SFWMD
COMPREHENSIVE
QUALITY ASSURANCE
PLAN

NOVEMBER 13, 1994

Inventory #318

COMPREHENSIVE QUALITY ASSURANCE PLAN

NOVEMBER 13, 1994

SOUTH FLORIDA WATER MANAGEMENT DISTRICT

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Comprehensive Quality Assurance Plan #870166G
for
South Florida Water Management District
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West Palm Beach, FL 33416-4680
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Prepared by
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10-12-94
Date

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11-10-94
Date

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3.0 STATEMENT OF POLICY

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

This CQAP is intended to be used as a reference and guide for those personnel collecting and analyzing samples and evaluating the results obtained for those analyses. It sets forth 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 QA/QC management practices to produce data of a 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, tissues and soils. The laboratory is capable of performing analyses for inorganic anions, metals, physical properties, organics (TOC), microbiology and other tests such as chlorophyll and macrobenthic invertebrates.

4.2 Key Personnel

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

Department Director, Department of Water Resource Evaluation: 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.

Department Directors, Department of Research and Department of Regulation: 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.

Division Directors, Hydrogeology, Kissimmee and Okeechobee Systems Research, Everglades Systems Research, Surface Water Management and Field Engineering: 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 Director, Water Quality Monitoring Division: Responsible for the allocation of resources, training of personnel, collection and analysis of samples, and reporting of results to meet the needs of the SFWMD for analytical services.

Senior Chemist, WQM Div. Quality Assurance Officer: Responsible for assuring that the laboratory and field personnel adhere to the approved methods of sample collection, analysis, maintenance of the Comprehensive Quality Assurance Plan, 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: Responsible for the supervision of the laboratory, review of quality control results, review of data, release of samples, training of personnel and adherence to required quality control procedures.

Senior Chemists: Responsible for the supervision of the assigned shift, review of quality control results, review of data, release of samples, training of personnel and adherence to required quality control procedures.

Senior Environmental Scientist, Water Quality Monitoring Division, Responsible for data management and assessment, and for the West Palm Beach Data Collection Group. Also responsible for overseeing organics monitoring for the division.

Staff Environmental Scientists, Water Quality Monitoring Division: Duties include supervision, report generation, and data review. Involves serving as project managers and collecting samples.

Hydrogeology, Kissimmee & Okeechobee Systems Research, Everglades Systems Research, Surface Water Management Field Engineering Division Quality Assurance Officers: Responsible for coordination of all project quality assurance plans and QA reports for the Division, review of quality control results for the projects, and training of division personnel in quality control procedures. The role of QA officer is separate and distinct from all other responsibilities for any specific project.

Supervising Professional-Environmentalists and Hydrogeologists: Responsible for the supervision of the project managers and field operations supervisors, training of personnel, coordination with divisional QA officers for QA/QC issues, development of sampling networks, review of quality control data and analytical results, and development of research projects.

Supervising Professional-Field Office, Water Quality Monitoring Division: Responsible for supervision of the Water Quality Monitoring Division's Okeechobee office, training of personnel in sampling and quality control procedures, design of sampling networks and research projects, review of quality control data and analytical results, and coordination with divisional QA officer.

Field Operations Supervisor, Hydrogeology Division: Responsible for the allocation of personnel for ground water sampling, drilling and logging of monitor wells, and training of personnel.

Field Operations Supervisor, Water Quality Monitoring Division: Responsible for the allocation of personnel and equipment for surface water sampling, training of personnel in sampling and quality control procedures, review of quality control data, review of analytical results for specified projects.

Staff Programmer Analyst, Water Quality Monitoring Division: Responsible for the maintenance and integrity of the laboratory information management system, programming computers, testing software packages, and operation of the LIMS.

Senior Technician Supervisor-Scientific, Water Quality Monitoring Division: Responsible for the supervision of technicians, sample site selections and data review.

4.3 Organization Charts

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

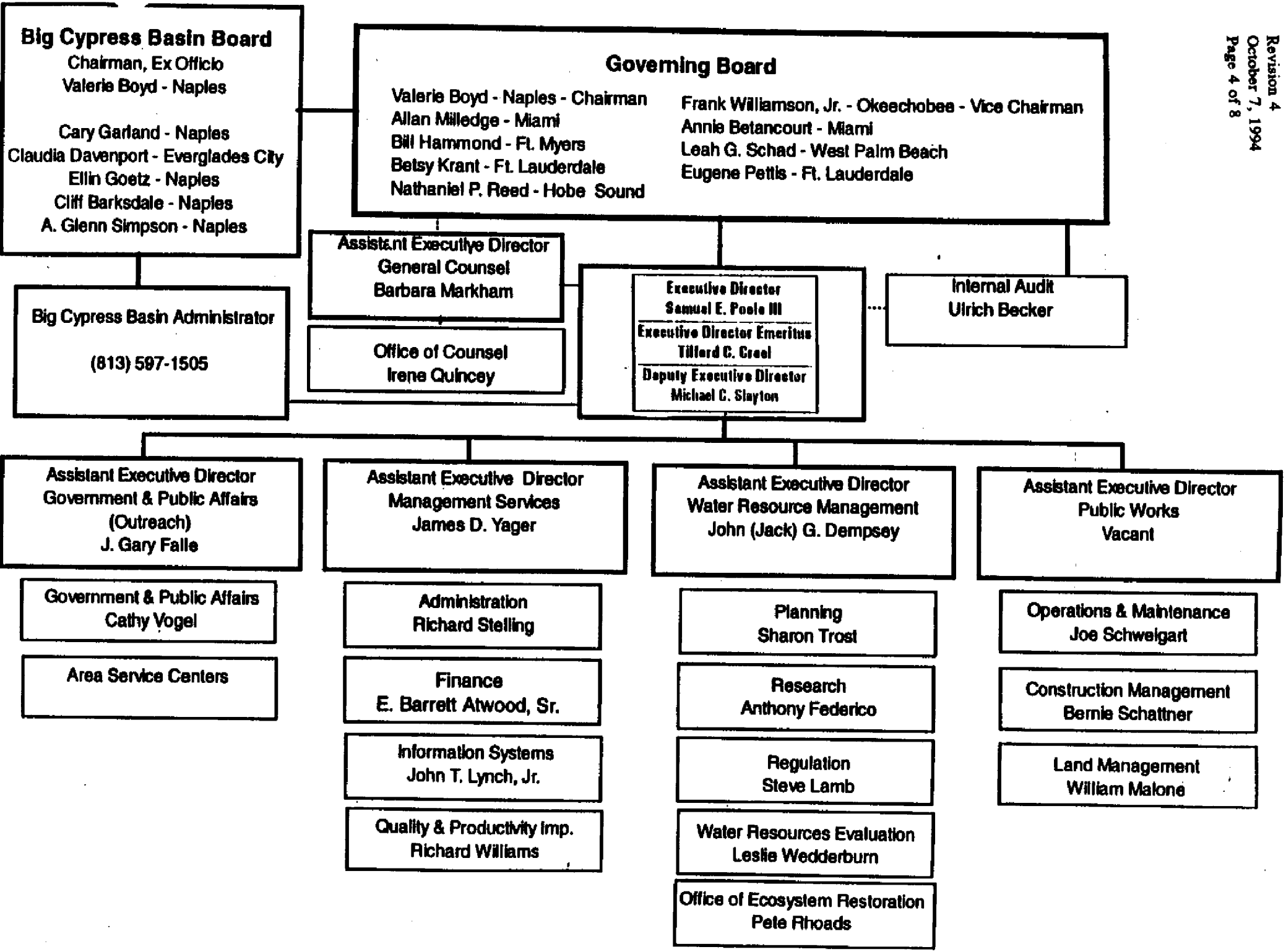
Figure 4.1 is the overall organization of the SFWMD showing the Governing Board, Executive and Assistant Executive Directors and the major departments and offices.

Figure 4.2 is the organization of the Department of Water Resources Evaluation showing the reporting relationships to the Department Director.

Figure 4.3 shows the organization of the Water Quality Monitoring Division through the supervisory levels.

Figure 4.4 shows the organization of the Hydrogeology Division through the supervisory levels.

Figure 4.5 shows the organization of the Department of Research and the Department of Regulation.


Big Cypress Basin Board
Chairman, Ex Officio
Valerie Boyd - Naples
Cary Garland - Naples
Claudia Davenport - Everglades City
Ellin Goetz - Naples
Cliff Barksdale - Naples
A. Glenn Simpson - Naples
Governing Board
Valerie Boyd - Naples - Chairman
Allan Milledge - Miami
Bill Hammond - Ft. Myers
Betsy Krant - Ft. Lauderdale
Nathaniel P. Reed - Hobe Sound
Frank Williamson, Jr. - Okeechobee - Vice Chairman
Annie Betancourt - Miami
Leah G. Schad - West Palm Beach
Eugene Pettis - Ft. Lauderdale
Big Cypress Basin Administrator
(813) 597-1505
Assistant Executive Director
General Counsel
Barbara Markham
Office of Counsel
Irene Quincey
Executive Director
Samuel E. Poole III
Executive Director Emeritus
Tilford C. Creel
Deputy Executive Director
Michael C. Slayton
Internal Audit
Ulrich Becker
Assistant Executive Director
Government & Public Affairs
(Outreach)
J. Gary Falle
Government & Public Affairs
Cathy Vogel
Area Service Centers
Assistant Executive Director
Management Services
James D. Yager
Administration
Richard Stelling
Finance
E. Barrett Atwood, Sr.
Information Systems
John T. Lynch, Jr.
Quality & Productivity Imp.
Richard Williams
Assistant Executive Director
Water Resource Management
John (Jack) G. Dempsey
Planning
Sharon Trost
Research
Anthony Federico
Regulation
Steve Lamb
Water Resources Evaluation
Leslie Wedderburn
Office of Ecosystem Restoration
Pete Rhoads
Assistant Executive Director
Public Works
Vacant
Operations & Maintenance
Joe Schweigart
Construction Management
Bernie Schattner
Land Management
William Malone

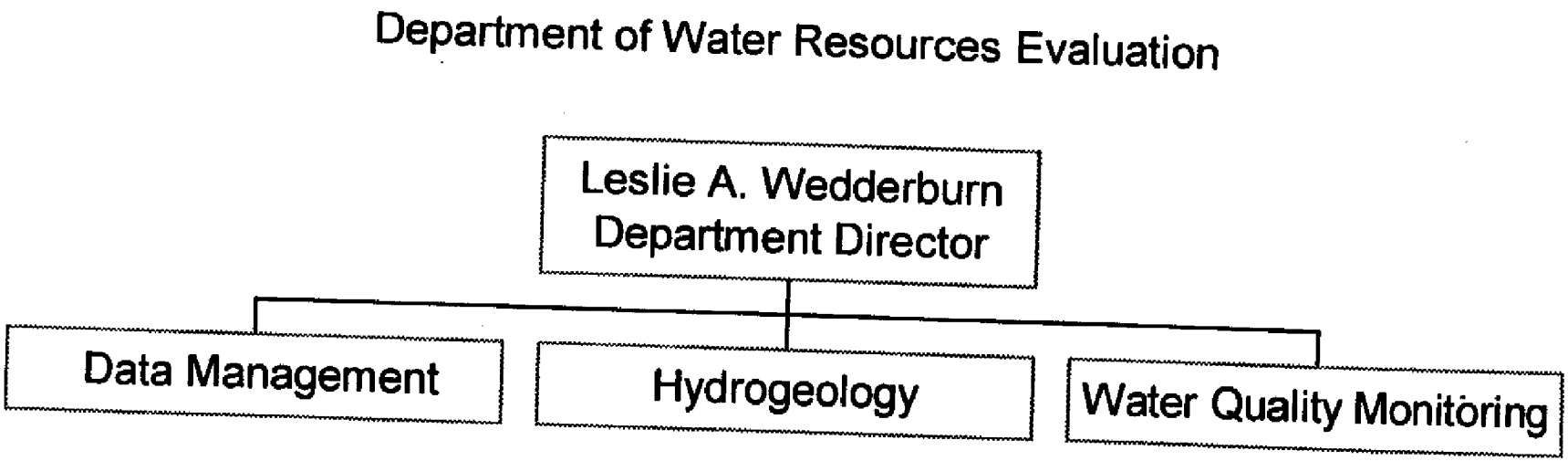


Figure 4.2 Department of Water Resources Evaluation

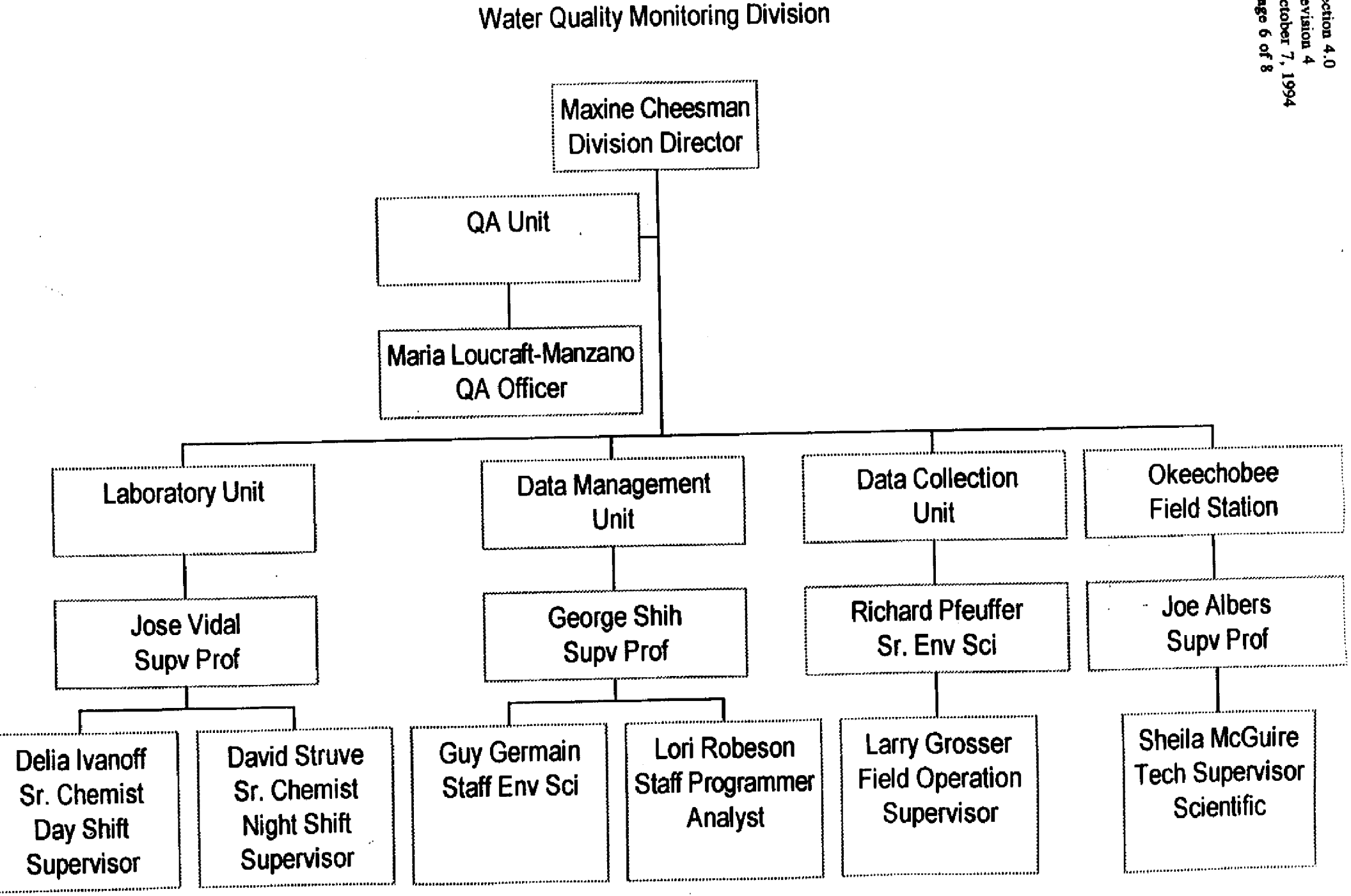


Figure 4.3 Water Quality Monitoring Division Organizational Chart

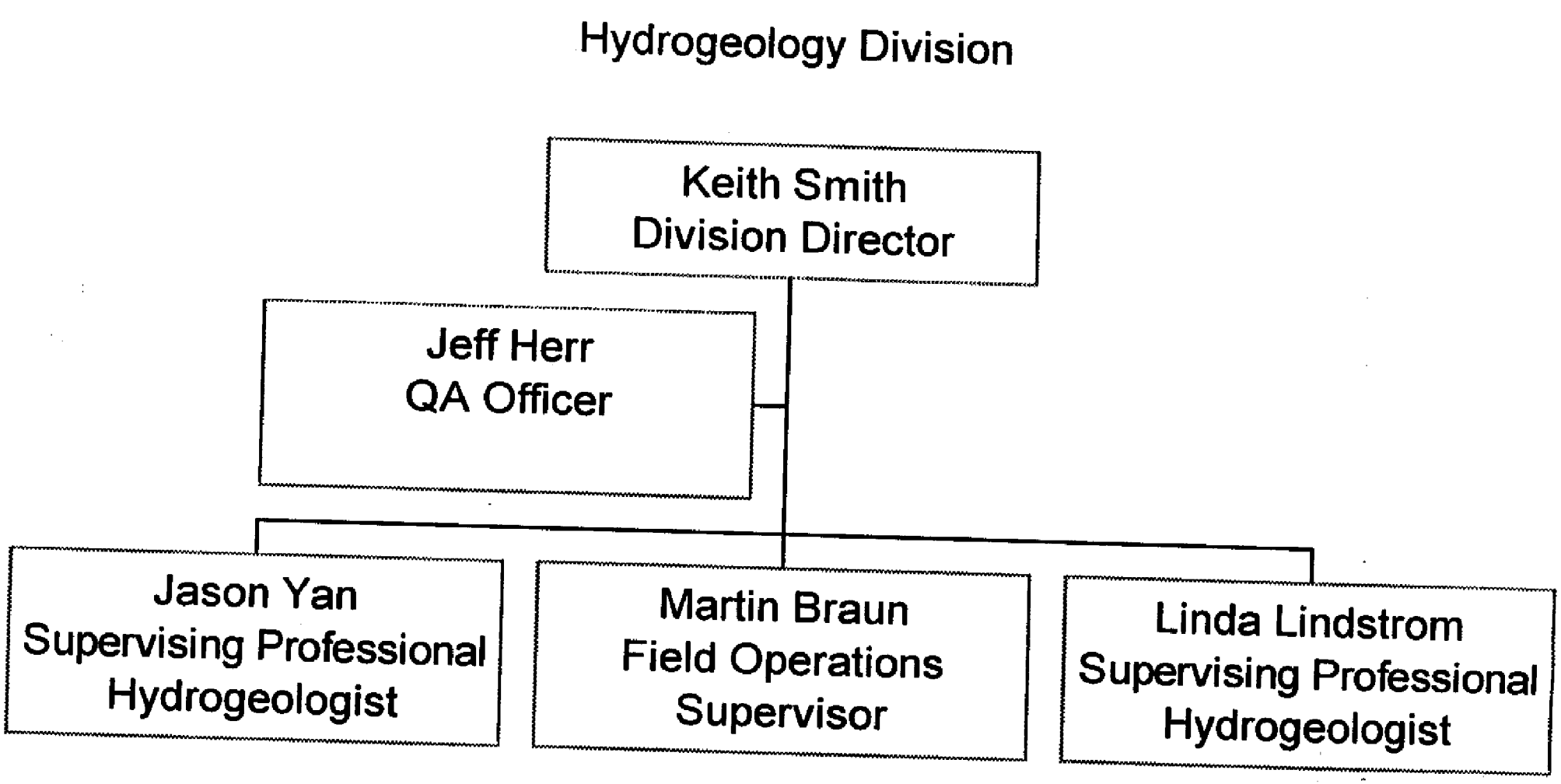


Figure 4.4 Hydrogeology Division Organizational Chart

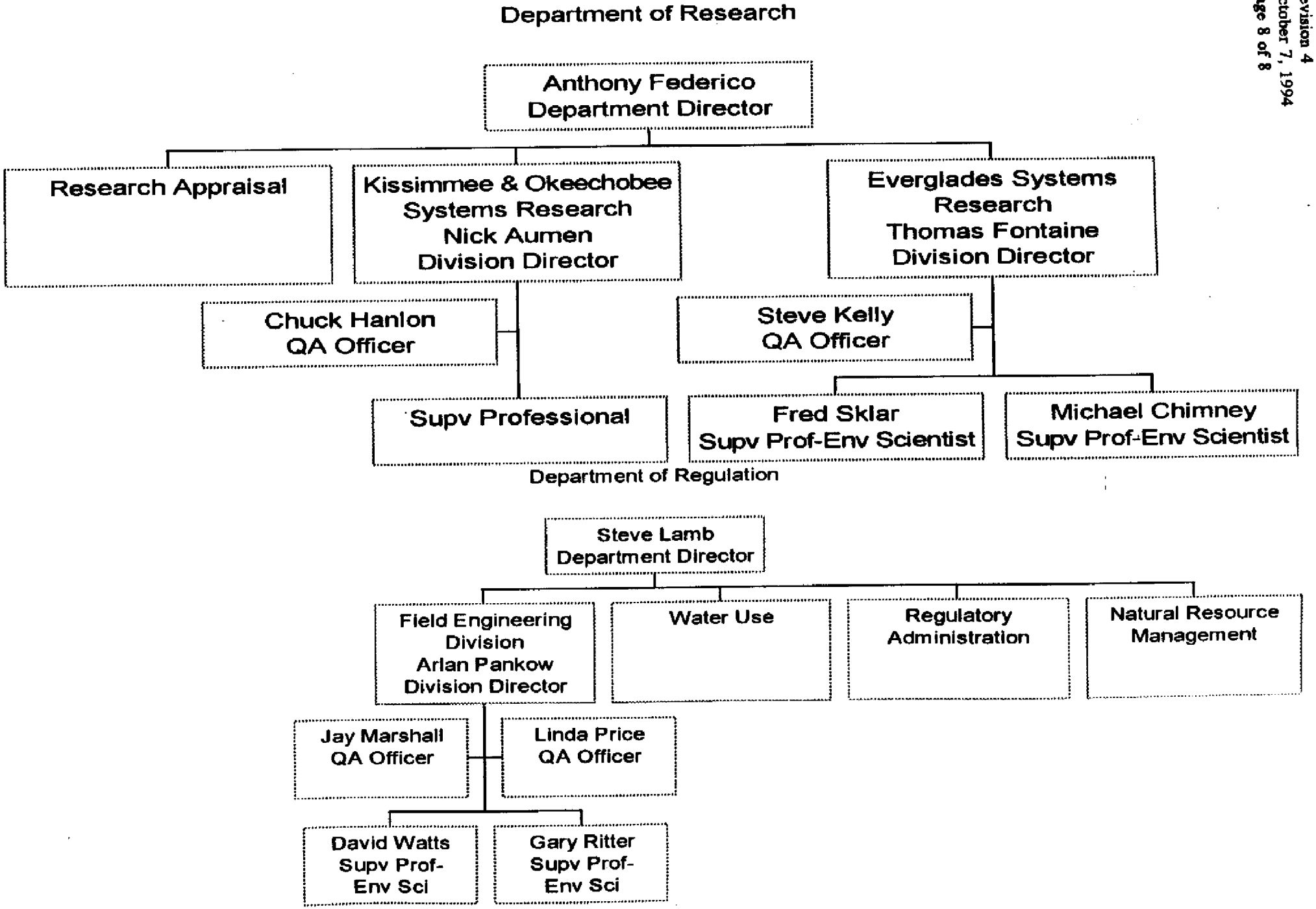


Figure 4.5 Department of Research and Department of Regulation Organiationl Chart

5.0 QA TARGETS FOR PRECISION, ACCURACY AND METHOD DETECTION LIMITS

Tables 5.1 and 5.2 present the laboratory quality assurance objectives and Table 5.3 presents the field quality assurance objectives used by SFWMD. The data is generated from historical data collected in the laboratory and field.

Table 5.1 - QUALITY ASSURANCE OBJECTIVES

Component	Matrix	Analytical Method #	Precision % RSD	Accuracy % Recvy	MDL mg/L
Alkalinity	Surface H_2O Ground H_2O	EPA 310.1	0 - 5.0	NA	1.0
Ammonia	Surface H_2O Ground H_2O	SM 4500-NH3H	0 - 5.9	78.5 - 116 L	0.01
Calcium, dissolved	Surface H_2O Ground H_2O	SM 3111B	0 - 4.0	93.5 - 106 M	1.0
Chloride	Surface H_2O Ground H_2O	EPA 300.A	0 - 2.0	94.7 - 104 M	0.5
Fluoride	Surface H_2O Ground H_2O	SM 4500F-C	0 - 8.5	79.0 - 115L	0.01
Iron, total & dissolved	Surface H_2O Ground H_2O	EPA 236.1	0 - 10.0	86.8 - 111 M	0.02
Nitrogen, Total Kjeldahl	Surface H_2O Ground H_2O	EPA 351.2	0 - 7.8	84.0 - 112 M	0.50
Magnesium, dissolved	Surface H_2O Ground H_2O	SM 3111B	0 - 4.0	96.6 - 104 M	0.2
Nitrate + nitrite	Surface H_2O Ground H_2O	SM 4500NO3F	0 - 5.0	98.0 - 101 M	0.004
Nitrite	Surface H_2O Ground H_2O	SM 4500NO2B	0 - 4.1	95.2 - 108 M	0.004
Nitrate	Surface H_2O Ground H_2O	By difference	NA	NA	0.004

Table 5.1 (cont'd) - QUALITY ASSURANCE OBJECTIVES

Component	Matrix	Analytical Method #	Precision % RSD	Accuracy % Recvy	MDL mg/L
Total phosphorus	Surface H_2O Ground H_2O	SM 4500PF	0 - 5.0	82.8 - 109 M	0.004
Organic carbon, total and dissolved	Surface H2O Groung H2O	EPA 415.1	0 - 10	80.0 - 120 M	1.0
Orthophosphate	Surface H_2O Ground H_2O	SM 4500PF	0 - 5.0	86.7 - 107 M	0.004
Potassium, dissolved	Surface H_2O Ground H_2O	SM 3111B	0 - 5.2	91.6 - 109 M	0.04
Residue, filterable	Surface H_2O Ground H_2O	SM 2540C	0 - 10	NA	3
Residue, nonfilterable	Surface H_2O Ground H_2O	EPA 160.2	0 - 10	NA	2
Residue, volatile	Surface H_2O Ground H_2O	EPA 160.4	0 - 10	NA	2
Silica, dissolved	Surface H_2O Ground H_2O	SM 4500SiD Modified	0 - 6.0	96.1 - 108 M	1.0
Sodium, dissolved	Surface H_2O Ground H_2O	SM 3111B	0 - 4.7	94.5 - 106 M	0.2
Strontium, dissolved	Surface H_2O Ground H_2O	SM 3111B	0 - 5.0	94.2 - 110	0.2
Sulfate	Surface H_2O Ground H_2O	EPA 300.A	0 - 2.6	96.3 - 104 M	2.0

Table 5.1 (cont'd) - QUALITY ASSURANCE OBJECTIVES

Component	Matrix	Analytical Method #	Precision % RSD	Accuracy % Recvy	MDL ug/L
Aluminum, total and dissolved	Surface H_2O Ground H_2O	EPA 202.2	0 - 10	80 - 120 M	2.5
Antimony, total and dissolved	Surface H_2O Ground H_2O	EPA 204.2	0 - 10	80 - 120 M	2.2
Arsenic, total	Surface H_2O Ground H_2O	EPA 206.5 + EPA 206.2	0 - 6.2	90 - 108 M	1.5
Barium, total and dissolved	Surface H_2O Ground H_2O	EPA 208.2	0 - 10	80 - 120 M	2.0
Beryllium, total and dissolved	Surface H_2O Ground H_2O	EPA 210.2	0 - 10	80 - 120 M	0.2
Cadmium, total and dissolved	Surface H_2O Ground H_2O	EPA 213.2	0 - 5.8	91.9 - 113 M	0.1
Chromium, total and dissolved	Surface H_2O Ground H_2O	EPA 218.2	0 - 5.0	80 - 113 M	0.5
Copper, total and dissolved	Surface H_2O Ground H_2O	EPA 220.2	0 - 5.0	84.2 - 114 M	0.5
Lead, total and dissolved	Surface H2O Ground H2O	EPA 239.2	0 - 5.5	83.5 - 112 M	0.5
Manganese, total and dissolved	Surface H_2O Ground H_2O	EPA 243.2	0 - 10	80 - 120 M	1.0
Mercury, total and dissolved	Surface H_2O Ground H_2O	EPA 245.1	0 - 17	94 - 121 L	0.2
Nickel, total and dissolved	Surface H_2O Ground H_2O	EPA 249.2	0 - 10	80 - 120 M	0.5
Selenium, total and dissolved	Surface H_2O Ground H_2O	EPA 270.2	0 - 10	80 - 120 M	1.0
Silver, total and dissolved	Surface H_2O Ground H_2O	EPA 272.2	0 - 10	80 - 120 M	0.5

Table 5.1 (cont'd) - QUALITY ASSURANCE OBJECTIVES

Component	Matrix	Analytical Method #	Precision % RSD	Accuracy % Recvy	MDL
Thallium, total and dissolved	Surface H_2O Ground H_2O	EPA 279.2	0 - 10	80 - 120 M	0.5 ug/L
Tin, total and dissolved	Surface H_2O Ground H_2O	EPA 202.2	0 - 10	80 - 120 M	0.7 ug/L
Zinc, total and dissolved	Surface H_2O Ground H_2O	EPA 289.1	0 - 5.0	99.4 - 108 M	20 ug/L
Hardness	Surface H_2O Ground H_2O	SM 2340B by calculation	NA	NA	5 mg eq $CaCO_3$/L
Alkaline Phosphatase MVP	Surface H_2O Ground H_2O	SFWMD 3160.1	0 - 10.0	NA	2 nmo/min/mL
Chlorine Residual, total	Surface H_2O Ground H_2O	EPA 330.4	0 - 10.0	NA	0.02 mg/L
Chlorophyll	Surface H2O	SM 10200H	0 - 35	NA	1 mg/m^3
Color	Surface H_2O Ground H_2O	SM 2120B modified	0 - 5.0	NA	1 Pt-Co unit
Macrobenthic Invertebrates	Surface H_2O Sediments	SM 10500	NA	NA	NA
pH	Surface H_2O Ground H_2O	SM 4500H+B	0 - 5.0	NA	0.5 pH unit
Specific Conductance	Surface H_2O Ground H_2O	SM 2510B	0 - 5.0	NA	0.4 uS/cm
Turbidity	Surface H_2O Ground H_2O	SM 2130B	0 - 5.0	NA	0.1 NTU

Table 5.2 - MICROBIOLOGY PARAMETERS QUALITY ASSURANCE OBJECTIVES

Component	Matrix	Analytical Method #	Precision %RSD	Accuracy % Recovery[1]	MDL[2]
Total Coliform	Surface H_2O Ground H_2O	SM 909A/9222B SM 908A/9221B	0 - 8.9 0 - 20	NA	NA
Fecal Coliform	Surface H_2O Ground H_2O	SM 909C/9222D SM 908C/9221C	0 - 15 0 - 20	NA	NA
Heterotrophic Plate Count	Surface H_2O Ground H_2O	SM 910B/9215B	0 - 40	NA	NA
Fecal Streptococci	Surface H_2O Ground H_2O	SM 907A/9230C	0 - 37	NA	NA

[1] There are currently no established accuracy data for relating analytical results to field populations.

[2] Since the ratio of culturable to unculturable cells depends on the sample, a generic MDL can not be determineed.

Table 5.3 - FIELD QUALITY ASSURANCE OBJECTIVES

Component	Matrix	Analytical Method #	Precision % RSD	Accuracy % Recvy	MDL
pH	Surface H_2O Ground H_2O	EPA 150.1	0 - 5	NA	0.5 pH unit
Oxygen, dissolved	Surface H_2O Ground H_2O	EPA 360.1	0 - 20	NA	0.1 mg/L
Specific conductance	Surface H_2O Ground H_2O	EPA 120.1	0 - 5	NA	50 uS/cm
Temperature	Surface H_2O Ground H_2O	EPA 170.1	0 - 3	NA	5°C
Salinity	Surface H_2O Ground H_2O	SM 2520B	0 - 5	NA	0.1 ppt

6.0 SAMPLING PROCEDURES

6.1 Sampling Capabilities

The sampling capabilities of SFWMD are shown in Table 6.1. The reference used in developing sampling procedures is the EPA Region IV Engineering Support Branch Standard Operating Procedures and Quality Assurance Manual (1991). This reference is available in the field and is referred to in this document as EPA SOP & QAM.

Table 6.1 Sampling Capabilities by Major Category

Matrix	Parameters
Surface Water	Inorganic Anions Metals Physical Properties Organics Extractable Organics Volatile Organics Microbiology Other (Macrobenthic Invertebrates/Chlorophyll)
Ground Water	Inorganic Anions Metals Physical Properties Organics Extractable Organics Volatile Organics Microbiological
Soil/sediments	Inorganic Anions Metals Physical Properties Organics Extractable Organics Volatile Organics
Atmospheric Deposition	Inorganic Anions Metals Physical Properties
Biological Tissues	Inorganic Anions Metals Physical Properties Organics

Samples are collected from the least to most contaminated areas whenever possible. Time limitations and distance between sites may make this impossible. However, the majority of the District sampling sites are ambient water sources with little variation in concentration levels within a sampling trip. For ground water sampling, if a well is suspected to have free product, then it is not sampled. A new unused pair of disposable latex/PVC gloves are 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, 9) inorganics, 10) turbidity and 11) macrobenthic invertebrates.

6.2 Field Equipment

6.2.1 Surface Water Sampling Equipment

Table 6.2 lists the equipment used for inorganic surface water quality sampling.

Table 6.2 Inorganic Surface Water Quality Sampling Equipment

Equipment Description	Type of Material	Use	Notes
Wildco 2.2 liter vertical sampling bottle	acrylic	collection	1
Wildco 2.2 liter horizontal sampling bottle	PVC	collection	1
Wildco 3.2 liter horizontal sampling bottle	PVC	collection	1
5.0 liter bucket	Polyethylene	collection	1
Nalgene sample bottles	HDPE	collection	1
Millipore Swinnex filter holder	acrylic/poly-propylene	filtration	1
Poretics prefilter	glass fiber	filtration	1
0.45 micron filter	polycarbonate	filtration	1
Millipore 50 ml syringe	plastic	filtration	1

[1]Not suitable for the collection of organics, extractable organics and VOCs

Field Instrumentation

1. Hydrolab Model 4031
2. Hydrolab Model 4041
3. Hydrolab Surveyor II
4. Hydrolab Surveyor III
5. Secchi Depth Disc
6. Licor spherical quantum sensors

Navigational Aids

1. Apelco DXL 6000 Loran with antenna and battery- for site location
2 USGS Quadrangle maps- for site location
3. Project location maps- for site location
4. WMD low band radio for communication
5. Mark Hurd Areal Photographs-for site location
6. Global Positioning Systems, Pathfinder Basic Plus- for site location

Boating Supplies

1. Safety equipment: life vests, horn, flare kit, oars, fire extinguisher and throwable cushion
2. Spare tire for trailer
3. Engine oil for boat

6.2.2 Ground Water Sampling Equipment

The following is a list of the equipment used for ground water quality sampling.

Table 6.3. Ground Water Sampling Equipment

Equipment Description		Type of Material	Use	Notes
Purging Equipment				
1.	Gorman Rupp/ Centrifugal Pump	Iron/Steel/ Rubber	Purge Only	1
2.	Suction Hose	Flex PVC	Purge Only	2
3.	Drop Pipe	Teflon	Purge Only	3
4.	Check Valve	Teflon Steel	Purge Only	3
5.	4 Gallon Bucket	Polyethylene	Purge Only	9
6.	Lufkin Tapes	Steel	Prior to Purge	4
7.	Sonin Electronic Tape	Plastic	Prior to Purge	5
Sampling Equipment				
1.	Norwell Bailer	Teflon	Purge/Sample	6
2.	Suspension Cable	Teflon Coated Stainless Steel	Purge/Sample	6
Field Filtration Units				
1.	QED FF-8200	Filter: Acrylic Copolymer with Polypropylene Body 0.45 micron. 1.0 micron is used for metals collected for permit compliance	Filtration	7
2.	Masterflex Model #7570-00 Peristal-tic Pump	Tygon Tubing Stainless Steel Housing	Air Source to force water through filter	8

Notes:

1. This equipment is used to evacuate the standing water from the well and does not contact the water within the well or sample water at any time.
2. This equipment does not routinely contact the water within the well and never contacts sample water at any time. The possibility of water that has come in contact with this equipment coming in contact with water within the well is minimized by the use of a drop pipe with a check valve. The purge pump is kept running while the drop pipe is withdrawn from the well to reduce the possibility of water draining back into the well from the inside of the suction hose.
3. This equipment contacts water within the well. It is cleaned in the laboratory and stored in aluminum foil until used. The cleaning procedures are dependent on the parameters being collected. The cleaning operations are recorded in the equipment logbook. Prior to the collection of the samples, the well is purged by removing three full bailers of water using a Teflon bailer.
4. This equipment contacts water within the well prior to the purging process. All water that contacts this equipment is removed during the purging process. This tape is cleaned with Liquinox™, rinsed with analyte free water, rinsed with isopropanol and rinsed again with analyte free water prior to use in the well. This operation is recorded and dated in the equipment logbook.
5. This device does not come in contact with the well or sample water at any time. It sends a sonic pulse down the well that is reflected off the surface of the water. The unit calculates the distance to the water surface by measuring the amount of time required for the sonic pulse to return to the sensor. It is temperature compensated so that changes in air temperature do not affect the accuracy.
6. This equipment is cleaned in the office and stored in aluminum foil until use. The cleaning procedures are dependent on the parameters that are being collected. This operation is recorded and dated in the equipment logbook.
7. Disposable, used once and discarded. Individually packed in plastic bags to prevent contamination prior to use.
8. Neither the peristaltic pump or Tygon™ tubing contacts the well or sample water at any time. This pump is used to force air into the top of the Norwell bailer which turn forces the water through the QED FF 8200 filter. The top two inches of water in the bailer, approximately 100 milliliters, is discarded because it was in contact with the air in the bailer.
9. This equipment used to collect and calculate amount of purge water only and will not be used to collect samples for analysis.

6.2.3 Soil/Sediment Equipment

The following equipment is used to collect soil/sediment samples.

Table 6.4 Soil/Sediment Sampling Equipment

Equipment Description	Type of Material	Use
Petite Ponar™	Stainless Steel	Sampling
Scoop	Stainless Steel	Sampling/ Compositing
Bowl/Tray	Stainless Steel	Compositing/ Homogenizing (not VOCs)
Core	Stainless Steel	Sampling
Core	PVC	Sampling (not for Organics)
Core attachment	PVC	Sampling (not for Organics)
Core stoppers	Rubber	Sampling (not for Organics)

6.2.4 Biological Tissues Sampling Equipment

The following equipment is used to collect biological tissue samples.

Table 6.5 Biological Tissues Sampling Equipment

Equipment Description	Type of Material	Use
Shears	Stainless Steel	Sampling (above ground biota)
Knife	Stainless Steel	Sampling (above ground biota)
Core	PVC	Sampling (below ground biota)
Opaque Bags	Plastic	Sample storage (biota)
Soil Sieve, 5mm mesh size)	Stainless Steel	Sample processing

6.2.5 Atmospheric Deposition Equipment

The following equipment is used to collect atmospheric deposition samples.

Table 6.6 Atmospheric Deposition Sampling and Processing Equipment

Equipment Description	Type of Material	Use	Notes
Aerochem Metric Wet/Dry Precipitation Collector	Aluminum	Hold sample collection buckets	1
Aerochem dryfall bucket and lid	PVC	Sample collection	2
Aerochem wetfall bucket and lid	PVC	Sample collection	2
5 liter bucket	Polyethylene	Sample processing	2
Rubber spatula/tweezers/ scoop	Plastic	Sample processing	2

Notes:
[1] Equipment will not contact sample.
[2] For inorganic ions, physical properties and Aluminum and Iron collection/processing only.

6.2.6 Autosampler Equipment

The following types of autosamplers and equipment are used:

Table 6.7 Autosampler Collection and Processing Equipment

Equipment Description	Type of Material	Use	Notes
American Sigma STREAMLINE Model 700 Autosampler	Polyethylene	Hold sample containers	1
American Sigma Model 6201 Autosampler	Polyethylene	Hold sample containers	1
Sample bottle 5 gal.	Polypropylene	Sample collection	2
Sample bottles 1 liter	Polypropylene	Sample collection	2
Pump tubing/Intake tubing	Silicon/PVC	Sample collection	2

Notes:
[1] Does not contact sample
[2] For Inorganic Anions, and physical parameters with long holding times only

6.2.7 Macrobenthic Invertebrate Sampling Equipment

The following equipment is used to collect macrobenthic samples. The equipment used will depend on the habitats available in the area.

Table 6.8 Macrbenthic Invertebrate Sampling Equipment

Equipment Description	Type of Material	Use
Hester-Dendy artificial substrates	Tempered hardboard	Sample collection
dip nets	Nylon	Sample collection
Petite Ponar	Steel	Sample collection
Ekman grab sampler	Steel	Sample collection
Sieve (U.S. Standard No. 30)	Steel	Processing
10% buffered formalin		Preservation
70-80% ethyl alcohol		Preseravation
Glass jars	Glass	Sample Storage
Sorting trays	Stainless Steel	Processing

6.2.8 Miscellaneous Equipment

Sample bottles
- 60 ml Nalgene polyethylene sample bottles - for inorganics only
- 175 ml Nalgene polyethylene sample bottles - for inorganics only
- 250 mL Nalgene polyethylene sample bottles - for inorganics only
- 1000 mL Nalgene polyethylene sample bottles - for inorganics only
- 125 mL amber Nalgene polyethylene rectangular sample bottles (mercury only)
- 250 mL Nalgene polyethylene sample bottles (trace metals only)

Note: Sample containers for VOCs organics & extractable organics are provided by contract laboratories.

Microbiology sample containers

125 ml Presterilized Whirlpaks™

Sample preservation supplies

1. 50% H_2SO_4 in 60 mL dropping bottle (fresh weekly, ACS reagent grade)
2. 50% HNO_3 in 60 mL dropping bottle (fresh weekly, Trace Metal grade)
3. pH strips, 0 - 3 range
4. Safety goggles
5. Neutralizing buffer solution, pH 6.9, for acid spill clean up

Note: Preservatives for VOCs, organics and extractable organics are provided by contract laboratories.

Hydrolab field calibration kit

1. Certified pH buffers - 4, 7, and 10
2. Certified conductivity standards - range appropriate for sampling sites for particular trip
3. Ring stand
4. Screwdrivers - straight edge and Phillips
5. Calibration cup with both hard and soft end caps

Coolers with wet ice

1. Igloo 48, 84 or 196 quart
2. Gott 60 or 80 quart

QA/QC supplies

1. QC Samples (prepared by lab)
2. Analyte free water - for field blanks and rinsing equipment

Miscellaneous supplies

1. Five (5) liter polyethylene bucket - for inorganic sample processing
2. Disposable latex/PVC gloves, powder free (PVC not for organics or VOCs)
3. Polyethylene trays - for providing clean working areas (does not contact sample)
4. Sample tags
5. #16 rubber bands
6. Waterproof pens (Sharpies)
7. Clipboard
8. Field notebook (bound, waterproof)
9. Chemistry field data log sheets
10. First aid kit
11. Watch (with seconds hand or timer)
12. Personal protective equipment

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 6.3.12 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, TRPHs, Whirlpaks™ for microbiology, and Oil and Grease.

Analyte free water is obtained from the laboratory or field prep areas which have 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, equipment blanks, and for the final decontamination rinse of field equipment. The reliability and purity of the analyte free water is monitored through routine conductivity measurements and the results obtained from the equipment and field blanks. The District does not provide a decontamination service to its clients.

6.3.1 Sampling Equipment Cleaning - Laboratory

In the laboratory the sampling equipment is cleaned using the following procedure.

1. Wash all surfaces thoroughly with a hot tap water and phosphate free soap (such as Liquinox™) solution. Use a brush to contact all surfaces and remove stubborn debris. Heavily contaminated equipment is acetone rinsed before regular decontamination.
2. Rinse thoroughly with hot tap water.
3. Rinse with 10% hydrochloric acid. Use 10% nitric acid for trace metal equipment only.
4. Rinse thoroughly with analyte free water.
5. Rinse thoroughly with pesticide grade isopropyl alcohol (equipment used for organic sampling only).
6. Rinse thoroughly with analyte free water.
7. Allow to air dry completely.
8. Wrap in aluminum foil (if applicable) 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, the date and initials of the person performing the procedure.

6.3.2 Surface Water Equipment (Inorganics Only)

Sampling equipment for nutrients, major ions and physical parameters that is reused from site to site is rinsed twice with analyte free water at the site and then rinsed three times with sample at the next sample site. Sampling equipment for both trace metals and nutrients is rinsed between sites with DI, rinsed with 10 % hydrochloric acid, and DI rinsed. When collecting metals only, 20% nitric acid is used instead of the hydrochloric acid. Before the next sampling event, all equipment must be cleaned as stated in Section 6.3.1. Hydrolab systems are to be rinsed in a light soap solution and stored in tap water.

6.3.3 Surface Water Equipment (Organics)

A subsurface grab sampler is used to collect organics in surface water. Samples are collected by immersing the sampler and bottle upstream into the surface water body until it is full. The subsurface sampler does not come into contact with the sample.

6.3.4 Ground Water Equipment

The sampling equipment is precleaned in the lab according to 6.3.1, used only once in the field, rinsed with analyte free water, tagged with the station location and returned to the sample prep area for thorough in-house cleaning. At a minimum, the first three bailer loads of water from a well are discarded to further rinse the bailer.

6.3.5 Sediment/Soils Equipment

The field sampling equipment is cleaned prior to being taken to the field and in between sites by following procedure: The dredge, scoop, bowl, and core (stainless steel) are washed with Liquinox™ 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 cores are washed with Liquinox™ detergent, rinsed with tap water, dipped in 10% HCl, rinsed with tap water, then rinsed with DI water and allowed to dry. The cores are bagged in polypropylene bags until taken into the field.

6.3.6 Sample Bottles and Filtering Equipment

In the laboratory, the reusable sample bottles (except for trace metals) and filter holders are detergent washed with Liquinox™, rinsed with hot tap water then with 10% hydrochloric acid, tap water, analyte free water, and finally air dried. Dry bottles are stored with the caps

on and filter holders are stored in a closed container. Unpreserved sample bottles are rinsed on site with sample three times before the final sample is collected.

Polyethylene trace metal bottles are detergent washed with Liquinox™, rinsed with hot tap water, soaked in 20% nitric acid overnight, rinsed with analyte free water, and stored with deionized water containing 1% nitric acid until sample collection. At the time of sampling, the acid is dumped and the bottle rinsed three times with sample water. The decontamination procedures are evaluated by checking 5% of the sample bottles. This is accomplished by filling the selected bottles with DI water and analyzing.

The filter holders are soaked in a weak sodium hypochlorite solution before washing to protect the laboratory from any bacteria which may be in the filter holders from the previous sampling process. Filter holders are then washed following the same procedure as inorganic sample bottles.

Filtering syringes are washed with Liquinox™, then rinsed with hot tap water, followed by analyte free water.

Clean bottles/equipment are collected from the lab by field crews and are not shipped.
Bottles for the collection of samples sent to contract laboratories are provided by the laboratory which will be performing the analyses. They have been cleaned by the contract laboratory according to that laboratory's procedures prior to shipment to the District. The laboratory must have approved cleaning procedures in their Comprehensive Quality Assurance Plan.

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 rather, replaced. The sampler and sampler tubing is dedicated to the site. The sampler is programmed to rinse the tubing twice with sample before collection and then purge the tubing after the sample is taken. For the American Sigma Model 6201 autosamplers located at pump stations, the sampler and pump tubing are replaced with clean tubing every four storm events, or, at a minimum, quarterly in the absence of storm events. The pump tubing for American Sigma Model 700 autosamplers is replaced at a minimum quarterly, or preferably, monthly. The entire sampler (American Sigma Model 6201 or 700) is cleaned when it is removed from the site for repair or transferred to another site. In an emergency, pump tubing may be cleaned by soaking in hot water and Liquinox® and scrubbing outside and ends with a small bottle brush. The tubing is then rinsed with hot tap water then DI water. If metals are required the tubing will be rinsed with 10% Nitric Acid. Finally, the tubing is rinsed with DI water and both ends capped with aluminum foil until ready for installation.

6.3.8 Atmospheric Deposition Equipment

Atmospheric Deposition dry and wetfall buckets are cleaned according to section 6.3.1, except for the acid rinse. Once dry, the buckets are capped and taken to the site. Each lot of cleaned buckets is tested for proper decontamination by pouring one liter of DI water into the bucket, swirling, and analyzing for the parameters of interest.

6.3.9 Teflon Tubing/Drop Pipe Decontamination

Teflon tubing and drop pipes are decontaminated in the lab by soaking in hot, soapy water in a stainless steel sink and using a brush to remove particulates on the exterior and inside the tubing ends. After rinsing the interior and exterior with hot tap water, tubing surfaces and ends are rinsed with Nitric acid, DI water, then methanol or isopropanol, and finally DI water. Tubing is then wrapped in fresh aluminum foil. The pre-cut lengths are connected with Teflon inserts or barbs. All cleaning is documented in a bound notebook. The isopropanol or methanol is containerized for proper disposal.

6.3.10 PVC Tubing/Hose

A PVC hose connects the pump to the Teflon drop pipe to collect groundwater samples. This hose is decontaminated by rinsing with DI water, and wiping with clean towels before purging the next well. This PVC hose does not come into contact with the sample or interior of the well. The drop pipe contains a check valve and is removed while the purge pump is still running to reduce the possibility of water draining back into the well from the inside of the suction hose.

6.3.11 Teflon Lanyards

Teflon coated, stainless steel lanyards are decontaminated by washing with liquinox^{R} and hot tap water, then rinsing with DI water and finally Isopropanol. The lanyards are decontaminated in the field by rinsing with DI water and allowing to air dry before the next use.

6.3.12 Analyte Free Water Containers

The analyte free water containers are cleaned in the laboratory using the standard bottle cleaning procedures described in Section 6.3.1 as per EPA SOP & QAM guidelines, Appendix B.

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, estuarine systems, storm water runoff, and agricultural point sources, sampling sites are chosen based on other criteria as described in the appropriate Quality Assurance Project Plans. In any case, the sample must be collected in such manner as to ensure that it is representative of the water body being studied.

6.4.1 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 boat or body.

3. Care is taken not the 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.

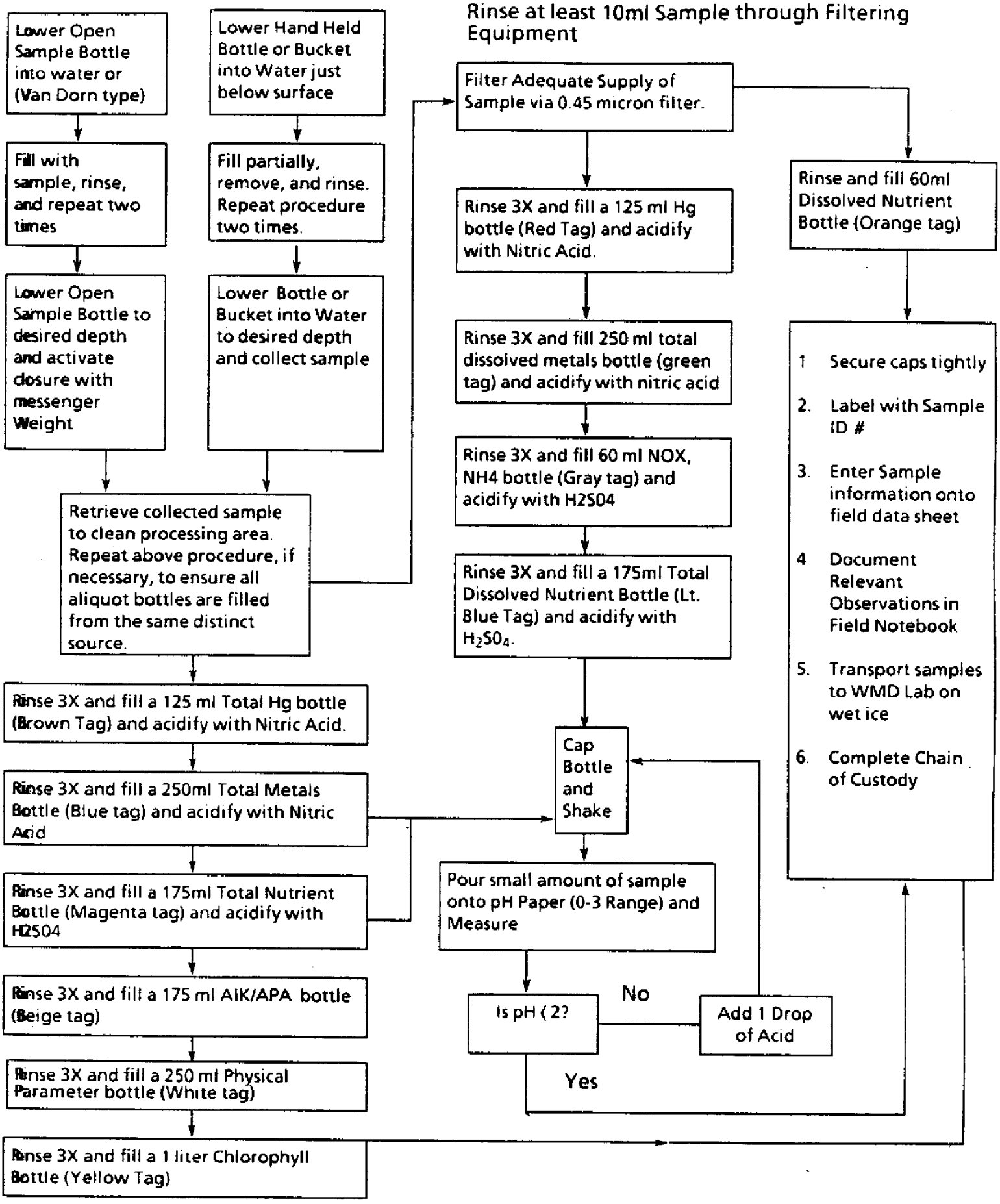
6. Preserve samples according to Table 6.9.

6.4.2 Surface Water - Organics

Surface water samples for organic analysis are collected using a subsurface grab sampler equipped with a precleaned glass bottle provided by the contract laboratory. Samples are collected inside the canal using a small boat. All unpreserved containers (except for VOCs) are rinsed three times before sample collection. The sample containers are immersed inverted to 0.5 meter below the surface, turned upright, pointing in the direction of flow, until full.

For Volatile organic samples, the water sample is poured slowly down the edge of the 40 mL Teflon-lined septum glass vial from the precleaned glass bottle to minimize aeration. The vial is filled to the point of creating a convex meniscus. The septum is placed, teflon side down, on

Figure 6.1 - Inorganic Surface Water Sampling Procedure



the meniscus and sealed with the screw cap. The vial is inverted and lightly tapped on the lid to dislodge any entrapped air bubbles. The absence of air bubbles indicates a proper seal. 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. Fumigant pesticides are collected in the same manner as VOC compounds.

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, and put in wet ice.

The samples are sent to the certified contract laboratory having a DEP approved Comp QAP with appropriate sample identification and chain of custody form provided by 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 for VOC analysis are placed into separate bubble-pack bags for each station. Coolers are taped shut with shipping tape and shipped to the laboratory using common carrier overnight delivery.

6.4.3 Surface Water - Autosamplers

Water quality autosamplers are used for the collection of daily composite or discrete samples at selected sample sites. The sampling procedure is controlled by the automatic sampler programming. The automatic sampler, American Sigma Model Streamline 700, Program Version 3.1, is programmed to rinse the sample collection tubing twice prior to sample collection and to purge the tubing following collection. The samplers are programmed for daily composite to collect an 80 mL sample at 144 minute intervals and add it to the correct composite sample bottle for a total of 10 samples per bottle. When samples are analyzed for total Kjeldahl nitrogen and total phosphorus only, one ml of 50% sulfuric acid is pre-added to the autosampler bottles in the field. This amount of acid has been determined to maintain pH <2 after sample collection. The pre-acidified bottles are capped and transported to the field, positioned in the autosampler, and uncapped.

Short holding time parameters are not routinely collected using an automatic sampler. Sampler bottles are not preacidified. The samples are collected within 24 hours after compositing has been completed, and analyzed within holding times.

After sample collection the bottles are capped, thoroughly mixed by inverting five times, labeled, placed on ice immediately and transported to the field laboratory and stored at 4°C. Within 24 hours, aliquots of the samples are transferred to 250 mL bottles, tagged, and stored at 4°C until transported to the analytical laboratory. Samples are submitted to the analytical laboratory within two days of the day the sampler was serviced. This procedure is only followed for long holding

time parameters.

The Sampler intakes at tributary sites are positioned six to eight inches from the bottom to avoid contamination from bottom sediments and a minimum of eight to ten feet from the tributary shoreline. Sampler intakes at water control structures are located 1 to 2 feet below the surface and 1 foot off the wing wall.

American Sigma Model 6201 autosamplers located at pump stations are dedicated to the site and work in synchrony with each of the pumps in the pumping battery. The autosampler is activated once any of the pumps becomes operational, and it collects a 50 ml aliquot for every 10,000 RPM on each operating pump. The aliquot is dispensed into a refrigerated five gallon polyethylene bottle. The refrigerated composite sample is homogenized by shaking the capped bottle. An aliquot is transferred unfiltered to a 250 mL sample bottle and another aliquot is filtered into a 60 mL sample bottle, for TKN, TPO_4 and NO_x, NH_4 testing, respectively. Both aliquots are preserved as indicated in Figure 6.9.

Autosamplers are dedicated to a specific location as long as they are working properly. 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.

6.4.4 Sediment/Soil

Sediment samples for organics are collected by hand grab using a stainless steel scoop, stainless steel petite Ponar™ dredge, or stainless steel core. The stainless steel scoop 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. Samples are not composited or sectioned into subsamples. The stainless steel core is used when collecting shallow sediment samples. Each sample (except VOC) is thoroughly mixed in the stainless steel bowl with a precleaned 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 precleaned stainless steel spool 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.

Duplicates are collected to measure the variability inherent in the sampling process. Duplicates

for sediments are collected from the same sampling device. 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 VOC are to be performed, the sample containers must be glass with teflon lined lids. VOCs bottles must have a teflon-lined septum. For other classes of analytes, glass or plastic jars may be used as sample containers. The containers are completely filled with sample so that air bubbles are not trapped in the container. This is necessary in order to minimize sample oxidation that could influence certain test results. The best way to minimize trapped air is to very gently pack the sample into the container with the spoon or scoop. Preserve according to Table 6.11.

Sediment samples are collected using PVC cores 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 that 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.

Field equipment is cleaned prior to the field trip and after each sample according to the procedures described in Section 6.3.5.

6.4.5 Ground Water

After collection the samples are tagged, preserved, and immediately placed on ice in a closed container. Exposure of the organic samples to sunlight is kept to a minimum. When VOCs are collected, trip blanks are kept with the organic 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. Filtered samples are collected using a Teflon bailer. The bailer has been modified so that a QED Sample Pro FF-8200 High Capacity 0.45 micron filter can be attached directly to the base of the bailer. The top of the bailer has an attachment so that the bailer can be pressurized to force the water through the filter (all parts are Teflon).

The first 100 mL of sample water 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. Unfiltered samples are collected in conjunction with filtered samples for metal analysis. A 1.0 micron filter is used for dissolved metals collected for permits.

Bottles are supplied by the SFWMD laboratory. If the analyses are to be performed by an outside contract lab, the bottles have been cleaned by the contract laboratory according to that laboratory's procedures prior to shipment to the SFWMD. The laboratory must have approved cleaning procedures in their Comprehensive Quality Assurance Plan, and perform a 5% analytical check on the washing procedure.

6.4.5.1 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 source and before any screens, aerators, filters, etc. The flow rate is reduced to less than 500 mL/min when collecting samples to avoid any undue disturbance. Unfiltered samples are collected directly into the sample containers from the spigot and filtered samples are collected from the spigot into the bailers.

Duplicates are collected by sampling from consecutive bailers. 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.

6.4.5.2 Flowing Artesian Wells

These wells are purged until three bore volumes have been purged, 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.

6.4.5.3 Monitoring Wells

A protective covering of visqueen plastic is placed on the ground at all sampling sites to reduce the potential for contamination. A fresh pair of disposable non-powdered latex gloves are worn at each sample site and while purging and collecting samples. The water depth relative to a measuring point is measured using a graduated steel tape and chalk, or a sonic distance measuring device. The depth to water is measured twice and both values are recorded in the sampler's field log. 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. The Sonin electronic unit is used only when the depth to water is less than 15 feet. In this range of 0 - 15 feet, the unit is accurate to within $\pm$ 0.1 foot. A steel tape is used for the depth to water if greater accuracy is needed or it the depth to water is greater than 15 feet.

The well is then purged by bailer or by a purge pump. Purge pumps are gas powered and extreme care must be used when handling and locating these pumps to minimize on-site contamination (placed away and downwind from any sampling activities). The purge pump consists of a centrifugal suction pump that never contacts the water within the well. A flexible PVC suction hose connects the pump to a three foot length of rigid Teflon drop pipe. The portion of the drop pipe to become in contact with the water column is cleaned prior to use as per the procedures outlined for other sampling equipment in section 6.3.1. The drop pipe 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 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, the drop pipe is lowered to the new water level. If the water level is drawn down too severely, the purging rate is decreased. The SFWMD does not collect samples at any well with a depth to water of more than 25 feet, thus submersible pumps are not used for sampling.

The well is purged until a minimum of three standing water volumes are removed. The volume of water to be purged is calculated using the following terms: Depth of well (DW) in feet, depth to water (DTW) in feet, and casing diameter (D) in inches. The minimum purge volume (three water column volumes) in gallons, is given by:

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

The volume of water removed from the well must be calculated to avoid excess purging. The flow rate is estimated by measuring the amount of time required to fill a container 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. Though a minimum of three water column volumes must be purged, the well is not considered purged until the well has chemically stabilized. Temperature, pH and conductivity are monitored and readings are recorded at 5 minute time intervals, or at shorter intervals if necessary. Irrigation well readings are taken at intervals required to purge one half the bore volume. These measurements are made in a flow through chamber to minimize atmospheric contact with the sample. The well is considered to be chemically stable when three consecutive sets or readings are within the following ranges: temperature +/- 0.2°C, conductivity +/- 5%, and pH +/- 0.1 unit. The purge volume is noted in the field log. All measurements that were recorded while waiting for the well to stabilize are recorded in the field

log. Only the final readings taken after the well has stabilized are input into the sample results database. The drop pipe is slowly raised while the purge pump is on 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, dry purged or slow recovery, for which recovery cannot be accomplished in 4 hours or less.

All samples are collected using a Teflon bailer. When handling bailers or sample containers, disposable latex gloves are worn. Prior to the collection of the samples, the well is purged three times with a Teflon bailer. This procedure is done to ensure that any water that was in contact with the Teflon drop pipe has been removed. The bailer is suspended by a Teflon coated stainless steel lanyard that is carefully lowered into the well. 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 to avoid sample aeration. The first few inches of sample in the bailer are discarded. The sample bottles are filled from the bailer.

The SFWMD does not use temporary well points or dedicated equipment for ground water monitoring. Samples are not collected from wells that have free product showing. Disposable lanyards are not used.

6.4.6 Biological Tissue

6.4.6.1 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.

6.4.6.2 Below Ground Macrophyte Biomass

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

6.4.7 Hazardous Wastes/Drums

The SFWMD does not sample hazardous waste or drums.

6.4.8 Waste Water

The SFWMD does not sample waste water.

6.4.9 Microbiological

Microbiological samples are collected with extra care in order to prevent sample contamination. The samples are not composited. The personnel collecting the samples do not touch the rims/ top of the whirlpaks™. Field personnel are instructed to discard a sample container if they think that the top was touched. Microbiological sampling is closely coordinated with the laboratory performing the analyses to ensure that samples are analyzed within holding times.

6.4.10 Oil and Grease

The SFWMD does not sample for oil and grease.

6.4.11 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 macrobenthic invertebrate 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.

a. 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 organism escapement. Visual inspection of each sample is necessary to ensure an adequate amount of sample is obtained.

b. 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.

c. 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 waterbody 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.

d. 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 perfromed 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.

6.4.12 Atmospheric Deposition

Atmospheric deposition samples are collected according to the National Atmospheric Deposition Program (NADP) guidelines.

The District uses Aerochem Metric Wet/Dry Precipitation collectors. The Aerochem is an aluminum structure with two 3.5 gallon PVC buckets which serve as receptacles for wet and dry deposition. An aluminum lid covers the wet side bucket under dry conditions. When the humidity sensor detects rain, the lid slides over the dry side bucket, uncovering the wet side bucket. All buckets are collected on Tuesdays only, according to NADP guidelines. 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 taken into the field, one bucket from each decontamination lot is checked by pouring one liter of DI water into the bucket and processing 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). Live frogs, insects and nonreprsentative foreign matter are removed with a clean scoop or tweezer. Any removed contaminants are documented in the field notebook. The sample is then processed as a routine surface water sample, including filtration and preservation as required. Processing equipment blanks, splits and field blanks are submitted according to routine QA procedures.

Dry side buckets are inspected for contamination as above. Only loose contamination is removed (with clean tweezers/spatula). Approximately 600 ml of DI water is added to the dry bucket contents rinsing the sides of the bucket. A precleaned spatula is used to rub the inside bottom and sides of the bucket. The total amount of DI water added should not exceed one liter and the volume must be recorded in the field notebook. The sample is then processed as a routine surface water sample, including filtration and preservation as required. Processing equipment blanks, splits and field blanks are submitted according to routine QA procedures.

6.4.13 Duplicates/Split Samples

Duplicates are collected to measure the variability inherent in the sampling process, and should be obtained by duplicating in rapid succession during the same sampling event, the entire acquisition technique used to obtain the first sample. Duplicates for water are collected by sampling from successively collected volumes. Duplicates for soils are collected from the same sample source (i.e., soil obtained from the same soil sampling device). Split samples are collected to measure the variability between laboratories, and should be obtained as subsamples taken from the same parent sample (a true split of soil, sediment or sludge is almost impossible to accomplish under field conditions; a split soil sample should be considered a duplicate and not a split sample). Split samples (for water) are taken from consecutive sample volumes from the same sampling device (i.e. from same bailer), or by mixing in a large intermediate vessel.

Note: 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 (the second half into the second set of containers), then first half volume of second bailer load is poured into the second set of containers (second half into first set of containers) etc. until both sets are full.

6.5 Documentation

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

1. Field Trip Checklist (surface water)
2. Chemistry Field Data Log
3. Bound field notebook (project specific)

6.6 Preservation

Holding times and preservation techniques for each parameter are given in Tables 6-9, 6-10, 6-11, 6-12 and 6-13.

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 the pH (0 - 3 pH units) test strip to ensure pH <2. If pH is not <2, additional acid is

Table 6.9 Holding Time and Preservation for Water Inorganics[1]

Parameter	Holding Time	Preservative	Container & Size
Alkaline Phosphatase[2]	24 hours	Cool, 4°C	Plastic, 175 mL
Alkalinity	14 days	Cool, 4°C	Plastic, 175 mL
Ammonia	28 days	Cool, 4°C, pH<2(H_2SO_4)	Plastic, 60 mL
Chloride	28 days	None required	Plastic, 60 mL
Chlorine, Total Residual	Analyze immediately	None required	Plastic or Glass, 250 mL
Color	48 hours	Cool, 4°C	Plastic, 60 mL
Fluoride	28 days	None required	Plastic, 250 mL
pH	Analyze immediately	None required	Plastic, 250 mL
Kjeldahl nitrogen	28 days	Cool, 4°C, pH<2(H_2SO_4)	Plastic, 175 mL
Mercury	28 days	pH<2(HNO_3)	Plastic, 125 mL
Metals	6 months	pH<2(HNO_3)	Plastic, 250 mL
Nitrate + nitrite	28 days	Cool, 4°C, pH<2(H_2SO_4)	Plastic, 60 mL
Nitrite	48 hours	Cool, 4°C	Plastic, 60 mL
Organic carbon	28 days	Cool, 4°C, pH<2(H_2SO_4)	Plastic, 250 mL
Orthophosphate	48 hours	Filter immediately, cool, 4°C	Plastic, 60 mL
Total phosphorus	28 days	Cool, 4°C, pH<2(H_2SO_4)	Plastic 175 mL
Residue, filterable, nonfilterable, volatile	7 days	Cool, 4°C	Plastic 250 mL
Silica	28 days	Cool, 4°C	Plastic, 60 mL
Specific conductance	28 days	Cool, 4°C	Plastic, 60 mL
Sulfate	28 days	Cool, 4°C	Plastic, 60 mL
Turbidity	48 hours	Cool, 4°C	Plastic, 250 mL

(1)From 40 CFR, Part 136, Table II (7-1-90)
(2)Alkaline Phosphatase is not listed in 40 CFR, Part 136, Table II (7-1-90)

Table 6.10 Holding Time and Preservation for Water Organics

Parameter	Holding Time	Preservation[1]	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, 1L, Teflon lined cap

(1) If residual chlorine is present, NA thiosulfate 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[1]

Parameter	Holding Time	Preservation	Container & Size
Volatile organics	14 days	Cool, 4°C	Glass, 4 oz. widemouth with Teflon/silicone septum
Semivolatile organics	14 days until extraction, 40 days after extraction	Cool, 4°C	Glass, 8 oz. widemouth with Teflon/silicone septum (50 grams)
Total metals	6 months	Cool, 4°C	Glass or plastic, 8 oz. widemouth (200 grams)
Mercury	28 days	Cool, 4°C	Glass or plastic, 8 oz. widemouth (200 grams)
Nutrients & Inorganics[2]	Not Specified	Cool, 4°C	Glass, 500 ml or plastic, 8 oz. widemouth with Teflon lined closure

(1) From Table 5, Chapter 17-160, F.A.C.
(2) From USEPA Standard Operating Procedures and Quality Assurance Manual (Appendix A).

Table 6.12 Holding Times and Preservation for Microbiologicals[4]

Parameter	Holding Time	Preservation[2]	Container[3]
Microbiologicals[1]	6 hours	Cool, 4°C/$Na_2S_2O_3$	Glass or Plastic > 125 ml

(1) Parameters included are: Fecal Coliform, Total Coliform and Fecal Streptococci.
(2) Addition of sodium thiosulfate is only required if the sample has a detectable amount of residual chlorine, as indicated by a field test using EPA Method 330.4 or 330.2 or equivalent.
(3) Presterilized Whirlpak bags (or equivalent) are typically used for sampling.
(4) From Table 8, Chapter 17-160, F.A.C.

Table 6.13 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, 4oC, dark filter with Mg CO3, (ii) Filter frozen (until testing)	Plastic, 1 L
Macrobenthic Invertebrates	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

added drop-wise, the bottle is capped and shaken, and the pH is tested again. This procedure is followed until 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 weekly for all sampling trips. Preservatives are taken into the field in polyethylene bottles.

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. Insulated coolers are used for sample shipment and are sealed with shipping tape to avoid tampering. If samples must be kept at 4°C, wet ice is used.

6.8 Field Waste Disposal

All field generated wastes and contaminated purge waters are segregated and containerized for proper disposal including the use of the services of a commercial disposal company, if required. 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/or neutralized and flushed down the sanitary sewer. The calibration standards for field parameters are flushed into the sanitary sewer.

6.9 Field Reagent and Standard Storage

Table 6-14 lists the storage procedures for reagents, standards and solvents.

Table 6-14. Reagent, Solvent and Standard Storage

Chemical	Method of Storage
Sulfuric Acid	Stored in original containers in vented acid storage cabinet. Note: Each acid is stored in a separate cabinet. Acid is transported in the field in polyethylene dropper bottles.
Nitric Acid	See above.
Phosphoric Acid	See above.
Hydrochloric Acid	See above.
Isopropyl Alcohol	Stored in original containers in vented solvent storage cabinet. No other solvents are stored in the same 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. No other solvents are stored in the same cabinet. Taken into the field in approved combustible containers.

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. SFWMD does not require legal custody procedures be used as the only samples analyzed in the District laboratory are not used in criminal court cases at this time.

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. This person, who may be an Assistant Scientific Technician, Scientific Technician, Senior Scientific Technician or Technician Supervisor, obtains the appropriate size precleaned bottles from the bottle storage area. This person signs the trip checklist (Figure 7-1) when all items necessary have been prepared and loaded into the vehicle.

The field sheets become a part of the project records maintained by the project manager with copies retained by the laboratory. Entries on all records, laboratory and field, are made in waterproof ink with errors deleted by crossing one line through them. All field documentation is signed or initialed by the field personnel.

Samples of the documentation are given in Figures 6-1 and Figures 7-1 through 7-4.

Figures 7.2 and 7.3 show the sample tags which include the preservation instructions, bottle size to use, and the parameters to be tested. Information on the tag includes the date the sample was taken and the sample number. The sample number is a unique sequential number for that project. Sample seals are not used by SFWMD.

Figure 7-4 shows the Chemistry Field Data Log used to record the field information. This data is manually entered into the laboratory information management system (LIMS) through the Sample Log-In screens shown in Figure 7-5 and 7-6. 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 for a given project on a given day. The sample number is used to track the progress of the sample through the laboratory.

The Chemistry Field Data Log includes the site name or station code, the date and time of

FIGURE 7.1

FIELD TRIP PREPARATION AND CHECK-OFF LIST

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

_____* Travel Request
_____* Sign Out Board
_____* Maps
_____* Vehicle Packet/Credit Cards

_____* Sign Out Vehicle
_____* Gas Vehicle
_____* Maintenance Check
_____* Coolers/Ice

_____* Pre-Cleaned Buckets
_____* Loaded Filters ____
_____* Yellow Tray

_____* Syringes
_____* Sampling Bottle

_____* Calibrated Hydrolab/Battery
_____* Field Notebook_____
_____* Tags/Rubber Bands

_____* Field Data Logs
_____* Waterproof Pens

_____* Fresh Acids- H_2SO_4 / HCl / HNO_3
_____* Goggles, Gloves
_____* 5 Gallons DI Water

_____* Trip Spikes
_____* pH Test Strips

_____* Bottles: 250ml- ___, 60ml- ___, 175ml-___, 250ml/TM-___
_____* Bottles: One Liter Bottle for EB(Equipment Blank)

_____* Stations: Routine / As Specified:_____
_____

_____* Keys:_____

PERSONAL ITEMS

_____* Watch
_____* Hat
_____* Food

_____* Sunglasses
_____* Sunscreen
_____* Mosquito Repellent

_____* Drinking Water
_____* Raingear

POST TRIP PROCEDURES

_____* Sort Samples in Sequence and by Tag Color
_____* Place Samples in Refrigerator(on Floor)
_____* Sign Chain of Custody on Header Sheet/Get Time Stamp
_____* Get Manager's Initials on Header Sheet & Turn In to Lab
_____* Return Clean Bottles to Bins in Trailer
_____* Separate Filter Holders and place in Soak Solution
_____* Place Dirty Bottles in Outside Closet at Lab
_____* Rinse Sampling Bottle with D.I. Water and Store
_____* Replace Water in Hydrolab Stand(Tap Water Only!)
_____* Clean Out Vehicle
_____* Park Vehicle at B113 Lot/Fill Out Trip Ticket/Return Keys
_____* Return Field Notebooks to Larry's Office
_____* Report Equipment(Vehicle,Hydrolab, etc.) Problems to Larry
_____* Return Signed Prep List to Larry

INITIALS-_____

Figure 7.2 SAMPLE SUBMISSION DIAGRAM FOR UNFILTERED WATER

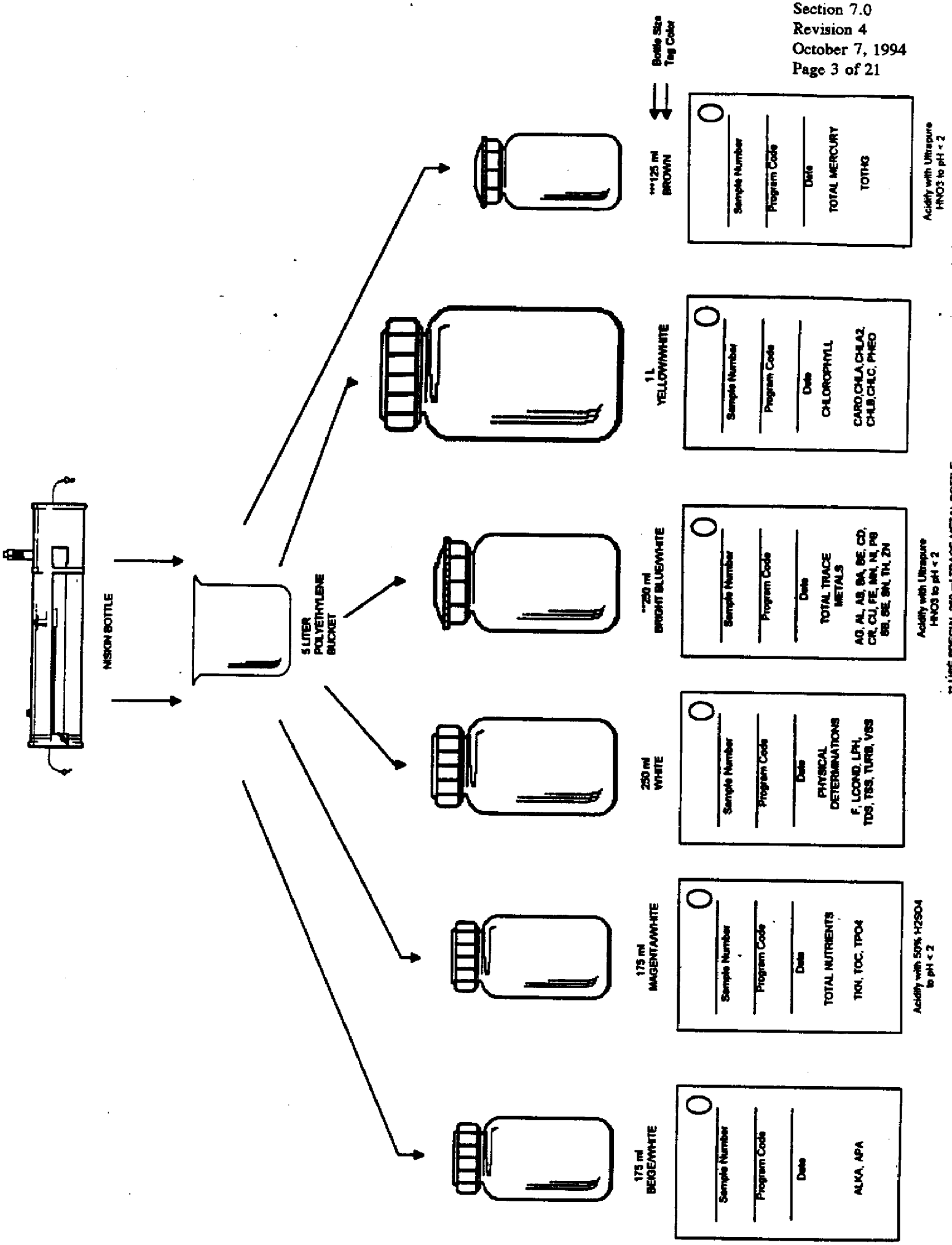


Figure 7.3 SAMPLE SUBMISSION DIAGRAM FOR FILTERED WATER

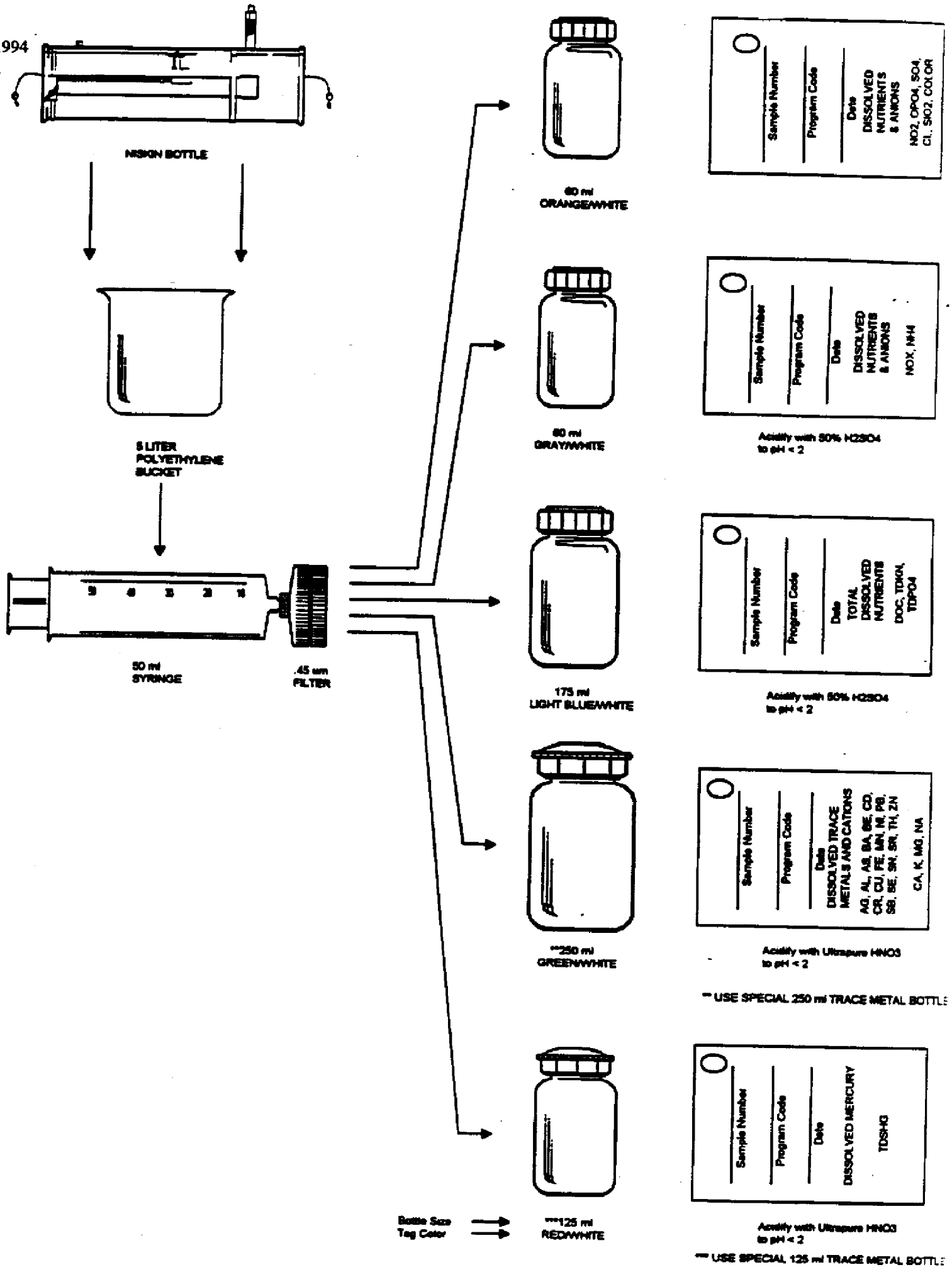
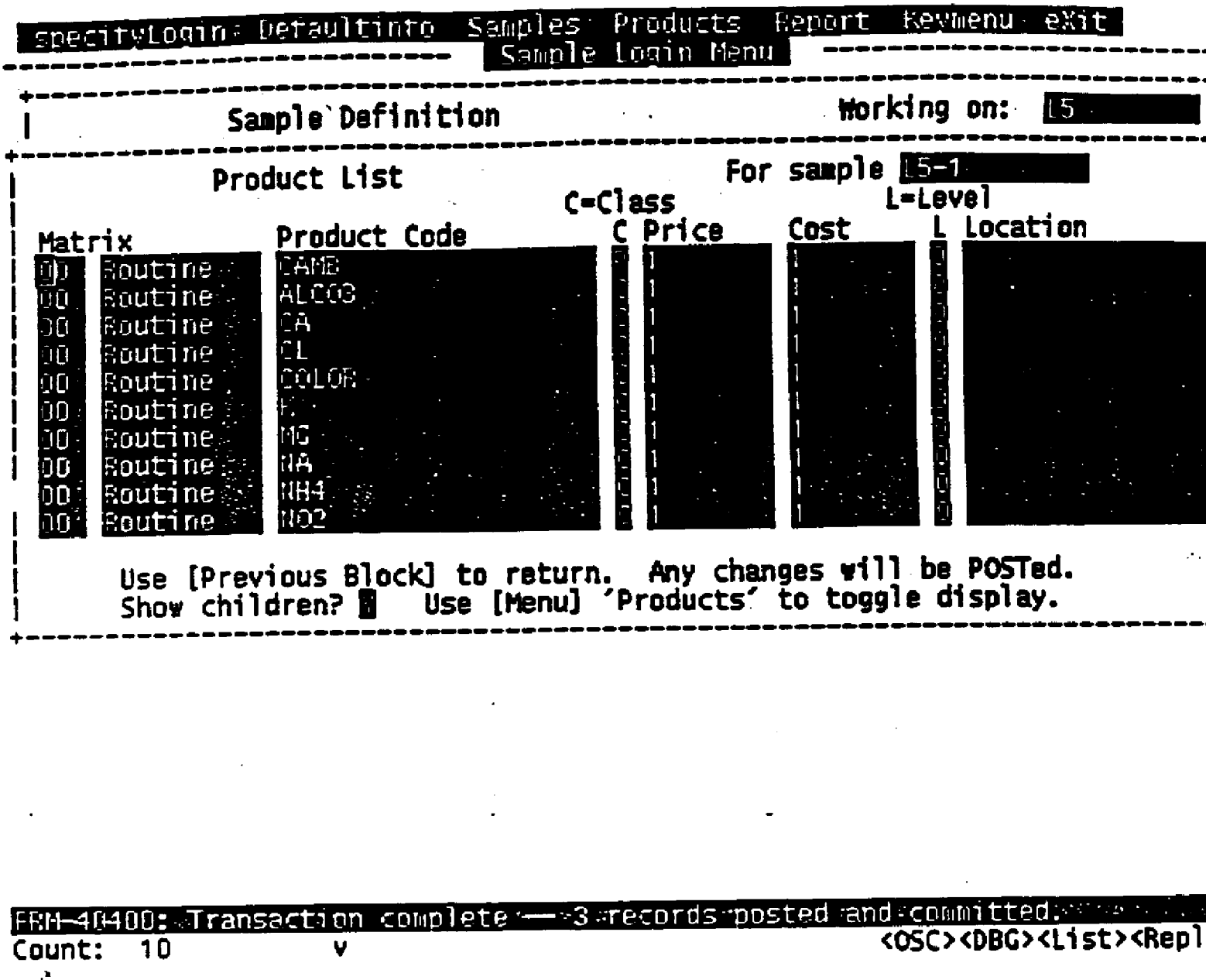


FIGURE 7.6 - SAMPLE PRODUCT LIST



FRM-40400: Transaction complete — 3 records posted and committed.
Count: 10 <OSC><DBG><List><Repl

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. Common carrier is not used for samples analyzed by the District laboratory.

The sample preparation (digestion) logs are maintained in bound laboratory notebooks. The information required is the laboratory sample number, standards, QC samples, dilution factors, signature or initials of person preparing samples, and the date of preparation. The analysis logs for each type of instrument are shown in Figures 7-7 to 7-10. The microbiology logs are shown in Figures 7-11 to 7-14.

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 precleaned sample containers received from the contract laboratory are delivered to the project manager who is responsible for their secure storage.

7.2 Field Custody Protocols

The samples are tagged at the time of collection using waterproof Tyvek™ tags which have been filled out with waterproof pens. The tags are attached with rubber bands to the neck of the sample bottle.

Each project has a unique four character project code. The sample field numbers are generated by a combination of this project code and up to a five digit sequential project number that unequivocally links the collected sample to the time and date of collection, and sampling point. The field sample 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, 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 shall be written on the Chemistry Field Data Log shown in Figure 7-4 at the time of sample collection. These measurements include temperature, pH, specific conductivity, dissolved oxygen, oxidation-reduction potential, secchi disc depth, total column depth, 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

CHEMISTRY FIELD DATA LOG

Figure 7.4

LIMS NUMBER	NB	SAMPLE NUMBER	DATE/TIME COLLECTED				STATION	FQC	UD	DS	WE	TYPE	FIELD WATER QUALITY DATA								TDEPTH	COMMENTS
			MO	DA	YR	TIME							DEPTH	TEMP	PH	COND	DO	SDD	SALINITY	REDOX		

Please circle the tests to be performed on the above samples.

ITE (250 ml)	MAGENTA (175 ml) H_2SO_4 pH < 2	ORANGE (60 ml)	LIGHT BLUE (175 ml) H_2SO_4 pH < 2	GREY (60 ml) H_2SO_4 pH < 2	BEIGE (175 ml)	YELLOW (1 L)	BRIGHT BLUE (250 ml) HNO_3 pH < 2		GREEN (250 ml) HNO_3 pH < 2			BROWN (125 ml) HNO_3 pH < 2	RED (125 ml) HNO_3 pH < 2
LPH	21 TKN	13 COLOR	26 TDPO4	16 NOX	67 ALKA	63 CARO	96 TOTAG	110 TOTMN	52 TDSAG	48 TDSMN	30 CA	102 TOTHG	49 TDSHG
LCOND	25 TP04	23 OPO4	22 TDKN	20 NH4	186 APA	61 CHLA	68 TOTAL	118 TOTNI	39 TDSAL	50 TDSNI	31 MG		
TURB	100 TOC	19 NO2	89 DOC			112 CHLA2	106 TOTAS	107 TOTPB	40 TDSAS	46 TDSPB	28 NA		
TSS		32 CL				62 CHLB	108 TOTBA	189 TOTSB	41 TDSBA	173 TDSSB	29 K		
VSS		33 SO4				113 CHLC	170 TOTBE	101 TOTSE	174 TDSBE	51 TDSSE			
F		27 SIO2				64 PHEO	103 TOTCD	172 TOTSN	42 TDSCD	178 TDSSN			
TDS							72 TOTCR	171 TOTTH	43 TDSCR	53 TDSSR			
							104 TOTCU	105 TOTZN	45 TDSCU	175 TDSTH			
							170 TOTFE		171 TDSFE	54 TDSZN			

Laboratory use only.

Received By (Initials) _____ Date _____

Login Group _____ Sample _____

Test List Code _____

WQM - 2

Relinquished By (Signature) _____ Date _____ Time _____

FIGURE 7.5 - SAMPLE LOG-IN TO LIMS

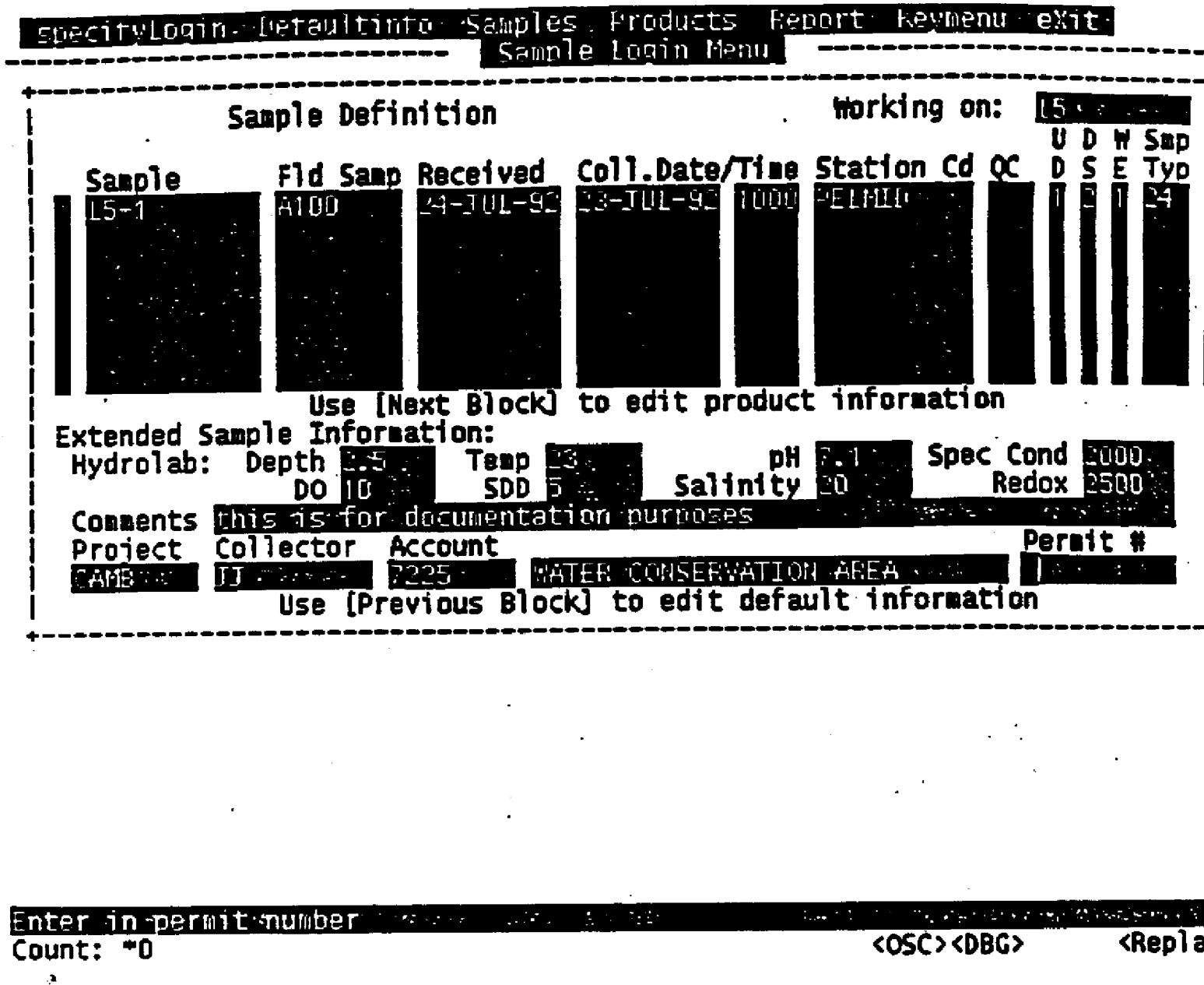


FIGURE 7.7 ATOMIC ABSORPTION ANALYSIS LOG

Parameter _____ Number of Samples _____ Date _____

High Standard _____ Operator _____

Detection Limit _____ Method file name _____ Flame Furnace (circle 1)

CALIBRATION INFORMATION

	CONCENTRATION	ABSORBANCE
S1		
S2		
S3		
S4		
S5		

FILE NAMES

ID/WT filename _____

Data filename _____

Name of file transferred to the LIMS _____

Samples _____

Comments/Problems _____

QUALITY CONTROL

QC1 _____ QC2 _____

Accepted Values: _____ _____

Repeat: X = _____

Std. Dev. = _____

Coef. Var. = _____

Stad. Add. % Recovery:

1. _____
2. _____
3. _____
4. _____

FURNACE PARAMETERS

Step	1	2	3	4	5	6
Temp °C						
Ramp (s)						
Hold (s)						
Read						
Rec.						
Baseline						
Int. Flow (ml/min)						

Graphite Tube: _____

Sample Volume: _____

Modifier Vol. _____

Replicates _____

Purge Gas _____

FLAME PARAMETERS

_____ : _____ (gas)

Burner _____

Modifier _____

Figure 7.8 P-E 3600 I.D./W.T. FILE

I.D. / W.T. FILE: _____ SAMPLE WEEK: _____

DATE: _____ DISC. #: _____

ANALYST: _____

PAGE: _____

PARAMETER				
ABSORBANCE				
DATA FILE				

	LIMS NUMBER		PROJECT CODE	SAMPLE NUMBER	DILUTIONS/RERUNS			
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								

Rapid Flow Analyzer Log

Figure 7.9

Technician _____ Date _____

Parameter _____ Std. Cal _____

High or Low (Circle One)

C F Method Number _____ Instrument# _____

Tray Protocol File Name	Sample Numbers
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____

Comments: _____

CALIBRATION:

CHANNEL 1: _____ CHANNEL 2: _____

_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

QUALITY CONTROL:

QC1: _____

QC2: _____

C.V.: _____

STAD: _____

_____

_____

_____

GAIN: _____

_____

FIGURE 7.10 - PHYSICAL PARAMETERS LOG

Calibration Log for Physical Parameters

ANALYST. _____ DATE _____

PARAMETER: _____

STANDARDS:

Known Value	Instrument Reading
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____

REP NO. QUALITY CONTROL SAMPLES:

	QC1 True Value _____	QC2 True Value _____
( )	_____	_____
( )	_____	_____
( )	_____	_____
( )	_____	_____
( )	_____	_____
( )	_____	_____

REPEAT SAMPLE READINGS:

( ) _____	( ) _____	( ) _____	( ) _____
( ) _____	( ) _____	( ) _____	( ) _____
( ) _____	( ) _____	( ) _____	( ) _____

SAMPLES ANALYZED: _____

_____

Figure 7.11 TOTAL COLIFORM MEMBRANE FILTER TECHNIQUE (SM #909 A)

SAMPLE ID	DATE -TIME		SAMPLE	WATER BATH	CFU/ 100 ml		LOT #-MANUFACTURER-pH				INCUBATION	CONFIRMATION			ANALYST
	COLLECTION	ANALYSIS	DIL. (ml)	DATE-TIME-TEMP. IN: OUT:	TC	NC	MEDIA	RINSE BUFFER	FILTER	PETRI DISH	DATE-TIME-TEMP. IN: OUT:	LTB	BGB	EC	
							GELMAN		GELMAN	GELMAN					
							GELMAN		GELMAN	GELMAN					
							GELMAN		GELMAN	GELMAN					
							GELMAN		GELMAN	GELMAN					
							GELMAN		GELMAN	GELMAN					
							GELMAN		GELMAN	GELMAN					
							GELMAN		GELMAN	GELMAN					
							GELMAN		GELMAN	GELMAN					
							GELMAN		GELMAN	GELMAN					
							GELMAN		GELMAN	GELMAN					
							GELMAN		GELMAN	GELMAN					
							GELMAN		GELMAN	GELMAN					
							GELMAN		GELMAN	GELMAN					
							GELMAN		GELMAN	GELMAN					
							GELMAN		GELMAN	GELMAN					
							GELMAN		GELMAN	GELMAN					
							GELMAN		GELMAN	GELMAN					

NOTE: T=TURBID G=GAS C=CLEAR NG=NO GAS

Figure 7.12 FECAL COLIFORM MEMBRANE FILTER TECHNIQUE (SM #909 C)

SAMPLE ID	DATE -TIME		SAMPLE	WATER BATH	COUNTS		LOT #-MANUFACTURER				INCUBATION	CONFIRMATION		CFU/	ANALYST
	COLLECTION	ANALYSIS	DIL. (ml)	DATE-TIME-TEMP. IN: OUT:	FC	NFC	MEDIA	RINSE BUFFER	FILTER	PETRI DISH	DATE-TIME-TEMP. IN: OUT:	24 hr	48 hr	100 ml	

NOTE: T=TURBID G=GAS NG=NO GROWTH NG=NO GAS

SAMPLE ID	DATE TIME OF	MEDIA	RINSE BUFFER	INCUBATION	DILUTION	PRESERVATIVE	CONFIRM	COMPLETE	MPN /100ML	ANALYST	COMMENTS
	COLLECTION: ANALYSIS:	LOT #: pH:	LOT #: pH:	DATE IN: OUT:							
				TIME IN: OUT:							
				TEMP DEG. C IN: OUT:							
	COLLECTION: ANALYSIS:	LOT #: pH:	LOT #: pH:	DATE IN: OUT:							
				TIME IN: OUT:							
				TEMP DEG. C IN: OUT:							
	COLLECTION: ANALYSIS:	LOT #: pH:	LOT #: pH:	DATE IN: OUT:							
				TIME IN: OUT:							
				TEMP DEG. C IN: OUT:							

FECAL STREPTOCOCCUS MEMBRANE FILTRATION (SM #910 B) **Figure 7.14** ANALYST

SAMPLE ID												
TIME &DATE COLLECTION												
TIME &DATE ANALYSIS												
DILUTION												
RAW COUNTS												
IN INCUBATION TEMP&DATE												
OUT INCUBATION TEMP&DATE												
MEDIA MANF& LOT#	Difco	Difco	Difco	Difco	Difco	Difco	Difco	Difco	Difco	Difco	Difco	Difco
FILTER MANF& LOT#	GELMAN	GELMAN	GELMAN	GELMAN	GELMAN	GELMAN	GELMAN	GELMAN	GELMAN	GELMAN	GELMAN	GELMAN
PETRI DISH MANF& LOT#	GELMAN	GELMAN	GELMAN	GELMAN	GELMAN	GELMAN	GELMAN	GELMAN	GELMAN	GELMAN	GELMAN	GELMAN
BUFFER LOT# &PH												
CONFIRMATION CATALASE												
MEDIA LOT# & PH BHI AGAR BHI BROTH BHI+40%BILE												
IN TIME DATE TEMP												
OUT TIME DATE TEMP												
CFU/ 100ML												

Bubbles indicates a + catalase (indicates presence of non streptococcus) No bubbles indicates a - catalase (streptococcus present

7.3.2 Sample Security, Accessibility, and Storage

The samples are accessible to the laboratory staff during working hours. The door to the exterior of the building and the door to the main hallway are locked when the last member of the staff leaves for the day. The door to the sample receiving area is opened at 7:00 A.M. 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 laboratory staff.

Samples are stored in refrigerators designated for sample storage only. No VOC's are stored in the laboratory refrigerators and standards are stored in refrigerators designated for standard storage.

Sample digestates are stored in the digestion laboratory until they are analyzed. Analysis takes place within 48 hours for nutrients and within 30 days for trace metals.

7.3.3 Sample Distribution and Tracking

The analysts check the database daily for samples requiring their assigned analyses and make work groups for these samples. They 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 review of the results, the laboratory supervisor removes the samples which are ready for disposal from the refrigerators. The status of the sample is changed from NEED to DONE in the disposal department in LIMS. Samples are disposed of by diluting and dumping into the sanitary sewer. The SFWMD does not analyze hazardous waste samples. Digestates containing hazardous materials, (i.e. the mercury in Kjeldahl nitrogen digestates), are treated as hazardous waste and are collected and stored for disposal by a commercial hazardous waste company.

7.3.4 Interlab Custody

The SFWMD has only one laboratory and does not transfer samples to any other laboratory. However, in the event of catastrophic failure, samples will be transported to a contract lab by common carrier accompanied by the log in sheets and the contract lab's chain of custody.

7.4 Electronic Data Records

A LIMS is used by SFWMD for sample tracking, data storage, and data reduction.

7.4.1 Security System

The LIMS has several levels of security. The Staff Programmer Analyst responsible for the operation and maintenance has the highest level of security and can access all information and programs in LIMS. The Division Director, Laboratory QA Officer, Supervising Professionals and Senior Chemists can access and modify all sample and results information. The analysts can enter analytical results but cannot modify the sample information or results. The project managers can only read and print results. User names and passwords are assigned to each person. Back up of both the file system and database is performed daily so that in the event of catastrophe, only one day of data would be lost. One week's worth of system files is stored in the vault.

7.4.2 Forms

Project Managers review weekly data results and identify tests for rework or field sample data for modification. These copies are stored by date produced and are kept according to the record management standards.

7.4.3 Electronic Data Transfer

All requests for copies of the data, electronic or hard copy, are made through the appropriate project manager. All data at SFWMD is public information. The project manager is responsible for requesting the data and submitting it to the requestor. 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 is maintained by the Staff Programmer Analyst who is responsible for maintaining the documentation records and the maintenance logs. 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 Staff Programmer Analyst.

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. The evaluation of the results must yield no

site ID, parameter analysis, types of QC samples collected (when and where collected), depth sample was collected, requested parameters and chain of custody documentation. Beginning and ending times of any composite sampling is noted. Optional information on this form includes upstream/downstream notation, discharge information, weather, sample type, depth and a comments section.

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 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, calibration information and standards used for calibration.

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, drillers 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 the sample is taken is recorded. Drilling/boring is not used for sampling.

7.2.1 Sample Transport

Following collection of the sample, the bottles are sealed, tagged, and returned to the contract laboratory along with appropriate sample identification (i.e., sample name and number), and chain of custody form. Samples 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. Coolers are taped shut

using packing tape and taken to the SFWMD shipping area for pickup by common carrier within one hour. 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, and limited comments about the sample or sample container. Sample seals are not used.

7.3 Laboratory Operations

The samples are brought to the laboratory by the field sampling personnel and put into the designated refrigerator. The person bringing them 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. ex: L1-1 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. As each sample is labeled, the technician checks the proper match of field and LIMS numbers, and 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

Samples are rejected if the bottle is leaking or cracked, if there is no Chemistry Field Data Log submitted with the samples, if the Chemistry Field Data Log is incomplete, or if holding times or preservation protocols have been violated.

significant statistical difference. 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.

8.0 Analytical Procedures

The procedures used by SFWMD are found in Section 5.0.

8.1 Field Screening Methods

A phosphorus screening method is used in the field to determine samples which may be exceeding established limits. The screening data is used only to determine which samples should be sent to the laboratory for testing (see appendix C). The criteria used to determine which samples are to be sent to the lab are project specific.

8.2 Laboratory Glassware Cleaning and Storage Procedures

For classics and nutrients, the laboratory glassware is cleaned by washing with a hot Liquinox™ solution, rinsing with D.I. water, rinsing with 10% hydrochloric, and finally rinsing with analyte D.I. water. Once dry, 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 air dry. 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 atomic absorption laboratory. Pipets are soaked in 1% Liquinox™, and cleaned in a pipet washer using three volumes of D.I. water followed by soaking in 10% HNO3, 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% HNO3, rinsed with analyte free water, allowed to air dry, and stored separately from other glassware in the metals analysis area. Polyethylene 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 which has been acidified to approximately 1% with double distilled nitric acid.

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 the spectrophotometer eliminates the natural variation in color perception found in the human eye allowing the lab to consistently report results regardless of which technician performs the analysis. The procedure used is given in Appendix A.

The adopted silica method is a modified method tested by Alpkem for use in Rapid Flow Analyzers. The adapted method reduces saltwater interferences and is found in Appendix B.

Alkaline phosphatase activity is measured using the Patterson and Jansson method, 1978. The procedure is found in Appendix D.

8.4 Laboratory Reagent Storage

The storage of the laboratory reagents and chemicals is given in Table 8-1.

Table 8-1. Reagent and Chemical Storage

Chemical	Method of Storage
Mineral acids	Stored in original conainers in vented cabinet designed for acid storage. Note: each acid is stored in a separate cabinet.
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 and phenol are collected for disposal by a hazardous waste company. As each waste is generated, the volume is entered on the monthly hazardous waste report required by the SFWMD Risk Management Division. When the volume collected reaches the level set by Risk Management, it is moved to the SFWMD hazardous waste storage area. The Risk Management Division is responsible for securing the services of the waste disposal company.

Any small amounts of reagents are transfered 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 and put into the sanitary sewer system with copious amounts of water. Samples are disposed of by washing them into the sanitary sewer system with copious amounts of water.

9.0 Calibration Procedures and Frequency

9.1 Instrumentation Lists

The following is a list of the laboratory instrumentation.

Manufacturer	Model and Description
Hach	Model 18900 Ratio Turbidimeter
Accumet	Model 50 Ion Analyzer
Radiometer	CDM83 Conductivity Meter
Mettler	P160 Top Load Balance AE163 Analytical Balance (2)AE100 Analytical Balance
Bausch & Lomb	Spectronic 501 Visible Spectrophotometer
Dionex	4000i Ion Chromatograph
Alpkem	(3)RFA300 Rapid Flow Analyzers with PC Workstation RFA 500 Injection Flow Analyzer
Perkin Elmer	1100B Flame Atomic Absorption Spectrophotometer with PC Workstation Z5100 Furnace Atomic Absorption Spectrophotometer with PC Workstation Lambda 6 uv-vis Spectrophotometer
Orion	Model 960 Autochemistry System
Rosemount Dohrmann	DC-190 Total Organic Carbon Analyzer
Millipore	Cytofluor 2350 Fluorescence Measurement System
Thermolyne	Type 37900 Culture Incubator
Blue M Electric Co.	Magic Whirl Constant Temperature Waterbath

Manufacturer	Model and Description
Fisher Scientific	Model 21K/R Morathon Centrifuge
Barnstead	Model 2250 Autoclave
Reichert	Model 40 Stereoscope Quebec Dark field Colony Counter

The following is a list of the field instrumentation.

Manufacturer	Model and Description
Hydrolab	Model 4031 pH, Conductivity, ORP, and Temperature Meter Model 4041 pH, Conductivity, DO, and Temperature Meter Model Surveyor II pH, Conductivity, DO, Temperature, Salinity, Model Surveyor III pH, Conductivity, DO, Temp., Salinity ORP, Turbidity and Depth Meter

9.2 Standard Receipt and Traceability

Standards are received by the Supervising Professional, Senior Chemists or Chemist, initialed, dated, and stored in the designated area for the particular standard.

The date of preparation of in-house primary stock solutions is recorded in a log book along with the following information regarding purchased stock solutions: 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. Manufacturers certificates of analysis and/or records of traceability for purchased stock solutions are filed in the appropriate instrument calibration notebooks. These notebooks are kept on file. The same procedure is followed for field samples.

Primary stock solutions prepared from freshly dried, ACS reagent grade chemicals are refrigerated and prepared monthly. Records of the preparation are kept in a logbook. Working calibration standards are prepared fresh daily.

The standard sources and preparation are given in Table 9-1.

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	Spex/JT Baker/ NIST	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_3 at room temp. NA	Weekly or as needed Daily
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
Organic Carbon	Commercial lab supplier	Dry, ACS analytical grade	Room temperature	Primary stocks, 1000 mg/L prepared from source Working stocks	Refrigerator Working Stocks	Monthly Daily
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	Class S weights	Dessicator, room temperature	NA	NA	NA

Table 9-2. Solutions Requiring Standardization

Test	Standard sources	How Received	Source Storage	Preparation from Source	Standardization procedure and Criteria	Standardization Frequency	Preparation Frequency
Alkalinity Titration	Commercial Lab Supplier	0.1 N Sulfuric Acid	Acid Storage Cabinet	Used as is from supplier	Standardized with 0.05 N sodium carbonate; must be within 5% of expected value	Weekly and each time a new bottle is used	Used as is from Supplier
Alkalinity Titration	Commercial Lab Supplier	0.1 N Sulfuric Acid	Acid Storage Cabinet	Diluted to 0.02 N from the 0.1 N solution	Standardized with 0.05 N sodium carbonate; must be within 5% of expected value	Weekly and each time a new batch is prepared	Prepared weekly and as needed
Chlorine Residual Titration	Commercial Lab Supplier	1 Titer FAS titrant	Refrigerator	Used as is from supplier	Standardization and certification provided by supplier	Standardization and certification provided by supplier	Prepared monthly and as needed

The calibration procedures for laboratory instruments are given in Table 9-3, for laboratory equipment in Table 9.4, and for field instruments in Table 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 for the field is recorded in the Field notebook or Calibration Book. Date and time of calibration, technician, standards used, standard results and temperature, and instrument used are recorded.

Calibration information for the laboratory is recorded in the individual instrument log and includes the analyst, date of analysis, standard values, millivolt or absorbance values for the standards, correlation coefficient, results of continuing and initial calibration standards, instrument gains, precision and accuracy results, and samples analyzed.

Table 9-3. Laboratory Instrument Calibration

Instrument	# Standards Initial Calib.	Accept/Reject Criteria - Initial Calibration	Frequency	# Standards Continuing Calibration	Accept/Reject Criteria - Cont. Calibration	Frequency
Atomic Absorption	3 - 5	Linear Regression Corr. Coefficient >0.995	Daily prior to use or failure of cont. calibration	3-5	Concentration within 5% of known value (mid-range)	Initial and every 20 samples
Continuous Flow and Ion Chromatograph	5 - 7	Linear Regression Corr. Coefficient >0.998	Daily prior to use or failure of cont. Calibration	5-7	Concentration within 5% of known value (mid-range)	Initial and every 20 samples
Carbon Analyzer	3	Concentration within 5% of known value	Daily prior to use or failure of cont. calibration	3	Concentration within 5% of known value (mid range)	Initial and 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	3	Concentration within 5% of known value (mid-range)	Initial and every 20 samples
Conductivity Meter	3	Concentration within 5% of known value	Daily prior to use or failure of cont. calibration	3	Concentration within 5% of known value (mid-range)	Initial and every 20 samples
Turbidimeter	3	Concentration within 5% of known value[1]	Daily prior to use or failure of cont. calibration	3	Concentration within 5% of known value (mid-range)	Initial and every 20 samples
Visible Spectrophotometer	5	Linear Regression Corr. Coefficient >0.998	Daily prior to use or failure of cont. calibration	5	Concentration within 5% of known value (mid-range)	Initial and every 20 samples
Fluorescence Spectrophotometer	4	Linear Regression Corr. Coefficient >0.998	Daily prior to use of failure of cont. calibration	4	Concentration within 5% of known value (mid-range)	Initial and every 20 samples
Analytical Balance	3	Weight within 2% of known value	Monthly	3	Weight within 1% of known value	NA

(1) Gel standards are checked monthly with Formazin control solutions of the same concentration, (i.e. 1.8, 18.0 and 180 NTU), to ensure integrity.

Note: Method Calibration requirements will be followed if more stringent than those listed in the QAP.

Table 9-4. Laboratory Equipment Calibration

Equipment	Calibration	Acceptance Criteria	Frequency
Analytical Balance	Calibrated with the 100g weight, then checked with entire set of Class S weights	All weights within 2 % of known value	Monthly
	Maintenance contract exists for calibration	NA	Semi-Annually
Autoclave	Check timer with stopwatch	Timer set for 15 min. maintains 121°C for at least 15 min. The entire cycle is completed within 45 min.	Quarterly
	Spore check	No visible spores	Monthly
Incubator	Temperature recorded from a calibrated thermometer. Adjustments made as needed	+/- 0.5 °C	Twice daily
Water Bath	Temperature recorded from a calibrated thermometer. Adjustments made as needed	+/- 0.2 °C	Twice daily

Table 9-5. Field Instrument Calibration (Hydrolabs[1,3])

Instrument Probe	# Standards Initial Calib.	Accept/Reject Criteria-Initial Calibration	Frequency	# Standards Continuing Calib.	Accept/Reject Criteria-Continuing Calib.	Frequency
pH	2 (1 pH 7 & 1 pH 4 or 10)[2]	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 in the expected Range	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
Dissolved Oxygen	Winkler titration	Concentration within 5% of known value	Annually	Saturated air	Concentration within 5% of known value	At the end of the day or withing 24 H of initial calibration
Temperature	1	Concentration within 2% of known value (NIST thermometer)	Daily	1	Concentration within 5% of known value - lab calibrated thermometer	Quarterly
Turbidity	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 prior to use

(1) The Hydrolabs all have automatic temperature compensation for pH, conductivity and DO measurements. Meters are check daily with NIST (NBS) Certified thermometers.
(2) Buffer pH 4 or pH 10 solution used, respectively, with acidic or basic samples.
(3) The calibratrion check is conducted weekly for instruments deployed in the field

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 Field Equipment Maintenance

Field maintenance procedures are given in Table 10-1. Maintenance that cannot be performed by SFWMD personnel is done by the manufacturer or his designee.

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, listed in Table 10-2, are documented in a 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 have been contracted to provide analytical services in the event of a catastrophic failure.

Table 10-1. Field Equipment Maintenance Schedule

Instrument	Specific Activity	Frequency
Hydrolabs (all models)	DO probe membrane and electrolyte changed	Quarterly/AN
	Conductivity sensors are sanded with emery cloth	Quarterly
	pH and reference electrodes cleaned with methanol	Quarterly/AN
	pH reference electrode refilled with 3M KCl	Quarterly/AN
	All outside surfaces cleaned and rinsed with analyte free water	Daily
Pumps (Gorman Rupp 2H Centrifugal)	Check oil and add if needed	Before use
	Drain pump of water	After use
	Wipe clean of mud and grease	After use
	Change oil & filter	Quarterly
	Change spark plugs & adjust carburator	Quarterly
Autosamplers	Check battery charge & replace as needed	Before use
	Check programming	Before use
	Magnet adjustment to seek bottle #1	After use
	Check pumping volume with a graduated cylinder	Before use
	Check indicating dessicant & change as needed	Before use
	Change pump tubing	Quarterly
	Calibrate Autosampler	Quarterly
	Distributor arm tubing replacement	Quarterly
	Liquid sensor cleaned	Quarterly
	Intake tubing strainers cleaned	Quarterly
Aerochem Collectors	Check temperature of sensor plate by touching	Before use
	Remove & cap collection buckets	Daily
	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	Daily

Table 10-2. Laboratory Equipment Maintenance Schedule

Instrument	Specific Activity	Frequency
Atomic Absorption	Check gases	Daily
	Flame: Nebulizer cleaned ultrsonically in Liquinox™ solution, rinsed with tap water, dipped in 10% HNO_3, rinsed with analyte free water.	Biweekly
	Burner head soaked in Liquinox™ solution.	After use
	Furnace: Windows inspected and cleaned with isopropyl alcohol.	Daily
	Tubes and platforms inspected and changed	AN
	Furnace decontamination as recommended by Perkin Elmer	Weekly/AN
	Service maintenance	Semiannual
Continuous Flow -Alpkem RFA300 -Alpkem RFA500	Inspect all tubing and fittings	Daily
	Wash manifold/flow cell	Daily
	Inspect filters	Weekly
	Replace pump tubes	Biweekly
	Clean rollers & grease	Monthly
	Service Maintenance	Semiannual
Ion Chromatograph	Check tubing and fittings for leaks	Daily
	Clean columns and change bed supports	Monthly
	Preventative maintenance by manufacturer	Semiannual

Instrument	Specific Activity	Frequency
Carbon Analyzer	Check/replace O-rings	Weekly/AN
	Change acid	When 2/3 empty
	Replace copper & glass wool	When discolored
	Replace injection port septa	Weekly/AN
	Inspect/replace combustion tube and catalyst	Biweekly
pH Meter	Rinse electrode with analyte free water	Before & after use
	Add reference solution	Daily/AN
Conductivity Meter	Rinse electrode with analyte free water	Before & after use
Turbidimeter	Clean cuvettes	Daily
	Adjust calibration	AN
Visible Spectrophotometer	Clean flowcell	Daily
	Change pump tubes	Semiannual
Fluorescence Spectrophotometer	Calibration Service & inspection	Annual
Analytical Balances	Clean weighing compartment	After each use
	Clean interior/exterior	Monthly
	Calibration check against class "s" weights	Monthly/ AN
	Calibration service & inspection	Semiannual
Ovens	Check temperature	Daily
	Calibrate thermometer to NIST thermometer	Annually
Refrigerators	Check temperature	Daily
	Calibrate thermometer to NIST thermometer	Annually

Instrument	Specific Activity	Frequency
Digestion blocks	Check temperature	Weekly
	Clean blocks	Monthly
	Calibrate thermometer to NIST thermometer	Annually
Centrifuge	Clean holder	After use
	Clean walls	After use
Autoclave	Check water level	Before use
	Clean interior and replace water	Before use
	Check pressure during operation	With each use
Colony Counter	Adjust focus and brightness	With each use
Incubator	Check temperature	Twice daily
Water Bath	Check temperature	Twice daily
	Change water	Monthly
Stereoscope	Replace bulb	AN
	Wipe lense	AN

AN - As Needed

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

The determination of the quality of a sample is dependent on the use of quality control samples in the field and laboratory. The definitions of each type of check can be found in DER QA-001/90, Appendix C.

11.1 Field Quality Control Checks

The field quality control 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. The SFWMD routinely provides known spiked solutions to take into the field at a rate of one per sampling trip. All field blanks are preserved and transported in the same manner as the samples.

The field quality control check samples consist of the following:

A. Field Blank - a deionized water sample poured directly into the sample container, preserved, and maintained open until sample collection is completed for that site.

B. Trip Spike - this is analyte free water spiked with a known amount of stock, prepared in the laboratory, taken into the field and handled like a routine sample (i.e. placed in coolers on ice), and returned to the lab without being opened.

C. Replicate Sample - Samples collected at the same time from the same source.

D. Split Sample - One sample which has been divided to make two samples which are analyzed by the laboratory.

E. Equipment Blank - after field cleaning of sampling equipment, the final deionized water rinse is collected and analyzed as an equipment blank. Equipment blanks are also collected before sample collection begins, and at a rate of one every twenty samples. Equipment Blanks are prepared by pouring one liter of DI water into the sample collection container and through each piece of sampling equipment. The Equipment Blank is filtered and preserved and handled as a routine sample.

The field quality control check samples described in A and D are included for each group of samples within the same project and are submitted each day samples are taken at a rate of 5%. These samples are submitted to the laboratory with the routine samples for that project. Equipment blanks (E) are submitted and analyzed before sampling begins and at a rate of 5%. Trip spikes are submitted to the laboratory at a rate of one per sampling trip. Replicate samples are submitted at a rate of 10%. Trip blanks are submitted with volatile organics (one in each

Table 11.1 Field Quality Control Checks

Type	# Samples /Event	Frequency (All Parameter Groups)
Equipment Blank, Precleaned Eqpt.	>10	1 prior to sampling, on-site 5% if >20 samples
	1-10	1 prior to sampling, on-site
Equipment Blank, Field Cleaned Eqpt.	>10	1 blank or 5% of equipment cleaned, whichever is greater
	5-10	1 blank on equipment cleaned
	<5	1 on either precleaned or field cleaned eqpt.
Trip Blank (VOC only)	1 or more	1 for each volatile organic method per cooler used to transport samples
Field Duplicate	1 or more	1 or 10% of the samples, whichever is greater
Field Blank	1 or more	1 or 5% of the samples, whichever is greater
Trip Spike	1	1 for each sampling trip
Field Measurements QC Check Stds.	1 or more	1 every 4 hours and at the end of the day

cooler) and are provided by contract labs. Trip spikes are prepared by the QA section in the laboratory by spiking analyte free water with known stock solutions, dispensing into sample bottles and preserving. The trip spikes are taken into the field and receive the same sample handling as the samples. Project managers request the trip spikes required for their trips in advance, reflecting their parameter test list. The left-hand margin of the Field QA/QC Sample Request form, shown in Fig. 11-1, is a check list of analytes for which trip solutions have been requested. The spiked solutions are prepared using purchased or prepared stock solutions. Trip spikes are submitted as routine samples to the lab.

Figure 11.1 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	0.4	
			TOTMN	10	
			TOTNI	10	
			TOTPB	10	
			TOTSB	20	
			TOTSE	20	
			TOTTH	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	0.4	
			TDSMN	10	
			TDSNI	10	
			TDSPB	10	
			TDSSB	20	
			TDSSE	20	
			TDSSR	2.0	
			TDSTH	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 02/9

11.2 Laboratory Quality Control Checks

The laboratory quality control checks are given in Table 11.2. The laboratory will meet or exceed the requirements for each method if greater than the minimum requirements. If the data from quality control check samples are not acceptable, results will be reported in the QA report to DEP.

11.3 Laboratory Quality Control Checks (Species Identification)

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

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 inhouse. The SFWMD maintains 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 Laboratory Quality Control Checks (Microbiology)

11.4.1 Laboratory Quality Control Checks for all Microbiology Tests

QC checks for microbiology include:

Annual Water Quality Test (Suitability Test) - Standard Methods 9020
Inhibitory Residue Test for each new lot of detergent (on file) - Standard Methods 9020
Monthly Heterotrophic Plate Count - Standard Methods 9215
Annual Metals Test - Standard Methods 9020
Monthly Chlorine Residual - Standard Methods 9020
Monthly Conductivity - Standard Methods 9020

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)	1 or 5% of samples, whichever is greater; if more than one matrix, 1 from each matrix.
Quality Control Check Samples	Blind Performance Evaluation Samples- analyzed in duplicate semiannually*
Quality Control Check Standards	Analyzed at the beginning of each analytical run to verify standard curve
Duplicate Samples	1 or 5% of samples, whichever is greater; if more than one matrix, 1 from each matrix
Continuing Calibration Standard	At a rate of 5% of the number of samples in an analytical set

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

The following QC checks are done for each microbiology test.

Table 11.3 Microbiology QC Checks

QC Check	Frequency	Purpose	Acceptance Criteria
Autoclave tape	with each sterilization batch	assure complete sterilization	Tape writing visible and dark
Spore check	monthly	assure complete sterilization	No viable cultures
Incubator temperature check	twice/day	maintain proper temperature	35.0 +/- 0.5 ° C
Water bath temperature check	twice/day	maintain proper temperature	44.5 +/- 0.2 ° C
Thermometer calibration with NIST thermometer	semi-annual	assure accurate temperature readings	< 0.2+/- ° C correction required

All materials such as filters, plates, whirlpaks™ and media are checked for sterility upon receipt or preparation using non selective broth and inoculating for 24 hours at 35.0 +/- 0.5°C. This information is documented in a bound log book. Logs are also used for media and rinse water preparation, autoclave cycles and checks, temperature checks, equipment maintenance and sample analysis.

A control blank is run at the beginning and end, as well as every ten samples, of each filtration series or sample set. Analysis duplicates are run every ten samples. Purchases positive and negative controls are run in duplicate monthly, and with each new lot of media, for all microbiology tests. The controls are taken to the confirmation/completed stage. Ten percent of all positive samples are counted by different technicians. Counts must agree within 5%.

11.4.2 Laboratory Quality Control Checks for Membrane Filtration Procedures

A control blank is run at the beginning and end of each filtration series. In addition, a carry over blank is run every ten samples. The log sheets used for the membrane filtration procedures are found in Figures 7.11, 7.12 and 7.14.

11.4.3 Laboratory Quality Control Checks for Most Probable Number Procedure (MPN)

With each MPN analysis, Lauryl tryptose broth is inoculated with ten mL of sterile phosphate rinse buffer and used as a blank control. The completed test is performed on ten percent of all coliform positive samples and at least once per quarter.

11.5 Routine Methods Used to Assess Precision and Accuracy

11.5.1 Field Reportable Data

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

Percent Relative Standard Deviation for precision of duplicates.

$$\%RSD = \frac{141.42 * |A-B|}{(A+B)}$$

Percent Recovery of Trip spikes

$$\%Recovery = \frac{[\text{Trip Spike Concentration}]}{\text{spike amount}} * 100$$

Percent Recovery of QC Check Standards

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

The quality control data is kept in table format with new limits calculated quarterly. The field staff is given the control limits for each quarter for ready reference as samples are collected. The formulas for calculating control limits are based on the standard deviation of the last 30 measurements for each type of sample. The standard deviation is calculated according to the following formula.

$$s = \sqrt{\frac{\Sigma(X_i-X)^2}{(n-1)}}$$

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

$$\text{Mean} = X = \frac{\Sigma X_i}{n}$$

The limits for field parameters are 2s for warning limits and 3s for control limits.

11.5.2 Lab Reportable Data

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

Accuracy can be defined as the agreement between the actual obtained result and the expected result. Two QC check samples, QC1 and QC2, having a known or "true" value and standard additions also with an expected result, are used to test for the accuracy of a measurement system. Accuracy may be quantified by comparing results obtained for QC1 and QC2 to their true values and calculating a percent recovery using the following equation:

$$\text{Percent Recovery} = \%R = \frac{\text{experimental result}}{\text{"true" value}} * 100$$

The values obtained for the matrix spike are used to calculate percent recovery using the following equation:

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

The percent recovery values may be used as an indication of bias. The control limits for accuracy are +/-2 standard deviations of the historical percent recoveries.

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 over a given time period. Because the SFWMD laboratory is highly automated and analyzes large numbers of samples in a short period of time, one sample is chosen as the repeat (or replicate) sample for each parameter and is analyzed several times over the course of the run. Since each replicate sample is analyzed more than two times during the analytical run, it is appropriate to use the percent relative standard deviation, or the coefficient of variation, as the basis of acceptability of an analytical run. The control limits for precision are +/-2 standard deviations of the historical percent relative standard deviation.

The mean and standard deviation are calculated as shown in Section 11.4.1. The % relative standard deviation is calculated by the following equation:

$$\%RSD = (s/X) * 100$$

where X is the mean and s is the standard deviation.

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. New limits are calculated quarterly, with

warning limits set at +/-1.5 standard deviations and control limits at +/-2.0 standard deviations of the most recent historical record for each type of QC check.

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

11.5 Method Detection and Practical Quantitation Limits

The method detection limits are determined by the procedures in 40 CFR Part 136, Appendix B. The method detection limits are updated annually.

The practical quantitation limit is 12 times the pooled standard deviations derived from the procedures to determine the method detection limit, and is updated annually.

Table 11.4 Procedures Used to Determine Precision and Accuracy

Method	Purpose	Concentration Level	Method References
Matrix Spike	Accuracy	Mid 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	Accuracy	Mid Level High Level	All parameters
QC Check Standards	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 the field measurement data are directly read from the instruments. These measurements include pH, specific conductance, dissolved oxygen, temperature, ORP, salinity, and depth. The data is 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

The laboratory measurements which are read directly from the instruments, requiring no calculations, are pH, specific conductance, turbidity, color and fluoride. The pH and conductivity meters have automatic temperature compensation. The conductivity cells are purchased with cell constants provided by the manufacturer and are checked monthly. 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 (Assistant Laboratory Technician, Laboratory Technician, Senior Laboratory Technician, or Chemist) is responsible for running the computer programs which provide the results in the appropriate concentrations and entering into the database.

The documentation for the results include the strip chart and chromatogram recordings and/or raw data files for the computerized calculations. The strip charts and chromatographs are identified with the date, the computer file name if applicable, 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 Senior Chemists are responsible for checking the raw data entries and calculations for correctness. The Laboratory Quality Assurance Officer is responsible for checking sample preparation logs, and instrument/analytical logs for adherence to QC protocols and sample identification. The QA Officer is also responsible for checking the calibration integrity by

Table 12.1 Formulas Used for Calculations

Parameter	Formula
Alkaline Phosphatase	Computer, linear regression
Alkalinity	Computer, ml of titrant X N X 50,000/ml sample
Ammonia	Computer, linear regression
Calcium, dissolved	Computer, logarithmic regression
Chloride	Computer, logarithmic regression
Chlorine Residual, Total	1 mL of FAS titrant = mg/L Cl
Iron, total and diss.	Computer, linear regression
Nitrogen, total Kjel.	Computer, linear regression
Magnesium, dissolved	Computer, logarithmic regression
Nitrate + nitrite	Computer, linear regression
Nitrite	Computer, linear regression
Nitrate	Computer, (Nitrate+nitrite)-Nitrite
Total phosphorus	Computer, linear regression
Organic Carbon, total and dissolved	Computer, Total - Inorganic, mean of 2 Repeats
Orthophosphate	Computer, linear regression
Potassium, dissolved	Computer, logarithmic regression
Residue, filterable	Computer, $\frac{\text{Final Weight-Tare,g}}{\text{Volume, mL}} \times 10^6$
Residue, nonfilterable	Computer, $\frac{\text{Final Weight-Tare,g}}{\text{Volume, mL}} \times 10^6$
Residue, volatile	Computer, $\frac{\text{Nonfilterable Final Weight-Weight(550°C),g}}{\text{Volume, mL}} \times 10^6$
Silica, dissolved	Computer, linear regression
Strontium, dissolved	Computer, linear regression

Parameter	Formula
Sulfate	Integrator, logarithmic regression
Trace metals	Computer, linear regression
Hardness	Computer, 2.497[Ca] + 4.118[Mg]
Chlorophyll	Chl. a = 11.85(OD664) - 1.54(OD647) - 0.08(OD630) Chl. b = 21.03(OD647) - 5.43 (OD664) - 2.66(OD630) Chl. c = 24.52(OD630) - 7.6(OD647) - 1.67(OD664) Pheophytin = (26.7(1.7*OD665)) - OD664 carotenoids = 4.0(OD480) Chla corrected = 26.7(OD664) - OD665 where: OD(wavelength) = absorbance (wavelength) - absorbance at 750 nm in non-acidified sample and : results are multiplied by volume of extract and divided by the volume of sample filtered in m^3
Total Coliform, membrane filter	# colonies/volume of sample (mL) X 100
Total Coliform, MPN	MPN tables[1]
Fecal Coliform, membrane filter	# colonies/volume of sample (mL) X 100
Fecal Coliform, MPN	MPN tables
Heterotrophic Plate count	# colonies/volume of sample tested (mL)
Fecal Steptococci	# colonies/volume of sample tested (mL)

(1) MPN tables found in SM 17th ed., Table 9221:V, p. 9-78.

comparing the present instrument responses to the historical values and the internal chain of custody for the samples to ensure that only authorized persons have analyzed or handled a sample.

12.2.2 Field Data Integrity

The Quality Assurance 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 took 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.

12.3 Specific Data Validation Procedures

12.3.1 Laboratory Data Validation

The analyst (Asst. Lab Technician, Lab Technician, Senior Lab Technician, or Chemist) 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 Quality Assurance Officer. The Senior Chemists are responsible for investigating the discrepancy and determining the cause. The Senior Chemists are also responsible for the review of all data to identify obvious anomalies. The Laboratory Quality Assurance Officer is responsible for reviewing the quality control results for each run, and insuring that all QC criteria are met. The Quality Assurance Officer must update the acceptable quality control limits for all parameters quarterly.

The laboratory quality control checks are used to validate the laboratory results. Each of the QC check samples will be discussed.

Method Reagent Blank - if the result is greater than the detection limit, the run is stopped and the blank is prepared again. All samples since the last acceptable blank are reanalyzed.

Matrix Spike Sample - if the result is outside the current acceptable limits, the sample will be prepared again. If the value is outside the range again, the sample is analyzed by means of standard additions. If a matrix problem is verified, it is noted in the database that the sample exhibits matrix interference.

Quality Control Check Standards - if the result is outside the current acceptable limits, the run is stopped and the instrument recalibrated. 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.

Quality Control Check Samples - if the result for these blind samples is incorrect, the entire procedure is checked for errors. The analytical results are reported in the semiannual report.

Replicate Sample - used to assure that the same results are consistently obtained throughout the analytical run. At a minimum, it is run three times (beginning, middle, and end) during the analytical run if there are more than 20 samples in the run (two times for 20 or less samples). The %RSD should not vary more than the acceptable limit for that parameter.

Duplicate samples - at least 5% of the samples received by the laboratory are done in duplicate. The sample will not achieve "complete" status until until the data is reviewed for precision.

Continuing calibration standard - used to confirm that the calibration curve remains constant throughout the analytical run. The value must remain within 5% of the initial value throughout the run.

12.3.2 Field Data Validation

The field sampling personnel (Assistant Scientific Technician, Scientific Technician, Senior Scientific Technician, Technician Supervisor, or Staff Environmental Scientist) is responsible for following the sampling procedures, reviewing the Chemistry Field Data Logs, and filling out all forms correctly and completely. The Technician is 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 Environmentalist or Senior Environmentalist 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.

The field quality control checks are used to validate the sample collection process and the field collected data. Each check will be discussed.

Quality Control Check Standards - used to check the calibration of the instruments on a continuing basis. Results must be within the established acceptable limits.

12.3.3 Project Data Validation

The Project Manager is responsible for the final review of data and its release to the database and to requestors. The Laboratory Quality Assurance 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 the review of the data for anomalous results.

12.4 Data Reporting

Following the data validation, the results are entered in the LIMS data base by the Analysts (Asst. Lab Technician, Technician, Senior Lab Technician or Chemist). The Senior Chemists check entered data, by means of automated computer programs, to ensure detection of aberrant data, e.g., $NO_2^- > NO_3^-$, to avoid its inclusion into final reports. All reports are generated electronically from this data base by the Water Quality Monitoring Division Programmer Analyst. Printouts are routinely generated for all electronically transmitted data (Fig. 12.2).

All requests for data reports must be made through Data Management. The Project Manager is responsible for reviewing the data before it is released to the requestor. An Example of the Final Report is given in Figure 12-1.

12.5 Data Storage

The records that will be retained are the strip charts, chromatograms, data files, Chemistry Field Data Logs, manual data entry records, daily QC reports, instrumentation logs and LIMS back up tapes.

The hard copy information is retained in the laboratory for no more than one year. After that it is sent to warehouse records storage and will be microfilmed if storage for longer than three years is needed.

The magnetic tapes used for weekly back-up of the laboratory information management system 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 for at least three years.

13.0 Corrective Action

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

The analyst (Asst. Lab Technician, Lab Technician, Senior Lab Technician or Chemist) or field sample collection technician (Asst. Scientific Technician, Scientific Technician, Senior Scientific Technician) is responsible for assessing each QC measure and initiating corrective action according to Tables 13.1 and 13.2, respectively. The Supervising Professional, Senior Chemists, Field Operations Supervisor, and the divisional Quality Assurance Officers are responsible for approving the corrective action taken or for initiating further steps to solve the problem.

External sources which may initiate corrective action are performance evaluation results, performance audits, system audits, split sample results, and laboratory/field comparison studies.

The problem and corrective action are documented in detail in one of the following: 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 Quality Assurance Officer who has the responsibility for determining if the solution is acceptable and if not, what further steps should be taken.

DEP recommended corrective action will be initiated as a result of systems or performance audits, split samples or data validation review.

Table 13.1 Corrective Actions for the Laboratory

QC Activity	Acceptance Criteria	Recommended Corrective Action
Initial Instrument Blank	Instrument response < MDL response	Prepare new blank, if same response determination cause of contamination: reagents, environment, equipment failure, etc.
Initial Calibration Standards	Coefficient of correlation >0.995 for AA, >0.998 Visible spectrometer, fluorometer	Reanalyze standards, if same response, reoptimize instrument, if same response, prepare new standards
QC Check Standards	Value within +/- 2 standard deviations of the historical value	Reanalyze QC check standard, if same response, prepare new QC check standard, if same response, prepare new primary and calibration standards
Continuing Calibration Standards	+/- 5% of expected value	Reanalyze standard, if same response, recalibrate and reanalyze run from last continuing calibration standard
Replicate Sample	Coefficient of variation within established limit	Determine cause: baseline drift, carryover, etc. Reanalyze all samples if correctable cause not found
Duplicate Sample	Coefficient of variation within established limit	Reanalyze duplicates, reanalyze all samples between duplicates
Matrix Spikes	Value within +/- 2 standard deviations of the historical value	Remake spike and reanalyze, if still not acceptable, spike a different sample, if acceptable reanalyze run if necessary. 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.
Microbiology Control Blanks	Control Blank < 1	Sample resubmitted

Table 13.2 Corrective Actions for the Field

QC Activity	Acceptance Criteria	Recommended Corrective Action
Initial Calibration Standards	Value within +/- 5% of expected value	Reanalyze standards, if same response, optimize instrument, if same response, use new standards.
QC Check Standards	Value within +/- 5% of expected value	Reanalyze QC check standard, if same response, prepare new QC check standard, if same response, recalibrate

Table 13.3 Corrective Actions resulting from Field Quality Control Checks

QC Activity	Acceptance Criteria	Recommended Corrective Action
Equipment/Trip Blank	Value < MDL	Laboratory should reanalyze blanks: If same response, project manager should check recorded cleaning procedures and mark sample trip results for affected and related parameters questionable or invalidate data, as required.
Trip Samples	Value within $\pm$ 2 standard deviations of the historical mean	Laboratory should reanalyze Trip Spikes: If Same Response, Sample Prep should be checked as well as other projects containing the same solution. If no other projects were affected, results for affected and related parameters should be invalidated or marked questionable, as required.
Duplicate Samples	Value within $\pm$ 2 standard deviations of the historical mean	Laboratory should reanalyze duplicates: If same response, mark sample trip results for affected and related parameters questionable or invalidate data as required. If reanalysis shows Field Collection to be acceptable, reanalyze all samples analyzed with the Field samples the first time.

14.0 Performance and Systems Audits

Audits are an essential part of the quality assurance program for both laboratory and field operations. A systems audit is conducted to measure compliance with the comprehensive and project quality assurance plans. A performance audit is 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

The systems audit is used to evaluate the entire measurement system, 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 Quality Assurance Plans. A list of deficiencies must be made and addressed to correct, improve, or modify the system as necessary.

14.1.1 Internal Systems Audits

Systems audits are performed using the forms shown in Figure 14.1. The audit is conducted Semiannually by one of the following persons: the Division Quality Assurance Officers, Water Quality Monitoring Senior Technician, Senior Scientific Technician Supervisor or Environmental Scientist.

14.1.2 External Systems Audits

There are no regularly scheduled external systems audit. The SFWMD will submit to audits conducted by the DEP Quality Assurance Section.

14.2 Performance Audits

A performance audit is used to evaluate the routine quality control program of the laboratory.

14.2.1 Internal Performance Audits

Internal performance audits are conducted semiannually by the Laboratory Quality Assurance Officer. The audit may consist of any or all of the following: resubmission of previously analyzed samples under a different LIMS number, preparation of additional QC samples, samples split with another laboratory, and submission of spike samples, all of which are blind to the analysts.

The audit may be conducted at any time on a suspect parameter in addition to the semiannual audits for the entire laboratory.

The results of the performance audits are included in the quarterly quality assurance reports issued by the Laboratory 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 the Department of Health and Rehabilitative Services, semiannual
2. United States Geological Survey, Denver, semiannual

FIGURE 14.1 - SYSTEMS AUDIT CHECKLIST

Project Name:_____ Project No:_____

Project Manager:_____ Date:_____

Project Code (field and lab use):_____

Field Auditor:_____ Lab Auditor:_____

Signature:_____ Signature:_____

	YES	NO
Planning and Preparation:		
1. Was QA Project Plan prepared for this project?	____	____
2. Was briefing held with project participants, both field and lab? Date:_____	____	____
3. Were Additional instructions given to participants (ie., changes in project plan)?	____	____
4. Was there a written list of sampling locations and descriptions?	____	____
5. Was there a map of sampling locations available to field personnel?	____	____
6. Was sampling scheduled with field technician supervisor in advance (minimum one week)?	____	____
7. Were analyses scheduled with laboratory in advance (minimum one week)?	____	____

Comments:_____

General Sampling Procedures:

	YES	NO
1. Were sampling locations properly selected?	____	____
2. Was sampling equipment protected from possible contamination prior to sample collection?	____	____
3. If equipment was cleaned in the field, were proper procedures used?	____	____
4. What field instruments were used?_____		
5. Were calibration procedures documented in the field notes?	____	____
6. Were samples chemically preserved at time of collection?	____	____
7. Was the preservative amount recorded in the field notes?	____	____
8. Were samples iced at the time of collection?	____	____
9. Were sample bottles rinsed with sample before filling?	____	____
10. Were field conditions recorded in the field notes?	____	____
11. Was filtering equipment pre-rinsed with sample?	____	____
12. Was waste material containerized and maintained separate from samples and equipment?	____	____

Comments:_____

Surface Water Sampling:

	YES	NO
1. What procedures were used to collect the surface water samples? _____		
2. Was a Niskin bottle used for sample collection?	____	____
3. Was sample collected in polyethylene bucket?	____	____
4. Did samplers wade in stream during sample collection?	____	____
5. Were autosamplers used?	____	____
6. Were Preventative maintenance protocols followed and documented?	____	____

Comments: _____

Well Sampling:

	YES	NO
1. Was depth of well determined?	____	____
2. Was depth to water determined?	____	____
3. Was measuring tape properly decontaminated between wells?	____	____
4. Were the above depths to water converted to water level elevations common to all wells?	____	____

5. How was the volume of water originally present in each well determined? ____ ____

6. Was the volume determined correctly? ____ ____

7. How was completeness of purging determined:
   Volume measure_____
   Time_____
   Flow rate_____
   Scond./pH/T_____

8. Was a sufficient volume purged? ____ ____

9. Was the well over-purged? ____ ____

10. Was the disposal of purge water handled properly? ____ ____

11. Was a dedicated (in-place) pump used? ____ ____
    If no: Describe method of purging:_____
    _____
    _____
    _____

12. How were the samples collected?
    Bailer? ____ ____
    Pump? ____ ____
    Other? Describe:_____
    _____
    _____
    _____

13. Construction material of bailer?_____

14. If a pump was used, describe how it was cleaned before and/or between wells:_____
    _____
    _____
    _____

15. Were the samples properly transferred from bailer to sample bottles (i.e., was the purgeable sample agitated, etc.)? ____ ____

16. Was the rope or line allowed to touch the ground? ____ ____

17. Was a teflon coated stainless steel cord used? ____ ____

Comments:_____

Sediment Sampling: YES NO

1. What procedures were used to collect the samples?

2. Were the samples well mixed prior to placing the sample in the sample container? ____ ____

3. Were the samples composited? ____ ____

Comments:

Other Sampling:

1. What other types of samples were collected during this investigation?

2. What procedures were used for the collection of these samples?

Comments: _____

_____

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_____

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Field Quality Control:

	YES	NO
1. Were QC samples specified in the QA Project Plan?	____	____
2. Were the QC samples collected in accordance with the QA project plan?	____	____
3. Did sampling personnel utilize any trip blanks?	____	____
4. Did sampling personnel utilize any preservative blanks?	____	____
5. Were any equipment blanks collected?	____	____
6. Were any duplicate samples collected?	____	____
7. Were any trip spikes utilized?	____	____
8. Check method used to collect split sample ____Filled one large container and then transferred portions ____Sequentially filled bottles		
9. Were chain of custody records completed for all samples?	____	____
10. Were all samples identified with appropriate tags?	____	____
11. Were sample I.D. tags filled out properly?	____	____
12. Did information on sample I.D. tags and Chemistry Field Data Log match?	____	____

	YES	NO
13. Were samples kept in a secure place after collection?	____	____
14. Was Chemistry field Data Log signed by sampling personnel?	____	____
15. Were amendments to the project plan documented (on the project plan itself, in a project logbook, elsewhere)?	____	____

Comments: _____

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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 aliquoted properly?	____	____

Comments: _____

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Analytical Methods:	YES	NO
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:	YES	NO
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?	____	____
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?	____	____

	YES	NO
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?	____	____
13. Is the completeness of the data acceptable?	____	____

Comments: _____

_____

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Data Validation and Reporting:	YES	NO
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: _____

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15.0 Quality Assurance Reports

The Divisional Quality Assurance Officers are responsible for preparing a quarterly internal quality assurance report. 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.

Quality assurance reports to DEP for SWIM projects are made on a variable schedule based on the frequency of sampling since these are on-going monitoring projects. For weekly, biweekly, or monthly sampling schedules, QA reports are submitted semiannually. For bimonthly, quarterly or semiannual sampling schedules, the QA reports are submitted annually. The reports to DEP are written by the Divisional Quality Assurance Officers, Laboratory Quality Assurance Officer and the Project Managers. The Project Manager is responsible for submitting the report to DEP.

If no project audits are performed and no significant quality assurance/quality control problems occur 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.

COLOR

Equipment: Spectronic 501 with ambient flowcell

Reagent: Platinum cobalt color standard, 500 APHA color units (Fisher #SO-P-120)

Standards:
1. 500 c.u. = undiluted stock reagent
2. 300 c.u. = 30 mLs stock diluted to 50 mLs with di H_2O
3. 100 c.u. = 10 mLs stock diluted to 50 mLs with di H_2O
4. 50 c.u. = 5 mLs stock diluted to 50 mLs with di H_2O

Procedure:

1. Calibration

   a. Let instrument warm-up for 30 minutes.
   b. The settings for the color procedure have been save in the 501's memory and will be automatically set-up when the instrument is turned on. It should go to 465 nm as the proper wavelength.
   c. Press "A" on the accessory module to activate the pump. Pump di H_2O through the flowcell until a stable reading is observed. Press "Second function" and "%A/A/C" keys on the main keyboard to zero the instrument.
   d. Pump the 500 c.u. standard through the flowcell until a stable reading of 500 +/-5 c.u. is obtained. If a reading of 500 +/-5 cu.u. is not obtained, consult the instrument manual or your supervisor for the recalibration procedure.
   e. Record the calibration results on the calibration log sheet in the notebook.
   f. check the remaining standard using the procedures in d and e. The 300 c.u. standard should read 300 +/-5 c.u. The 100 c.u. standard should read 100 +/-3 c.u. The 50 c.u. standard should read 50 +/-3 c.u.

2. Sample Measurement

   a. Sample should be at or near room temperature to prevent condensation on the flowcell.
   b. Pump sample through the flowcell until the reading is stable. It takes approximately one milliliter of sample to get a stable reading.
   c. Record the reading on the computer sheet for manual data entry.
   d. Check a standard after every 10 samples. If the result is not correct, check with your supervisor before continuing with the analysis of samples.

3. Quality Control

   a. The QC check standards are run at the beginning of the run after calibration. Continue if results are in the acceptable range, if not, recalibrate the instrument.
   b. Duplicate samples are run every 20 samples.
   c. A replicate sample is run at the beginning, middle, and end of each day's run.

General Description

The color of the sample is determined by spectroscopic comparison to platinum-cobalt standard solutions. The use of spectroscopy allows more samples to be analyzed and it also eliminates the variation in color readings taken by the human eye reducing the potential for error in the test. The method is applicable to waters which are colored naturally due to vegetative decay. One unit of color corresponds to 1 mg/L platinum in the form of the chloroplatinate ion.

Samples

The sample matrices analyzed using this procedure are limited to ambient surface water, ground water, rainfall, and agricultural storm water runoff.

SILICA

This method is provided by ALPKEM Corporation for use with the Rapid flow Analyzer.

Summary of Method

B-molybdosilicic acid is formed by the reaction of silicate with molybdate at a pH of 1 to 1.8. The B-molybdosilicic acid is reduced by tin (II) to form molybdenum blue with an absorbance maximum at 820 nm (1).

Interferences

Interference from orthophosphate and tannin is eliminated by the use of tartaric acid. Filter turbid samples before determination. Color absorbing at the analytical wavelength will interfere.

Sample Handling and Preservation

Collect samples in plastic containers. The samples are unpreserved. Store them at 4 degrees C. The holding time is 28 days (3).

Equipment: Rapid Flow Analyzer 300 @ 820 NM

Reagents: Filter all Reagents prior to use

Sodium Lauryl Sulfate 5% solution: Dissolve 5 g of dodecyl sulfate $\{CH_3(CH_2)_{10}CH_2OSO_3NA\}$ in 95 ml of DI water in a 250 ml erlenmeyer flask.

Working Molybdate Reagent: Mix 1.080 g or ammonium molybdate, 0.3 ml H_2HO_4, and 1 ml sodium lauryl sulfate. Dilute to 100 ml with DI water. Prepare daily.

Tartaric Acid: Dissolve 100 g of tartaric acid $(CHOH)_2(CO_2H)_2$ in approximately 700 ml of DI water in a 1L volumetric flask. Dilute to the mark and mix well. Add 2 drops of chloroform. Store the reagent in a plastic container and refrigerate at 2 - 6 degrees C.

Stock Stannous Chloride: Cautiously add, while stirring, 10 ml of HCL to 10 ml of DI water. Dissolve 10 g of stannous chloride ($SnCl_2$ $2H_2O$) in the acidic solution. (Heat if necessary) Store the solution in a tightly closed plastic container and refrigerate at 2 - 6 degrees C.

Hydrochloric Acid 1.2N: Cautiously, while stirring, add 100 ml of concentrated (12N) hydrochloric acid (HCL) to approximately 800 ml of DI water in a 1L volumetric flask. Dilute to the mark with DI water, mix well and store in a plastic container.

Working Stannous Chloride Reagent: Mix 0.5 ml of stock Stannous Chloride with 50 ml of 1.2N HCl in a plastic container. Prepare fresh daily.

Standards:

Stock Standard: The stock standard is a 10 mg/ml Si of 21.3 mg/ml SiO_2 NBS standard.

Intermediate Stock (Solution A): Dilute 5 ml of NBS stock to 100 ml = 10.6 mg/l.

Working Standards:

STD 1: 2 ml of Solution A in 100 ml of water = 21.30 mg/l
STD 2: 1 ml of Solution A in 100 ml of water = 10.65 mg/l
STD 3: 1 ml of Solution A in 200 ml of water = 5.33 mg/l
STD 4: 50 ml of STD 3 in 100 ml of water = 2.67 mg/l
BLANK: DI WATER

NOTE: STORE ALL STANDARDS IN PLASTIC BOTTLES. DO NOT ACIDIFY.
NOTE: The use of glass containers should be avoided. Transfer all reagents and calibrants to plastic containers immediately following preparation.

References:

1. Truesdale, V.W., C.J. Smith, "The Formation of Molybdosilicic Acids from Mixed Solutions of Molybdate and Silicate," Analyst, March 1975, Vol. 100, pg. 203-212.

2. Standard Methods for the Examination of Water and Wastewater, Fourteenth Edition, Pg. 487, American Public Health Association, Washington, D.C.

3. Methods for Chemical Analysis of Water and Wastes, March 1984, EPA-600/4-79-020, "Sample Preservation" Pg. xviii, Environmental Monitoring and Support Laboratory, Office of Research and Development, U.S. Environmental Monitoring and Support Laboratory, Environmental Protection Agency, Cincinnati Ohio, 45286.

4. Patton, C.J., Design, Characterization, and Applications of a Miniature Continuous Flow Analysis System, Doctoral Dissertation, Michigan State University, 1982, Pg. 63 - 64.

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 PO4-P = 4.394 grams potassium phosphate, monobasic (KH2PO4) 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 H_2O
2.0 mg/L = 20 ml stock diluted to 1000 ml with di H_2O
1.5 mg/L = 15 ml stock diluted to 1000 ml with di H_2O
1.0 mg/L = 10 ml stock diluted to 1000 ml with di H_2O
0.5 mg/L = 5 ml stock diluted to 1000 ml with di H_2O
Blank = 1000 ml di H_2O

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 ammmonium 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	Pattersson and Jansson, 1978	DRAFT
PAGE 1 OF 7 Appendix D				DATE 8-01-94

APPROVALS/DATE			
DIVISION DIRECTOR	LAB SUPERVISOR	QUALITY ASSURANCE	METHODS

ECTION 1.0 - TABLE OF CONTENTS

ECTION 2.0 - METHOD DESCRIPTION/HISTORY

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

$$R\text{-}PO_4 + H_2O ====== ROH + H_2PO_4$$

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 then 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.

CTION 7.0 - QUALITY CONTROL

Run a duplicate set of each working standard for each analysis. Record the fluorescence value on the instrument

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.

CTION 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 Cytofluour 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.**

SECTION 8.0 (CON'T)

8.6 Alternatively, a new protocol can be created by following these steps:

a. On the well displayed on the screen, click the well you want to use.

b. On the upper right hand corner of the screen, click the well assignment you need (Bl=Blank, Un=Sample, St=Standar Co=Control, Em=Empty)

c. On the edit bar located at the upper portion of the screen, edit the correct I.D. You will need to enter the concentratio 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 μL of MUP into each sample wel **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 fir well is on the top right position. Scan within 10 seconds (Click RUN, COLLECT DATA, then ente WORKGROUP number under file name). Record the exact time of the start of the incubation. The syste will automatically scan for time 0 reading, then a message "50 % completed will be displayed" on the sca 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 giv you an option to CLOSE DOOR or IGNORE DOOR. Choose IGNORE DOOR if another plate is to b 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 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 no highlighted. IMPORTANT: Only highlighted well (blackened background) will be calculated with th standard curve.

8.13 After highlighting each well, depress the DATA button on the right hand corner of the screen. Th 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 correction (At this stage, any outlier standard or sample can be hidden to exclude from calculations. Press the H button).

APPROVALS/DATE			
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ECTION 9.0 - DATA HANDLING

9.1 Cytofluour 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.

ECTION 9.0 - DATA HANDLING (CON'T)

2 LIMS Database

9.2.1 Prior to running samples: Go into the ACS LIMS via the command s1 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.

CTION 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 a paper towel, to dry. Discard the plate if any visible crack or scratches is observed.

CTION 11.0 - REFERENCES

11.1 Pattersson, K. and M. Jansson. 1978. Determination of phosphatase activity in lake water-a study of methods. Verh. Internat. Verein. Limnol. 20:1226-1230.

11.2 Prof. Robert G. Wetzel. 1994. Personnal Communication. Department of Biological Sciences, The University of Alabama, Tuscaloosa, Alabama 35487-0344, USA.

11.3 Cytofluor 2300 Manual. 1992. Millipore Corporation, Bedford, MA.

DER Biology Section

v. 1—7/6/93

SOP #BA-7
Benthic Macroinvertebrate Dip Net Sample Collection

(based on Plafkin, 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.	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.
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.	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.
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: $\text{Number of sweeps per Major Habitat} = \frac{20}{(\text{Number of Major Habitats}) + 1}$ 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).	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.

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STEPS	COMMENTS
4. Perform 20 discrete 0.5 meter sweeps with the dip net. Sample the available substrates as determined by the above procedures.	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.
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.	Catch organisms by allowing them to flow into the net and also by sweeping the net towards disturbed material.
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.	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.
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.	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.
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.	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.
5. Record the number of sweeps for each habitat on the *Field Physical / Chemical Characterization Data Sheet.*	Ideally, control and test sites will be sampled the same number of times in the same habitats.
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.	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".

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.

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.

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SOP #BA-8
Benthic Macroinvertebrate Qualitative (Dip Net) Sample Handling

STEPS	COMMENTS
Materials	
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. *Benthic Macroinvertebrate Bench Sheet*	
Methods	
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 (fist 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® 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.

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STEPS	COMMENTS
5. Thoroughly mix the sample so that a homogenous 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 numbe. 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.

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SOP #BA-8.1
Preparation of 80% Ethanol

STEPS	COMMENTS
Materials	
1. 100% Ethanol (HPLC grade) 2. D.I. water 3. 4000-mL graduated cylinder 4. 4-L glass amber jug 5. Plastic funnel to fit into 4-L jug	
Methods	
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.	

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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	
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).	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.
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.	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).
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 taught, 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 disgorge the contents into the sieve, rinsing to assure complete sample purging.	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. Check to make sure the jaws are fully closed and that no sample was lost while lifting the dredge.

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STEPS	COMMENTS
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 disgorge the contents into the sieve, rinsing to assure complete sample purging.	Check to make sure the jaws are fully closed and that no sample was lost while lifting the dredge.
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.	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.
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.	Take care to rinse the entire contents of the sample into the pan. Some organisms may to stick to the screen.
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.	
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.	Rose bengal dye may be added to the sample, as a picking aid, if desired.

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SOP #BA-10
Benthic Macroinvertebrate Grab Sample Handling
(Modified from *Standard Methods 10500C*)

STEPS	COMMENTS
Materials	
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-6.1
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. *Benthic Macroinvertebrate Bench Sheet*	
Methods	
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 *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.	

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STEPS	COMMENTS
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.	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.
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).	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.
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.	Picking accuracy should be checked by a co-worker in 10% of the samples.

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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^2). 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 tubiculous worms which are generally large in size) considered useful in impact determination.

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STEPS	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.	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.
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.	Take care to rinse the entire contents of the sample into the pan. Some organisms may to stick to the screen.
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.	Rose bengal dye (use a very small amount) may be added to the sample, as a picking aid, if desired.

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SOP #BA-12
Benthic Macroinvertebrate Core Sample Handling
(Modified from *Standard Methods 10500C*)

STEPS	COMMENTS
Materials	
1. Waterproof paper and permanent marker	For making labels
2. U.S. 30 mesh sieve	
3. Ethanol filled squeeze bottle (80%)	
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. *Benthic Macroinvertebrate Bench Sheet*	
Methods	
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 sample container (wide mouth jug or Whirl-pak bag) over a U.S. 30 mesh sieve. Rinse the container 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, twigs, 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 *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.	

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STEPS	COMMENTS
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.	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.
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).	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.
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.	Picking accuracy should be checked by a co-worker in 10% of the samples.

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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® tool with fasteners	
5. Whirl-pak® 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.	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 snags will deflect sand from being deposited on the samplers. This can be determined by close examination of the bottom topography.
2. Attach cable to a point on the bank sufficiently high to enable recovery even if the water level increases.	Wrap the cable around the base of a tree on the bank and use the Nico-press® 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® tool is unavailable, the fasteners may be crimped by hammering (two hammers are needed).
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.	Wade or use a boat. DO NOT pull the block up from the shore.
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.	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.

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SOP #BA-14
Benthic Macroinvertebrate Hester-Dendy Sample Handling
(Modified from *Standard Methods 10500C*)

STEPS	COMMENTS
Materials	
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. *Benthic Macroinvertebrate Bench Sheet*	
Methods	
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.

STEPS	COMMENTS
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.	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.
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).	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.
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.	Picking accuracy should be checked by a co-worker in 10% of the samples.

Macrobenthic Invertebrate Keys

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