyl alcohol soaked swab.

Re-install the six o-rings (replace if o-rings are flattened). Re-install the white cell block, tightening the screws just enough to make sure the cell block is seated flat against the specific conductance sensor body. After rinsing with deionized water, the sensor is ready for calibration.

5.3.2.3. Sensors Used

5.3.2.3.1. Hydrolab Surveyor III / H20 Datasonde Conductivity Specifications

RANGE:	0 to 100 mS/cm
ACCURACY:	1% of range
SENSOR:	6-electrode cell
COMPENSATIONS:	automatic for temperature (25 C)
RESOLUTION:	four digits
CALIBRATION:	KCl or seawater standards
RESPONSE TIME:	< one minute
STABILITY:	six months

5.3.2.3.4. Calibration Procedures

Conductivity calibration is accomplished by filling the calibration cup with the standard that most closely represents the anticipated range of the waters to be measured. Typing a "C" while in the basic menu will access the "calibrate" function which will result in the message: **PCS%ORDLTIM:**

Then, typing "C" (for conductivity) will result in the message: **Std:**

This stands for standard. Type in the specific conductance calibration standard's value in milliSiemens/cm (same as millimhos/cm). For instance, a standard of 720 micromhos/cm would be typed in as 0.720. Hit the return key to set the calibration and return to the SOM. This procedure also simultaneously calibrates the salinity function because the salinity parameter is algorithm-generated from the conductivity reading.

5.4. Hydrolab Operating Procedures - Dissolved Oxygen

5.4.1 Introduction

5.4.1.1. Theory

The dissolved oxygen (DO) content of waters results from (1) the photosynthetic and respiratory activities of the biota in the open water, the benthos, and the aufwuchs; and (2) the diffusion gradient at the air-water interface and distribution by wind-driven mixing. Generally, 3 mg/l DO or less is stressful to aquatic vertebrates and most other aquatic life.

5.4.1.2. Instrument Siting and Exposure (see Section 5.1.1.2.)

5.4.1.3. Measurement Standards

The rebuildable polarographic electrode is accepted for field use by FDEP (Florida Department of Environmental Protection) provided that the dissolved oxygen is air calibrated daily and calibrated against the Winkler method annually (see Section 5.4.2.2.).

The standard unit of measurement of dissolved oxygen is milligrams per liter (mg/l). The accuracy of the Hydrolab dissolved oxygen measurement is 0.2 mg/l. The accepted tolerance as stipulated in the SFWMD Comprehensive Quality Assurance Plan is 5% of the known value. A Hydrolab whose dissolved oxygen value falls outside of the tolerance range requires recalibration.

5.4.2 Instrumentation--Manual Measurements

5.4.2.1. Principle of Operation

There are generally two methods used to determine the level of dissolved oxygen in water. The SFWMD uses the iodometric (Winkler) method only to verify the accuracy of the Hydrolab instruments on an annual basis as stipulated in the SFWMD Comprehensive Quality Assurance Plan (January, 1992). The Hydrolab instruments utilize the electrometric method which employs the membrane electrode procedure that is based on the rate of diffusion of molecular oxygen across a membrane.

5.4.2.2. Maintenance

Maintenance is performed on the dissolved oxygen sensor on a quarterly basis as stipulated in the SFWMD Comprehensive Quality Assurance Plan (November,1995). Additional maintenance is required when the sensor becomes wrinkled, bubbled, torn, dirty, or when calibration is "out of range". Visual inspections of the membrane should be made daily to ensure that there are no air bubbles under the membrane or that the membrane is not torn or wrinkled.

To change membranes, remove the white DO sensor guard and the o-ring securing the membrane. Shake out the old electrolyte, rinse with deionized water, and refill with fresh electrolyte (provided in the Maintenance Kit, or use 2M potassium chloride) until there is a perceptible meniscus of electrolyte rising above the entire electrode surface of the sensor. Make sure that there are no bubbles in the electrolyte. Hold one end of a new membrane against the body of the DO sensor surface and hold it in place with your index finger. Secure the membrane with the o-ring. There should be no wrinkles in the membrane or bubbles in the electrolyte. Trim away the excess membrane extending below the o-ring. The DO sensor is now ready for calibration, but it should be allowed to soak overnight to give the membrane time to relax to its final shape. The dissolved oxygen electrode should be stored in tap water when not in use.

5.4.2.3. Sensors Used

5.4.2.3.1. Hydrolab Surveyor III / H20 Datasonde Dissolved Oxygen Specifications

RANGE:	0 to 20 mg/l
ACCURACY:	0.2 mg/l
SENSOR:	rebuildable polarographic; 1 mil teflon
COMPENSATIONS:	automatic for temperature and salinity
RESOLUTION:	0.01 mg/l
CALIBRATION:	saturated air or Winkler
RESPONSE TIME:	< one minute
STABILITY:	one month

5.4.2.4. Calibration Procedures

DO calibration is accomplished by filling the inverted calibration cup with tap water until the water is just below the o-ring used to secure the membrane. Any water droplets are then carefully removed (blotted) with a soft tissue (kimwipe). The hard white calibration cup lid is then placed (concave end upward) on top of the calibration cup. The sensor is ready for calibration once the temperature and oxygen readings have stabilized.

Typing a "C" while in he basic menu will access the "calibrate" function which will result in the message: **PCS%ORDLTIM:**

Then, typing "O" will result in the message: Std:

This stands for Standard. Then, type in the local barometric pressure in millimeters of mercury and hit the return key to get the message: **Std:**

The actual dissolved oxygen reading which is derived from the "Table of Oxygen Solubility" is then entered. Once the return key is pressed the user is returned to the SOM.

APPENDIX A

APPENDIX A

GRAB SAMPLE PARAMETERS for USSO and USL3BRS

Chemical Parameters

Biweekly flowing/monthly:
Total Phosphorous (TP), Ortho Phosphorus (OPO_4), Total Kjeldahal Nitrogen (TKN), Nitrate+Nitrite (NOX), Ammonia (NH_4), Turbidity (Turb), Color, Chloride, and Alkalinity

Quarterly:
Add to the above: Total Suspended Solids (TSS), Sulfate (SO_4), Silicate (SiO_2), Calcium (Ca), Magnesium (Mg), Sodium (Na), Potassium (K), Total Iron (TotFe)

Bi-annual:
Add to all above: Total Arsenic (TotAs), Total Cadmium (TotCd), Total Copper (TotCu), Total Lead (TotPb), Total Zinc (TotZn), and Total Mercury (TotHg)

Physical Parameters

Hydrolab: Temperature, pH, Dissolved Oxygen and Conductivity