LABORATORY QUALITY ASSURANCE PROCEDURES

For the

ENVIRONMENTAL SYSTEMS ENGINEERING INSTITUTE
DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING
UNIVERSITY OF CENTRAL FLORIDA
ORLANDO, FLORIDA 32816

GENERAL INFORMATION

INTRODUCTION

Quality assurance as discussed in this section refers to the practices of the Environmental Systems Engineering Institute for sample bottle preparation, sample storage after receipt from the field, analysis, and data reporting. General laboratory practices include the use of suitable grades of reagents, gases, glassware, and standard materials. All reagents will be of at least reagent grade for the inorganic analyses. ACS or HPLC (or higher) grade solvents will be required for all organic analyses. Gases and standards will be of the highest purity obtainable; with the exact purity of the primary standard materials being known. Primary standard material is purchased fresh at least every six months with working standard solutions being replaced in accordance with the particular analytical methods. All volumetric glassware will be Class A grade. Periodic checks on performance of the laboratory equipment are performed regularly as a part of the quality control program. Likewise the performance of the analytical balances are monitored on an semi-annual basis by weighing a series of Class S weights and making any necessary adjustments.

SAMPLE COLLECTION AND CUSTODY

Containers

Sample containers are to be cleaned in accordance with Table 1. Each sample bottle receives a label which is to be filled out with the project name, date and time of sampling, preservatives, work order number, sort code, and initials of person taking the sample. Field personnel will receive all sample bottles from the laboratory manager just prior to the sampling event in order to insure that uncontaminated bottles are being used. Table 2 lists the sizes and types of bottles to be used for each parameter.

Table 1

Sample Bottle Cleaning Procedures

Analysis/Parameter	**Cleaning Procedure (in order specified)**
pH, Color, UV-254, Solids, Turbidity	1-4
Inorganics (anions, silica, etc.)	1-4
Metals, Alkalinity	1-4, 10, 4
NPDOC	1-4, 9
THM	1-4, 9
Haloacetic acids	1-4, 9
Pesticides Group A	6-8
Pesticides Group B	6-8

Cleaning Procedures:

1. Remove all labels with tap water and scrub brush.
2. Wash with tap water and a suitable laboratory-grade detergent, i.e. Liquinox and a scrub brush.
3. Rinse a minimum of three times with tap water.
4. Rinse a minimum of three times with deionized water.
5. Rinse with ACS grade 1:1 HCl
6. Rinse a minimum of three times with acetone.
7. Rinse a minimum of three times with petroleum ether.
8. Air dry for at least 30 minutes, or blow dry with high purity helium gas.
9. Bake for at least 4 hours at 400 C, then cool slowly to room temperature.
10. Rinse with 1:1 HNO_3

Labeling

Sample bottles, at the time of collection, should have labels affixed to them which contain sufficient space or fields in which relevant information concerning sample nature and custody can be entered with a pen or pencil. This information includes the project name, the initials of the project manager, the sample identity and matrix type (e.g. groundwater, surface water, etc), the work order number, the sort code, and the sample date. Information on the sample nature and type should be entered immediately or as soon as possible after sample collection in the field. Information pertaining to sample custody (work order number, sort code) may be entered upon submission of samples to the laboratory, and may be entered by the project manager (or his/her designee) upon sample submission. A suggested format for sample labels is shown below in Figure 1.

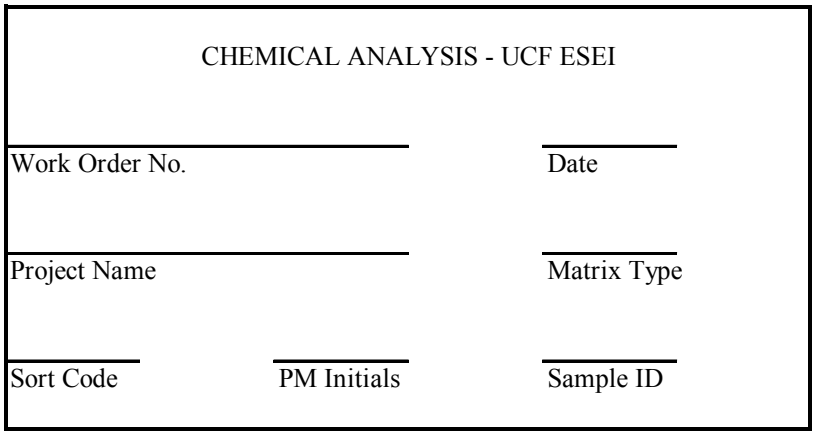

Figure 1 Suggested label format for sample bottles submitted to laboratory.

A template is available from the laboratory which will permit generation of entire sheets of these labels that are suitable for printing via computer.

Field Analysis

The following table shows a list of parameters to be analyzed on-site within the scope of the project, along with the methods and their dynamic ranges of determination.

Table 2

Summary of field parameters and methodologies

Parameter	Method	Method Reference	Approx. Range
Alkalinity	Titration	SM 2320 B	5 - 500 ppm
Ammonia-N	Membrane Probe Method	SM 4500-NH3 C	0.1 – 3 ppm
Chlorine, free	DPD colorimetric	SM 4500-Cl G or Hach 8021	0.1 - 2 ppm
Chlorine, total	DPD colorimetric	SM 4500-Cl-G or Hach 8167	0.1 - 2 ppm
Color, apparent	Visual Comparision (by spectrometer)	SM 2120 B	1 - 50 cpu
Conductivity	Probe	SM 2510 B	variable
Hardness (total, calcium)	EDTA Titration	SM 2340 C	5 - 500 mg/L
Iron, dissolved	Phenanthroline	SM 3500-Fe D	0.005 - 3 mg/L
Nitrate	Cadmium reduction	Hach 8192	0.1 – 0.5 mg/L
Nitrite	Diazotization	Hach 8507	0.1 - 0.3 mg/L
Oxygen, dissolved (DO)	Membrane probe	SM 4500-O G	0.1 - 20 mg/L
Ozone	Indigo	SM 4500-O_3 B	0 - 1.5 mg/L
pH	Electrometric	SM 4500-H^+ B	2 - 13
Phosphate, ortho	Ascorbic Acid	SM 4500-P E	0 - 2.5 mg/L
Silica	Silicomolybdate	Hach 8012	0.3-100 mg/L
Sulfide	Iodometric	SM 4500-S^{2-} F	0.1 - 5 mg/L
Temperature	Direct reading		0 - 100 deg C
Turbidity	Nephelometric	SM 2130 B	0.02 - 200 ntu
UV-254	UV spectrometry	SM 5910 A	0-0.5200 cm^{-1}

SM = Standard Methods of Water and Wastewater Analysis, 19th ed (1995)

Hach = DR4000 Spectrometer Method Handbook

Preservation, Storage and Transport to the Laboratory

Samples are to be preserved at the sample site, in accordance with Table 3. Samples are transported from the sample site to the laboratory in an ice chest containing wet ice or several cold packs. Following inspection and log-in at the laboratory the samples will be refrigerated at 4°C if called for by procedure. Sample holding periods will be in accordance with Table 3. Please note that all times listed are in terms of the sampling event that may or may not be the same day as when the samples arrive at the laboratory. Holding time begins at time of sample collection, not sample delivery to the laboratory. Samples requiring parameters not specified in Table 2 will be stored at 4°C in plastic or glass containers until the time of analysis.

LABORATORY CUSTODY AND ANALYSIS

Log-In

At the time of collection, sample information are entered into a laboratory log book. There shall be a log book for each individual parameter that is analyzed on site. Relevant information shall be entered into each log book that is used (i.e. the log book for each parameter analyzed). This information includes sample location, initials of sampler, date and time sampled, and preservation of the sample (if needed). The results of any field analyses shall be included in the appropriate field log book. Field analyses include chemical parameters specified in Table 3, as well as pressure, flow, and/or any other relevent parameters that are most accurately determined on-site. Field determination is particularly important for parameters whose values may change during sample transport to the laboratory (such as sulfides). The field information is to accompany the samples to the laboratory, with the appropriate Custody Sheet (see Figure 2). Upon arrival at the laboratory, the samples are examined for broken or leaking containers, proper preservation and sampling technique. This process is illustrated in the flow chart given in Figure 3. If sample integrity is questionable, re-sampling is requested at this time.

Table 3

Sample containers, preservatives, and holding times

Parameter	Container[a]	Preservative	Holding Time
UV Absorbing Organics, Color, Turbidity	100 mL plastic or glass	None	Analyze Immediately
pH	100 mL plastic or glass	None	Analyze Immediately
Anions (Cl, SO_4, Br, F, PO_4) by IC.	500 mL plastic or glass	Refrigerate 4 C	28 days
Alkalinity	100 mL plastic or glass	Refrigerate 4 C	24 hours
Metals	250 mL plastic or glass	HNO_3 to pH < 2	28 days
THM & HAA formation potential	4 liter amber glass jugs with screw caps	Refrigerate at 4 C	None, analyze immediately
THM (following incubation for formation potential)	60 mL amber glass vials with Teflon-lined screw-caps	Refrigerate 4 C 0.5 mL of 0.4 *M* $Na_2S_2O_3$	Extract within 7 days, analyze immediately following extraction
HAA (following incubation for formation potential)	125 amber glass bottle with Teflon-lined screw caps	1.25 mL 0.4 *M* NH_4Cl, Refrigerate	Extract within 7 days, analyze immediately following extraction
KIWA Pesticides	1 liter amber glass bottle with Teflon lined screw caps	Refrigerate at 4 C	Extract within 7 days, analyze extract within 40 days
NPDOC	100 mL glass	Refrigerate 4 C pH < 2 with HCl	28 days

[a]Volumes listed by each parameter are minimum requirements for accurate determination and inclusion of necessary quality control (spikes, duplicates, etc.) for that specific parameter. Total sample size may be estimated by adding volumes of parameters desired.

Chain of Custody

Once the samples are deemed acceptable the laboratory manager assigns the sample (or group of samples within a given experiment) a Work Order Number. The project manager then generates and submits a formal Chain of Custody document, or Custody Sheet for that sampling event. In addition, each sample within a given Work Order is assigned a Sort Code, in addition to any other sample identification number that the project manager assigns for his/her own purposes.

The custody log serves as a tracking tool to assist project and laboratory staff in monitoring the progress of analysis for each work order proceeding through the laboratory. The analyst checks this log at the beginning of his/her work shift to determine which samples need analysis for which parameters, so that they may proceed with these analyses. Analysts can review the custody sheets for each work order within the log, obtain unanalyzed samples, and carry out necessary analyses. As the analyses are completed satisfactorily, the analyst initials and dates the appropriate column on the custody sheet and submits the Analysis Sheet to the Laboratory Manager for approval. This process proceeds until each parameter on a given work order is analyzed. At this point, the work order is said to be "filled", and the Laboratory Manager generates a

Summary Sheet for the completed work order. This process is illustrated graphically in the flow chart in Figure 4.

Work order numbers are assigned based on year (first two numbers), month (next two numbers), and chronological order of sampling event (next three numbers). For example, a sample receiving the number 0505001, was received during 2005, in May, and was the first sampling event received that month. Furthermore, a Sort Code is assigned by the Project Manager to each sample within a given work order (before submitting the sample). This number consists of an integer ranging from one to the total number of samples within the work order. For example, a work order consisting of eight samples would have sort codes of values one through eight assigned to each sample sequentially according to the original order on the custody sheet as prepared by the project manager. This order, once established on the custody sheet, is never changed throughout the history of that work order, and is retained on every report referring to that sample. This number is added solely to expedite the process of electronically reporting, transferring, and managing data, so that all sample results for all parameters could be conveniently placed and/or electronically copied in the same order (to minimize clerical errors) on the Summary of Analytical Results and Progress Report (Summary Sheet).

It is the responsibility of the submitting party (Project Manager, etc) to be sure that a properly-completed Custody Sheet accompanies each sample set submitted to the laboratory. Any samples that are not listed on a Custody Sheet will not be analyzed.

ESEI Laboratory
University of Central Florida
P.O. Box 25000
Orlando, Florida, 32816
Phone: 407-823-5092
Fax: 407-823-3315

Workorder: 9804005
Date: 4/24/98

Chain of Custody

						Analysis Requested					
Client		Dietz/Wayson									
Address:		UCF CEES									
Phone/Fax:		x5304				NPDOC	Alkalinity	Iron	Sulfate		
Contact:		J. Dietz									
Sort Code	Sample ID	Date Sampled	Time Sampled	Matrix Type	Client id						
1	K06KB	4/24/98		GW							
2	L06LB	4/24/98		GW							
3	B07B0	4/24/98		GW							
4	C07C0	4/24/98		GW							
5	D07D0	4/24/98		GW							
6	E07E0	4/24/98		GW							
7	F07F0	4/24/98		GW							
8	G07G0	4/24/98		GW							
9	H07H0	4/24/98		GW							
10	I07I0	4/24/98		GW							

Relinquished by: Date/Time:

Received by: Date/Time:

Comments:

Figure 2 Sample of Custody Sheet format

STAGE 1

SAMPLE SUBMITTAL AND ASSIGNMENT

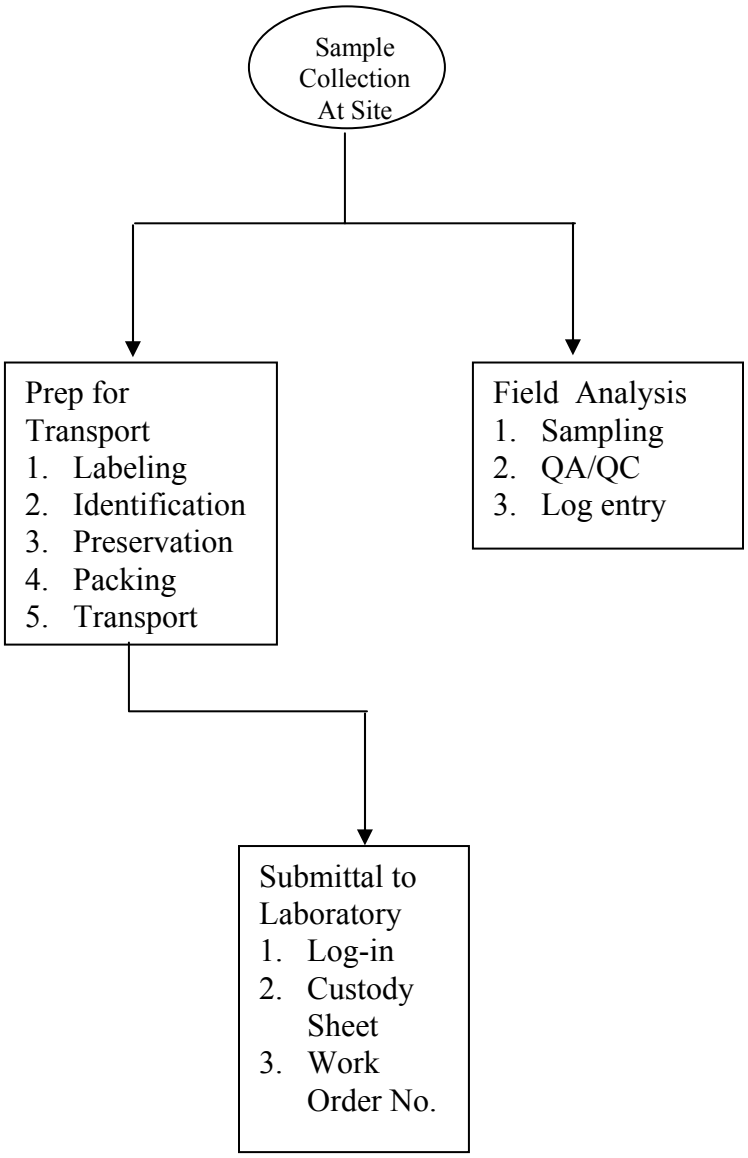

Figure 3 Flow chart of field sample collection and analysis protocol

STAGE II
SAMPLE ANALYSIS AND DATA REPORTING

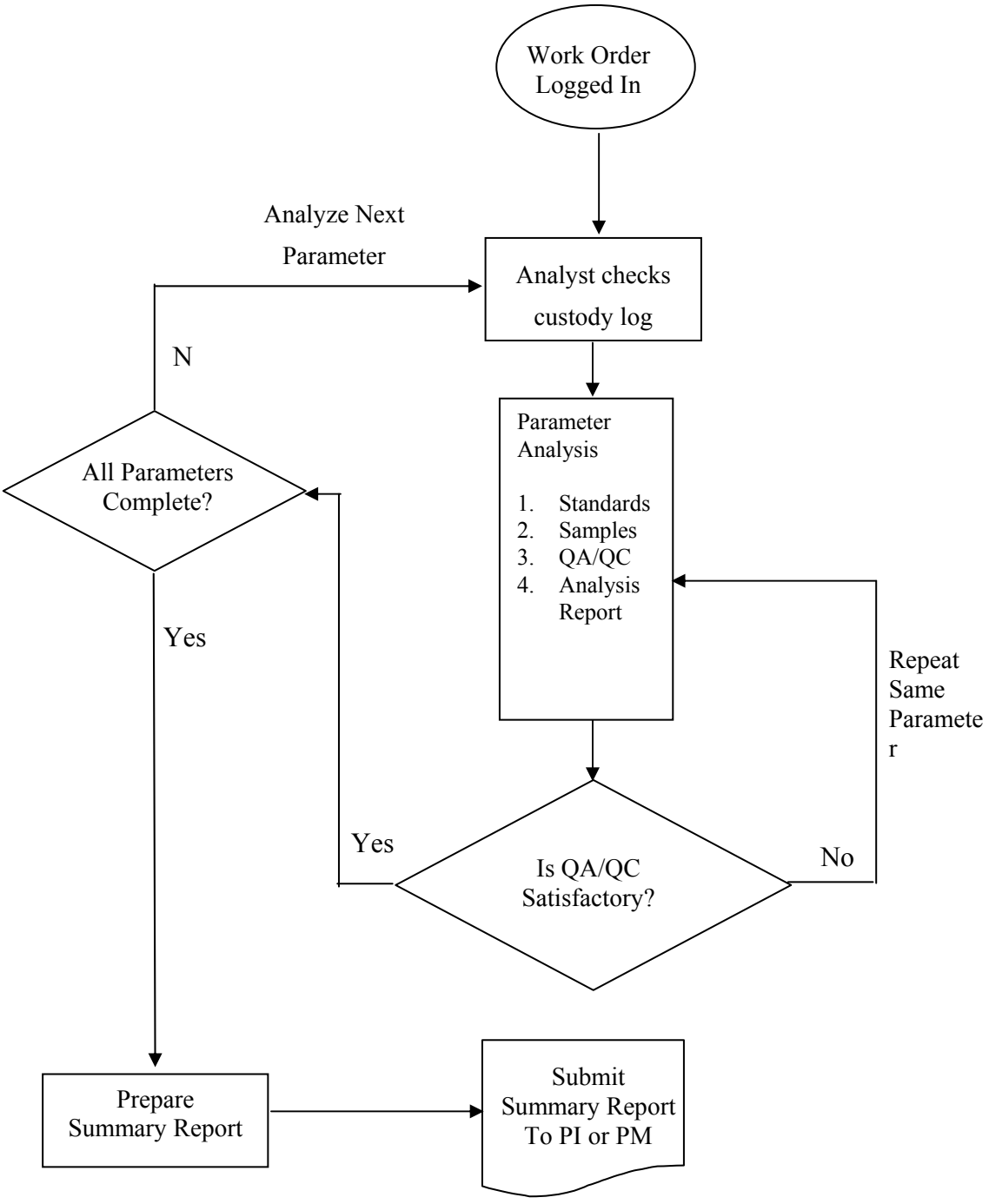

Figure 4 Flow chart of laboratory chain of custody, analysis, and reporting

Parameter Analysis

As a given work order is filled (i.e. analytical results for that work order are submitted and approved by the Laboratory Manager) the results are printed out on an Analysis Sheet. This information includes sample identification and measurement information. As each analysis is carried out, the analyst is responsible to assure that proper standards and quality control samples are analyzed and recorded in accordance with the paramater's requirements. Standard results do not need to be recorded on the analysis sheet but must be logged in the appropriate log book or maintained in the appropriate data file. QA/QC results must be shown on the Analysis Sheet. The Analysis Sheet contains all information pertinent to a given parameter for a given work order. This information includes sample identification and measurement information. The example below demonstrates the format in which that information is presented. Analytical data for each individual parameter requested within a given work order is presented in this format on its own sheet. Each analysis sheet is present in both printed and electronic form to the Laboratory Manager for approval and filing. If the quality control provisions are not met, the analysis is not approved, and the analysis is repeated until satisfactory QA/QC results are obtained.

LABORATORY REPORT

Pb

Client: IMS
Work Order: 9709007
Sample Date: 10/1/97
Date: 10/25/97

Metal Analyzed & Wavelength: Pb @ 283 nm

Sort Code	Sample ID	Dilution Factor	Mean Absorbance	Concentration (ppb)*	
1	FTM-R	-	0.1523	35.7	
2	FTM-F	-	0.1491	34.1	
3	FTM-P	-	0.1122	19.6	
			.		
	SPIKES	**CONCENTRATION (mg/L)***			
	SAMPLE ID	SPIKED WITH	RECOVERED	% RECOVERY	%RSD
9001-2	Filtrate	40.00	48.2	113	x
	DUPES				
Dupe 2	FTM-F	x	30.9	x	9.8

Analyst

Approved by

Figure 5 Example of an Analysis Sheet

Summary Reports.

As analyses are satisfactorily completed, they are submitted the Laboratory Manager and copied to a Summary Sheet. The Summary Sheet serves as a running progress report for the work order as it is filled, and is updated with new information each time an analysis is completed. The Summary Sheet contains the measurements for each parameter requested, the minimum level as quantified by the standard curve for that analysis, the scheduled date of completion of each analysis, and the actual date of completion of each analysis. The Summary Sheet is updated regularly and kept in a binder or folder in the laboratory. This binder or folder is kept available for review by the Project Manager or any other laboratory staff at any time, and is used to track the progress of analyses for all outstanding work orders. Samples remain in the custody of the laboratory until completion, review, and approval of analytical results by the laboratory manager and the project manager. When all relevent parties approve of the results, custody of samples is released to the project manager for disposal. Upon completion of the last analysis for a given work order, the Summary Sheet (Figure 6) is inspected and signed by the Laboratory Manager and relinquished to the Project Manager.

SUMMARY OF ANALYTICAL RESULTS
PROJECT: USEPA
START DATE: 7/20/99
COMPLETE DATE: 7/30/99

		NPDOC	UV-254	Color	TS
9907001		(mg/L)	(cm^{-1})	(cpu)	(mg/L)
1	Raw	8.07	0.2747	46	244
2	ZMF Permeate	3.36	0.0859	8	246
3	ZMF Bleed	NR	NR	NR	1282
4	CSF	2.13	0.0391	3	NR
5	NF1 Permeate	0.94	0.0155	1	NR
6	NF2 Permeate	0.10	0.0046	1	NR
7	NF1 Concentrate	5.83	0.0761	NR	NR
8	NF2 Concentrate	6.12	0.0936	NR	NR

Figure 6 Sample of Summary Sheet

LABORATORY EQUIPMENT AND PREVENTIVE MAINTENANCE

In order to prevent down time due to equipment failure spare parts for several analytical instruments will be kept on hand. Instruments which are available in this laboratory are: HP 6890A gas chromatograph equipped with an ECD detector, autosampler, and dedicated PC, HP 5890-II GC with FID detector, Model 3000 purge and trap sampler Model 2016 concentrator, three Shimadzu GC-14 gas chromatographs for SOC and VFA analysis, Dohrmann Phoenix 8000 Total Organic Carbon Analyzer with Gilson autosampler, Hitachi Z-9000 graphite furnace atomic absorption spectrophotometer with autosampler, cooled by Neslab CFT-33 recirculating cooler, TJA/Unicam Model 969 flame atomic absorption spectrophotometer, two Hach Ratio Turbidimeters (Model 2100AN), four Hach DR/4000U ultraviolet/visible spectrophotometers, Dionex Ion chromatographs (Model DX-120) with autosampler, and several Fisher Accumet pH meters (Model AR50 and others). Instrument logs detailing the routine maintenance and performance of the instruments will be kept during the project. Two Barnstead/Thermolyne distillation units provide water for reagent preparation.

ANALYTICAL QUALITY ASSURANCE

METHODOLOGIES

All analyses are performed in accordance with the methodologies listed in Table 3. Each analytical method to be used during the course of this project has certain quality control guidelines that will be observed in order to produce quality data. The precision and accuracy measurements are statistically manipulated and graphed in order to further assess the quality of the data on an on-going basis. Where applicable, standard curves are constructed and analyzed for correlation. Further assessment of accuracy are made by the use of reference samples of known concentrations and statistically generated 95% confidence intervals. The following is a discussion of precision and accuracy assessment as it pertains to this project and the current precision and accuracy data which is available for the parameters of interest.

Quality Control for Field Methods

Introduction

Maintenance of good analytical practice in the field will be carried out according to the same statistical principles as in the main laboratory. While facilities available in a field laboratory are somewhat less sophisticated than those in a full-scale laboratory, the same guidelines are applied to obtain the maximum quality possible from the data gathered in the field. For the benefit of access to the reader, the theoretical background that is presented in the ESEI Quality Assurance plan is inserted here for reference, with additions in each section that apply specifically to field analysis practices.

A discussion of the theory and basis for quality control of accuracy and precision follows in the next section. Quality control as applied to field analysis is intended to describe the development and enforcement of good analytical and handling practices as they pertain to field analysis. Measures taken in the field will be carried out as closely as feasiily to those used in the main laboratory. All parameters in the field will be assessed for precision. However, the principle of accuracy based upon recovery of standard addition does not apply to many of the field parameters; and for still other parameters, accuracy is not feasible or practical to analyze in the field, even though the parameter is a discreet species (such as sulfide). Table 4 summarizes the appropriate QA measures to be taken for various field analyses.

Table 4

Appropriate quality control provisions for field parameters

Parameter	Accuracy	Precision
Alkalinity	Y	Y
Chlorine, free	N	Y
Chlorine, total	N	Y
Color, apparent	N	Y
Conductivity	N	Y
Hardness (total, calcium)	Y	Y
Iron, dissolved	Y	Y
Oxygen, dissolved (DO)	N	Y
pH	N	Y
Temperature	N	Y
Turbidity	N	Y
UV-254	N	Y
Nitrate	Y	Y
Nitrite	Y	Y
Ozone	N	Y
Phosphate, ortho	Y	Y
Silica	Y	Y
Sulfide	N	Y

Application and Enforcement of Precision Criteria

Quality control requirements for the analytical methods listed in this field QA plan require ten percent of all samples be analyzed (analytical plus field) in duplicate with at least one duplicate pair being analyzed each day sample analyses are performed. Duplicates will be selected by the Co-PI in charge, or his/her designee, on site during the sampling event unless otherwise instructed by the Co-PI or his designee. Field duplicates will be collected "blindly"; their identity will not be given to the analyst(s). The sample(s) will be labeled with a neutral identity suitable to the sampling event, such as "QA1" or the like. The Co-PI(s) or designee in charge of quality control on each given day/event will keep a confidential log that will contain a record of the selected duplicates

for each event/day. This log will be kept out of reach of all analysts, in a location other than the field laboratory, and will be reviewed on a routine basis by the Co-PI.

Field assessment of quality assurance will be carried out using NIST ranges for precision. If results are found to be out of compliance (RPD >10% except where reasonable, such as very low permeate values), the Co-PI will meet with the appropriate personnel to discuss corrective actions as necessary.

Application and Enforcement of Accuracy Criteria

Quality control requirements for the analytical methods listed in this field QA plan require ten percent of all samples be spiked, with at least one spike being analyzed each day sample analyses are performed. Spikes will be prepared by the Co-PI in charge, or his/her designee, on site during the sampling event unless otherwise instructed by the PI or his/her designee. Selection and preparation of spikes will be done "blindly"; their identity will not be given to the analyst(s). The sample(s) will be labeled with a neutral identity suitable to the sampling event, such as "QA1" or the like. The Co-PI(s) or designee(s) in charge of quality control on each given day/event will keep a confidential log that will contain a record of the selected duplicates for each event/day. This log will be kept out of reach of all analysts, in a location other than the field laboratory, and will be reviewed on a monthly basis by the Co-PI's or designees.

Field assessment of accuracy will use the NIST default range (80-120% recovery). If results are found to be out of compliance (less than 80% or greater than 120% recovery), the Co-PIs will meet with the appropriate personnel to discuss corrective actions as necessary.

Other Means of Quality Control Assessment

Trip Blanks

In order to assess the prospect of contamination, a "trip blank" will be utilized. A clean bottle will be filled with deionized (blank) water and carried into the field. The cap to this bottle will be opened for a length of time comparable to that of collecting a sample in a similar bottle. The cap is then replaced, and the trip blank is submitted to the laboratory along with the other samples being submitted to the laboratory. If the results for the requested parameters show levels that are significantly above those known for clean deionized water, corrective action will be taken to determine the source and/or cause of contamination.

Check Standards

A secondary check for accuracy is to analyze a known standard solution (analyte prepared by the laboratory in deionized water). This check serves to verify adequate instrument performance, particularly when the response of the instrument is suspect, or is subject to variation during long periods of operation. As needed, a check standard is

analyzed, and the recovery is calculated in the same way as a spike. Recovery is determined by comparing the response of a check standard to that of DI water blank.

Comparability and Completeness

Data comparability is assured by the use of standard methodologies. For pH, bromides, nitrates, calcium, sulfates, chlorides, sodium, bicarbonate, and NPDOC, the specific analytical methods from the 19th edition of Standard Methods (APHA, AWWA, and WEF 1995) are cited in Tables 3 through 6. THM and haloacetic acid measurements will be made in accordance with EPA methods 501.2 and 552. Completeness will be determined by comparison of the project objectives and required outputs during the various phases of the project

Spare consumables for analytical equipment

Adequate supplies of expendable parts must be kept available for laboratory and field equipment. Spare parts for equipment (pH meters, DO probes, spectrophotometer, etc.) are kept in the lab trailer for immediate replacement. Once a spare part has been used, the user must contact the main ESEI laboratory facility to arrange for a replacement spare. At no time should necessary equipment be lacking spare parts crucial to maintenance of continuous quality operation. Needs for replacement parts should be coordinated on a monthly basis (or more often as needed) by a Co-PI or designated personnel at the site.

Chemical reagents and glassware supplies

Several techniques in use for this project utilize reagents that must be prepared and standardized on a regular basis. Examples include standards, titrants, and other reagents that have finite shelf lives. These materials are summarized in the following table. Some of the listed reagents (ex. Iodine titrant for sulfides) do not have a defined shelf life in the literature, however they will degrade under certain conditions. For example, iodine decomposes upon exposure to direct sunlight, hence it is kept in a dark bottle. The analyst responsible for these techniques, as well as to the supervising co-PI, should be aware of the storage and usage conditions of reagents in Table 5. Care must be taken to store and use them properly to obtain maximum usage.

Table 5

Reagents to be provided by the main ESEI lab on a regular basis

Parameter	Reagent	Purpose	Shelf Life
Alkalinity	Sodium Carbonate	Standard	1 week
Alkalinity	0.02N sulfuric acid	Titrant	6 months
Color, apparent	Chloroplatinate	Standards	1 month
Conductivity	0.01 M KCl	Standard	6 months
Hardness (total, Ca))	EDTA solution	Titrant	6 months
Hardness (total)	Ammonia buffer	Adj. to pH 10	1 month
Nitrate	1000 ppm $NaNO_3$	Standard	6 months
Nitrite	1000 ppm $NaNO_2$	Standard	6 months
pH	Buffer concentrates	Standard	6 months
Sulfide	0.025 N iodine	Indicator	6 months
Sulfide	0.025 N sodium thiosulfate	Titrant	1 month
Turbidity	Formazin (primary)	Calibration	1 day
Turbidity	Gelex (secondary)	Daily check	N/A

Field lab trailer users must also be aware of the rate and extent of usage of pre-prepared reagents that do not necessarily require further treatment. These items must be monitored, and re-ordered well in advance of supply depletion. A Co-PI or his designee should oversee a monthly inventory of reagents, and designate the appropriate personnel to collect ordering information and transfer the information to the lab manager at the main ESEI facility. Items such as pre-packaged reagents (Hach pillows, chemical stock standards, etc.) must not be depleted unknowingly.

The same consideration should be given to supplies (glassware, accessories, etc.) that are subject to misplacement, transport back to the main lab, breakage, or loss. Adequate spare supplies for these commodities are currently on hand in the lab trailer, but these reserves will be depleted as things get used (broken, etc). A Co-PI or his designee should oversee a monthly inventory of supplies, and designate the appropriate personnel to collect ordering information and transfer the information to the lab manager at the main ESEI facility.

Table 6

Inorganic Analytical Methods and Reporting Limits

Parameter	Method	Reporting Limit
Aluminum	SM 3113 pages 3-22 to 3-27 Electrothermal Atomic Absorption	20 ppb
Bicarbonate	SM 2320B, pages 2-26 to 2-28 Titration Method	5 mg/L
Bromides	SM 4110 pages 4-2 to 4-6, Ion Chromatography with Chemical Suppression of Eluent Conductivity	0.1 mg/L
Calcium	SM 3111B pages 3-13 to 3-15 Direct Air/Acetylene Flame AAS	0.1 mg/L
Chloride	SM 4500-Cl B pages 4-49 to 4-50 Argentometric Method SM 4110 pages 4-2 to 4-6, Ion Chromatography with Chemical Suppression of Eluent Conductivity	1.0 mg/L 0.1 mg/L
Copper	SM 3113 pages 3-22 to 3-27 Electrothermal Atomic Absorption SM 3111B pages 3-13 to 3-15 Direct Air/Acetylene Flame AAS	5 ppb 0.3 mg/L
Hardness, Calcium	SM 3500-Ca D. pages 3-57 to 3-58 EDTA Titrimetric Method	5 mg/L
Hardness, Total	SM 2340C pages 2-36 to 2-38 EDTA Titrimetric Method	5 mg/L
Iron	SM 3111B pages 3-13 to 3-15, Direct Air/Acetylene Flame AAS SM 3113 pages 3-22 to 3-27 Electrothermal Atomic Absorption	0.3 mg/L 5 ppb
Lead	SM 3113 pages 3-22 to 3-27 Electrothermal Atomic Absorption	5 ppb
Magnesium	SM 3111B pages 3-13 to 3-15 Direct Air/Acetylene Flame AAS	0.1 ppm
Manganese	SM 3113 pages 3-22 to 3-27 Electrothermal Atomic Absorption	1 ppb
Nitrate	SM 4110 pages 4-2 to 4-6, Ion Chromatography with Chemical Suppression of Eluant Conductivity	0.1 mg/L
Nitrite	SM 4110 pages 4-2 to 4-6, Ion Chromatography with Chemical Suppression of Eluant Conductivity	0.1 mg/L

Table 6
Inorganic Analytical Methods and Reporting Limits (continued)

Parameter	Method	Reporting Limit
Nitrogen (trivalent)	SM 4500-Norg pages 4-92 to 4-94 Macro-Kjeldahl Method	5 mg/L
Oxygen, Dissolved	SM 4500-O G., pages 4-102 to 4-104	0.1 mg/L
pH	SM 4500-H^+ B pages 4-65 to 4-69 Electrometric Method	0.1 pH units
Phosphorus	SM 4500-P C, pages 4-111 to 4-112 VM Colorimetric Method	0.3 mg/L
	SM 4500-P E. pages 4-113 to 4-114 Ascorbic Acid Method	0.01 mg/L
Silica	SM 4500-Si D, pages 4-118 to 4-120 Molybdoslicate Method	1 mg/L
Sodium	SM 3500-Na B, page 3-96 to 3-98 Flame Emission Method.	0.1 mg/L
Sulfate	SM 4500-SO_4^{2-} pages 4-136 to 4-137, Turbidimetric Method	1.0 mg/L
	SM 4110 pages 4-2 to 4-6, Ion Chromatography with Chemical Suppression of Eluant Conductivity	0.1 mg/L

All techniques designated with "SM" referenced in Standard Methods are from the 20th Edition (1998).

Table 7

Organic Analytical Methods and Reporting Limits

Parameter	Method	Reporting Limit
AOC	SM 9210B, pages 9-53 to 9-64 P17/NOX Method	1 ppb C
BDOC	NPDOC Determination Before and After Incubation	0.1 mg/L
Haloacetic acids	EPA Method 552, Determination of Haloacetic Acids in Drinking water by Liquid-Liquid Extraction Derivatization, and Gas Chromatography with Electron Capture Detection, Methods for the Determination of Organic Compounds in Drinking Water, Supplement I, EPA/600/4-90/020, July 1990.	1 ppb for all compounds except 2,4 chlorophenol acid which has a detection limit of 20 ppb.
NPDOC	SM 5310C pages 5-19 to 5-21 Persulfate/UV Oxidation Method	0.1 mg/L
Pesticides (simazine, atrazine, bentazone, diuron, DNOC, pirimicarb, metamitron, metribuzin, MCPA, mecoprob, vinchlozolin)	Acidification and SPE/ HPLC Determination at 230 and 270 nm. KIWA protocol	0.1 ppb each.
THM	EPA Method 501.1, Analysis of Trihalomethanes in Drinking Water by Liquid/Liquid Extraction, U.S. Environmental Protection Agency, 40 CFR Part 141, Appendix c, Part II, 1980.	0.5 ppb each

All techniques designated with "SM" referenced in Standard Methods are from the 20th Edition (1998).

Table 8

Aggregate Analytical Methods and Reporting Limits

Parameter	Method	Reporting Limit
$CaCO_3$ Saturation (SI)	SM 2330B pages 2-29 to 2-33 Saturation Index	NA
Color	SM 2120A pages 2-2 to 2-4 UV Absorption at 254 nm	1 cpu
Conductivity	SM 2510B pages 2-45 to 2-46 Laboratory Method	0.1 umho/cm
ORP	SM 2580B pages 2-74 to 2-77 Measurement in Clean Water	0.1 mV
Particle Counts	SM 2560D pages 2-66 to 2-67 Light-Scattering Method	1 particle/mL
Silt Density Index (SDI)	ASTM Method D-4189-82 ASTM Test Method	NA
Solids (TDS, TSS, TS)	SM 2540 pages 2-53 to 2-58 Gravimetric Methods	1 mg/L
Turbidity	SM 2130B pages 2-9 to 2-11 Nephelometric Method	0.02 ntu
UV-254	SM 5910 pages 5-60 to 5-62 UV Absorption at 254 nm	0.0001 cm^{-1}

All techniques designated with "SM" referenced in Standard Methods are from the 20th Edition (1998).

Table 9

Microbiological Analytical Methods and Reporting Limits

Parameter	Method	Reporting Limit
Coliforms (Fecal, Total)	SM 9222 pages 9-53 to 9-64 Membrane Filtration Technique	20 CFU
HPC	SM 9215B pages 9-34 to 9-35 Pour Plate Method	30 CFU

All techniques designated with "SM" referenced in Standard Methods are from the 19th Edition (1995).

Precision

Precision is assessed by measuring the reproducibility observed between duplicate analyses. Duplicates are two determinations of the same analyte for the same sample made by repeating the analytical procedure in its entirety. Precision is expressed as percent relative deviation for each pair of analyses and is calculated by the following formula:

$$\%RPD_{99.9} = \left(\frac{S}{\mathbf{X}}\right) X\ 100 \qquad (1)$$

where:

S = range
X = mean (average for a pair)

The range (S) for a data pair is calculated at 99.9% confidence using the following equation:

$$S = |X_1 - X_2| \qquad (2)$$

To estimate the standard deviation at 95% confidence, a ratio of B factors at p = 0.001 vs. p = 0.05 is taken and found to be 0.89. The RPD above is multipled by this ratio to estimate the standard deviation at 95% confidence.

$$\%RPD_{95} = \%RPD_{99.9} * 0.89 \qquad (3)$$

Precision of a given analytical method is continuously determined by plotting the mean range and variance determinations on a graph known as a Control Chart. An example follows. The range is defined as the absolute value of the difference between the two duplicates. The normalized mean range, $\overline{R}$, is calculated using the following equation:

$$\overline{R} = \frac{\sum_{n=1}^{N} R}{N}$$

where:

$\sum_{n=1}^{N} R$ = sum of the relative standard deviations

N = number of data pairs

The variance, S_R^2, was calculated by:

$$S_R^2 = \frac{\sum_{n=1}^{N} R^2 - (N\,\overline{R}^2)}{(N-1)}$$

where:

$\sum_{n=1}^{N} R^2$ = sum of the relative standard deviations

$\overline{R}^2$ = square of the mean range

N = number of data pairs

The warning limits (WL) and control limits (CL) were calculated by the following equations:

$$WL = \overline{R} + 2S_R$$

$$CL = \overline{R} + 3S_R$$

where:

$\overline{R}$ = mean range

S_R = square root of variance

Data is assessed by interpreting the mean range (also referred to as the central line), with regard to the warning and control limits. A graph of concentration versus sample number is used to aid the interpretation. The mean range, WL and CL are shown as horizontal lines on the graph. The results of an individual paired duplicate analysis are entered on the graph and are assessed by where they fall within the boundaries on the graph. A minimum of twenty pairs of duplicate analyses are used to construct the graph. In the event that a new technique is being introduced or applied, experimentation is done on 20 aliquots of one or more trial matrices (tap water, raw water, etc.) to generate an initial control chart.

The graph is used in the following manner:

If six successive samples exceeded the central line another duplicate pair is analyzed. If the additional duplicate did not exceed the central line analyses proceed; if not the procedure is investigated and more duplicates are analyzed until satisfactory operation is achieved.

If four out of five successive data points exceed one standard deviation, or if a pattern of always deviating positively or negatively is observed, an extra duplicate is analyzed. The system is considered out of control if the trend continues or if the one standard deviation is again exceeded.

If two out of three successive data points exceed the warning limit, an extra duplicate is analyzed. Sample analyses are discontinued if the additional analysis exceed the warning limit.

A sample set is reanalyzed if one data point exceeds the control limit. If the repeated analyses are below the limit, analyses are continued. If the repeated analysis exceeds the control limit, sample analyses are discontinued until the problem is corrected.

Quality control requirements for the analytical methods listed in this quality assurance plan require ten percent of all samples be analyzed in duplicate with at least one duplicate pair being analyzed each day sample analyses are performed.

Accuracy

Accuracy evaluation will encompass the use of spikes, known reference samples, and control standards. Ten percent of all samples, with a minimum of one sample per day whenever analyzes are performed, will be spiked with all analytes being tested for. Percent recovery will be calculated by the following formula:

$$\%R = \left(\frac{A - B}{C}\right) X\ 100 \qquad (4)$$

where:

%R = percent recovery
A = response of spiked sample
B = response of unspiked sample
C = amount of spike

As with the duplicates, the mean, variance, warning and control limits are calculated using at least twenty data points. For the spikes, percent recovery is used instead of relative standard deviation; and as with the duplicates the mean, variance, warning and control limits are calculated using the previously mentioned equations. One additional difference between the presentation of the spike and duplicate data is that the warning and control limits are expressed in terms of plus or minus standard deviations. The upper limits are positive deviations while the lower limits were are negative standard deviations. A graph of the data and statistically calculated points are developed by plotting concentration versus sequence number. This graph is used to access the acceptability of the data in the same manner as previously described for the duplicate analyses. The graphs for precision and accuracy data are redrawn at least annually.

In addition to the duplicate and spike data, purchased reference check samples will be used to assess analytical accuracy. The samples come with preparation instructions, a true value, and a ninety-five percent confidence interval that is computed by the vendor. Most of the samples can be stored and reanalyzed on a daily basis for three months if refrigerated. Sample analysis is not to take place if the results of the reference samples are outside the given confidence interval. Additionally some analytical methods make use of a check sample that is prepared by the laboratory staff to monitor analytical performance. An acceptable result must be obtained for the check standard before an analysis may proceed. What follows is an analyte by analyte view of the analytical quality control that is currently in place at the UCF laboratory.

Method Detection Limits

Since analytical detection limits vary from method to method, and from analyte to analyte, an initial demonstration of capability will be performed for each method and for the individual analytes. For instrumental methods, analyte detection limit is estimated to be five times the detector signal noise at each analyte's retention time. An estimate of each analyte's concentration will be made and laboratory control samples consisting of deionized water spiked with the analytes will be taken through the analytical process and statistically evaluated. Seven laboratory control samples are analyzed for each method.

The mean ($\overline{R}$) and the standard deviation (S) for the percent recovery for each analyte is determined by the following equations.

$$R_i = \left(\frac{(M/A)\ X\ 100}{N}\right)$$

where:

R_i = mean percent recovery
M = measured analyte concentration
A = actual analyte concentration
N = number of laboratory control samples analyzed

$$S = \sqrt{\frac{\int_{n=1}^{N} R^2 - (N\ (R_i^2))}{(N-1)}}$$

where:

R = mean percent recovery
R_i = individual recovery of each sample (in percent)
N = number of samples analyzed

In order for the system performance to be considered acceptable the recovery value for each analyte must be within R +/- 30% or within R +/- 3S depending on the analyte. This procedure is used to set the detection limits on an annual basis. For the wet analytical methods, an estimate of the detection limit based upon the values observed for the blank analyses is made and the analysis of the seven samples as stated above was made. the current method detection limits observed at the UCF laboratory are listed previously in Table 6 to Table 9.

For the purposes of result reporting, in lieu of varying detection limits, a 'lower limit' is established for each parameter for which a standard curve can be developed. The lower limit is defined as the concentration of the lowest standard solution that is used to construct the standard curve routinely for a given analysis. Sample measurements that show a value less than that lower limit are reported as such. For example, the linear response range for standard calcium solutions typically observed in the laboratory extends from 0.1 ppm to 20 ppm calcium ion. A permeate sample that is analyzed, and whose absorbance yields a calculated concentration of 0.05 ppm is simply reported as "< 0.1 ppm", since the standard curve observed does not cover the range of this sample.

LABORATORY PROCEDURES

INORGANIC PARAMETERS

Alumimum

Low-levels of aluminum (<100 ppb) are analyzed for on a Hitachi Z-9000 Simultaneous Multi-Element Graphite Furnace Atomic Absorption Spectrophotometer. (See Iron section for theoretical explanation). A small volume of sample (10-40 μL) is injected by the instrument into the cuvette, and then heated in several stages to 710^{o}C electrothermally. The absorbance is measured before and during atomization, and the difference is reported as the sample absorbance. At least five standards between 0-100 ppb are analyzed daily. Typical recoveries for aluminum from tap water are 95% accurate, with a precision of less than 1%, but insufficient data have been collected at this stage for statistical analysis.

A second method used to determine aluminum in water uses a visible-range spectroscopy technique (SM 3500-Al D). Samples (25 mL) known to contain aluminum are added to a 50-mL volumetric flask which has been cleaned with 1:1 HCl. The sample is acidified with 0.02M sulfuric acid (1 mL). Interfering iron is complexed with 1 mL of an ascorbic acid solution (0.1 grams in 100 mL water). Ten mL of acetate buffer, and 5 mL of Eriochrome Cyanine R dye solution are added to the sample. The sample color is allowed to develop as the dye complexes with the aluminum present for 5-10 minutes. An aliquot of sample is poured into a 1-cm quartz cell and its absorbance is read on a Hach DR/4000 UV/visible spectrophotometer at 535 nm. Three such readings are taken. At least five standards within the range of 0-300 ppb Al are prepared and measured in the same fashion as the samples. Standards must be prepared daily from either aluminum metal, or from aluminum potassium sulfate salt. Duplicate samples are taken and developed separately, and spikes are prepared using the sample matrix to be analyzed, with the appropriate interference (fluoride, phosphate) considered. All glassware must be washed with 1:1 HCl prior to use, to remove any potential aluminum contamination.

Bicarbonate

Bicarbonate is measured by the alkalinity titration method. The alkalinity of a water sample is a measure of its acid-neutralizing ability, and is the sum of all titratable bases. Alkalinity was determined by neutralization of the titratable bases following titration with standardized acid to a specific pH. Bicarbonate alkalinity is present when the phenolphthalein alkalinity (end-point at pH 8.3) is greater than half the total alkalinity (pH end-point at 4.5). The alkalinity analysis depends on the proper standardization of the acid titrant, use of a representative sample size, and the precise determination of pH during the course of the analysis. A Fisher Accumet model 950 pH meter is calibrated daily as stated above. The titrant is standardized daily by titrating a solution of 15 mL 0.05 N sodium carbonate (Na_2CO_3) and 60 mL of deionized water. The sodium

carbonate solution is prepared from approximately 3 grams of primary standard which has been dried at 400 ^{O}C for 4 hours and cooled in a desiccator. Two and one-half grams of the dried sodium carbonate is weighed to the nearest milligram and placed in a one liter volumetric flask and dissolved and diluted to a final volume of one liter. This solution serves as the standardizing titer for the acid solution, and is discarded weekly. A 0.1 N sulfuric acid solution is prepared by diluting 2.8 milliliters of concentrated (36 N) sulfuric acid to one liter with deionized water. Two hundred milliliters of this solution are then diluted to one liter with deionized water to make a 0.02 N sulfuric acid solution which is standardized with 0.05N sodium carbonate. Normality is determined using the given equation.

$$\text{Normality (N)} = \left(\frac{0.05 \text{ X } 5.0}{\text{mls titrant}}\right)$$

The standardization of the acid titration is repeated until values differing by less than five percent are obtained. The unpreserved samples are analyzed within twenty-four hours after collection. Each sample is brought to room temperature and stirred gently before analysis. Titrations are repeated until a sample aliquot that required at least five but no more than one hundred milliliters of titrant to reach end point was found. The initial pH is measured and recorded in the laboratory bench notebook. The volume of titrant is recorded at the two (8.3 and 4.5) end-points of interest. The following equation is then used to calculate alkalinity.

$$\text{Alkalinity, mg/L } CaCO_3 = \left(\frac{\text{A X N X } 50000}{\text{ml sample}}\right)$$

where:

A = mL standard acid used

N = normality of standard acid

Quality control for alkalinity analysis involves duplicating and spiking one sample for every ten analyses. A minimum of one sample is and spiked every day alkalinity titrations are performed, as well as the quarterly analysis of reference quality control samples. A detection limit of 5 mg/L was determined by analyzing deionized water blanks on a daily basis. A RSD mean of 1 is a typical quality control target for precision while accuracy has a mean % recovery of 100 +/- 5.

Bromide

Bromide analyses are conducted using a Dionex ion chromatograph in accordance with SM 4110. Samples containing bromide are injected into the instrument and carried by an eluent solution (Na_2CO_3/$NaHCO_3$) through an anion-separating chromatography column (Dionex AS-14 or equivalent). Ions are then converted to their respective haloacids in the instrument's suppresser. As the acids pass through the detector, the conductivity of the sample (which is monitored continuously) increases. This increase in

conductivity is detected and represented as a peak whose area corresponds to the concentration of ion in the sample. The bromide peak in the sample chromatograph has a retention time of about 3.5 minutes using the analytical column. The proposed QA/QC scenario includes using at least three standards to calibrate the ion chromatograph on a daily basis. At least one blank analysis daily along with duplicates and spikes is performed to assess precision and accuracy. Reference standard ion solutions are purchased through and external vendor.

Calcium Hardness

Calcium hardness is determined by ethylenediaminetetraacetate (EDTA) titration. The EDTA forms a chelated soluble complex with calcium and/or magnesium that can be stoichiometrically quantified by titration at a controlled pH and known sample volume. The sample pH is adjusted between 12 and 13 by the addition of 1.0 mL of 3 N NH_4OH solution followed immediately by the addition of two drops of Eriochrome Black T indicator, and titrated with EDTA (0.01 N) to a purple end point. A sample volume requiring less than fifteen milliliters of titrant is used (for most samples 50 mLs of sample is sufficient). The EDTA solution was prepared by weighing 3.723 grams analytical reagent-grade disodium ethylenediaminetetraacetate dihydrate and diluting to one liter with deionized water. The end point of the hardness titration is taken as when the initial purple color disappears and a lasting blue color first appears. The following formula is used to calculate calcium hardness:

$$\text{Hardness as mg/L } CaCO_3 = \left(\frac{\text{(A - B) X C X 1000}}{\text{ml sample}} \right)$$

where:

A = mL titrant for sample
B = mL titrant for blank
C = mg $CaCO_3$ equivalent to 1 mL EDTA titrant

The titrant is standardized before use by titrating five milliliters of a standard calcium solution. The solution is prepared by adding 1+1 HCl to 1.000 gram of anhydrous $CaCO_3$ powder followed by addition of two hundred milliliters of deionized water. The resulting solution is boiled for two minutes. Five drops of methyl red indicator are then added, and the solution was shaded to the intermediate orange color by the addition of a 3N NH_4OH and 1+1 HCl. The standard solution was made by dilution to one liter giving a final concentration of 1 mL = 1 mg $CaCO_3$. The titrant is always standardized at least twice, with the average value being used in the calcium hardness calculation.

Quality control for calcium hardness involved duplicate, spike, and reference analyses. The number of duplicate and spike analyses are ten percent of all samples or one per day whichever is greater. A precision mean of 2 % RSD and an accuracy of 99

+/- 5 % are typical quality control observations. Reference samples are used on a daily basis with fresh samples being acquired quarterly.

Calcium (as Ca^{+2} Metal Ion)

Atomic absorption spectrophotometry is used to analyze for calcium. Analysis is carried out at 422.7 nm daily. The standards are prepared by serially diluting a 1000 ppm stock solution of acidified calcium nitrate. The stock solution is purchased from a vendor and is accompanied by a certificate verifying the concentration to within +/- 1 percent. Following the analysis of the standards, the correlation coefficient for the linear curve is calculated by the instrument. The coefficient for the curve must be 0.99 % before analyses are to proceed. All samples are analyzed in triplicate with a statistical analysis of the data including mean, standard deviation, and RSD being reported by the instrument. Blanks, spikes, duplicates, and reference samples are used to assess quality control with reference samples being replaced quarterly. Typical precision data shows a mean of 3 % RSD while accuracy has a mean of 92 % recovery.

Chloride

Determination of chloride in samples is carried out by two different techniques, For chloride between 0.1 and 100 mg/L, the same ion chromatography technique is used (SM 4110) as is for bromides. Retention time for chloride elution is about 2.3 minutes.

Alternatively, the argentometric titration of chloride may be used. One hundred mL of sample are titrated with 0.014 N $AgNO_3$ until chloride neutralization is reached. Sample analysis or dilution and analysis is repeated until the volume of titrant used is between 5 mL and 25 mL. The 0.0141N silver nitrate titrant is prepared by dissolving and diluting 2.395 g $AgNO_3$ to one liter with deionized water. The titrant is standardized on a daily basis by titration of a 5 mL sample of 0.0141 *M* sodium chloride. Two drops of potassium dichromate indicator are added to all samples before titration. The standard chloride solution is prepared from an externally purchased standard, or by dissolving 824 mg NaCl (dried at 140^{o}C overnight) with deionized water and diluting to one liter. The actual concentration of the titrant is then calculated using the following equation:

$$N\ AgNO_3 = \left(\frac{A}{B - C}\right)\ X\ 0.0141$$

where:

A = mL of 0.0141N NaCl used

B = mL of $AgNO_3$ titrant used

C = mL required to titrate the blank

A blank of 100 milliliters of deionized water is titrated for background correction. The titrant is standardized in duplicate until a difference of two percent or less is obtained. The normality of the silver nitrate solution is determined by averaging the acceptable titrations. Sample chloride concentrations are also determined from an average of duplicated samples with a difference of two percent or less. The following equation is used to determine the chloride concentration in the original sample:

$$\text{mg/L } Cl^- = \left(\frac{(A - B) \text{ X } N \text{ X } 35450}{\text{ml sample}} \right)$$

where:

A = mL titration for sample

B = mL titration for blank

N = normality of $AgNO_3$

Quality control for chlorides consists of duplicate, spike, and reference sample analysis. One duplicate and spike analysis is made for every ten chloride analyses completed or a minimum of one duplicate and spike analysis is performed every day chlorides are analyzed. The duplicate analysis, spike analysis, percent relative deviation, and percent recovery are reported, and used for quality control. A detection limit of 5 mg/L has been established for chlorides. Accuracy data for chlorides has ranged from 88-112% recovery with a mean of 101% while precision has a average mean of 2% RSD. A new lot of reference samples are obtained quarterly.

Iron

Atomic absorption spectrophotometry of two varieties is used to analyze for iron, depending on the level of iron in the samples being studied. Analysis is carried out in the laboratory by one of two available atomic absorption techniques. Samples known to contain greater than 0.1 ppm (hereafter, "high-level") of iron are analyzed using a direct air-acetylene flame method (SM 3111B); while samples known to contain less than 0.1 ppm of iron (hereafter, "low-level" iron) are analyzed by an electrothermal technique (SM 3113B). If background information on sample ranges is unavailable, a high-level determination is carried out first, and then a low-level determination is carried on those samples too low in iron to be determined by the flame technique

High-level iron samples are analyzed on a TJA/Unicam 969 flame atomic absorption spectrometer set at 248.3 nm, and employing a air-acetylene flame. Samples are aspirated into a laminar flow burner head which supports a flame fueled by a mixture of air and acetylene. Iron present in the sample is atomized. A monochromatic light source (a hollow cathode lamp) emitting light at 248.3 nm is directed through the flame. Iron atoms in the flame will selectively absorb at 248.3 nm. The difference between absorbances as read by the detector before and during sample aspiration is

reported as the sample absorbance. At least three standards between 0.1 and 10 ppm are prepared for calibration of the spectrophotometer daily. The standards are prepared by serially diluting a 1000 ppm stock solution of acidified ferric nitrate. The stock solution is purchased from a vendor and is accompanied by a certificate verifying the concentration to within +/- 1 percent. Following the analysis of the standards, the correlation coefficient for the linear curve is calculated by the instrument. The coefficient for the curve must be at least 0.99 before analyses are to proceed. All samples are acidified (2-3 drops concentrated nitric acid) and analyzed in triplicate with a statistical analysis of the data including mean, standard deviation, and RSD being reported by the instrument. Blanks, spikes, duplicates, and reference samples are used to assess quality control with reference samples being replaced quarterly.

Low-level iron is analyzed for on a Hitachi Z-9000 Simultaneous Multi-Element Graphite Furnace Atomic Absorption Spectrophotometer. The technique by which sample absorption is measured is identical in theory to that of flame absorption described above, except that the flame and fuel gases are replaced by a graphite tube (cuvette) within a furnace. A small volume of sample (10-40 μL) is injected by the instrument into the cuvette, and then heated in several stages to very high temperatures (as high as 600-700^{o}C) electrothermally. This heating program dries and atomizes the sample, as does the flame in the high-level technique. The absorbance is measured before and during atomization, and the difference is reported as the sample absorbance. At least five standards between 0-100 ppb are analyzed daily. Data and quality control are reported and handled in the same fashion as in the flame technique.

Magnesium

Flame atomic absorption spectrophotometry is used to analyze for magnesium. Analysis is carried out at 285 nm with at least three standards between 0 and 2 ppm for calibration of the spectrophotometer daily. The standards are prepared by serially diluting a 1000 ppm stock solution of acidified magnesium nitrate. The stock solution is purchased from a vendor and is accompanied by a certificate verifying the concentration to within $\pm$1 percent. Following the analysis of the standards, the correlation coefficient for the linear curve is calculated by the instrument. The coefficient for the curve must be at least 0.99 before analyses are to proceed. All samples are analyzed in triplicate with a statistical analysis of the data including mean, standard deviation, and RSD being reported by the instrument. Blanks, spikes, duplicates, and reference samples are used to assess quality control with reference samples being replaced quarterly.

Manganese

Manganese is determined using the Hitachi Z-9000 Graphite Furnace Atomic Absorption Spectrophotometer (see Iron section for theoretical explanation). Absorbance is measured before and during atomization at 279.5 nm. At least five standards between 0-30 ppb are analyzed daily. The standard curve is constructed from these data by the instrument, and is accepted only if its correlation coefficient exceeds 0.99.

Nitrate

Nitrates are also measured in the laboratory using the same ion chromatography technique that is used to measure bromides, with some small differences. At concentrations of 0.1 to 1 ppm, the same technique that is used for bromides (above) is used here, except that the retention time for the nitrate peak is at 3.0 minutes. At concentrations above 1 ppm, a slightly different eluent is used (1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$), and the nitrate peak appears at 3.5 minutes.

Nitrite

Nitrites are analyzed using the same procedure on the same column as (and simultaneously with) the procedure given above for nitrates. The retention time for the nitrite peak appears at about 2.0 minutes. All other attributes of the analysis are comparable.

Nitrogen (trivalent species)

Species containing nitrogen in the trivalent state are measured using the Macro-Kjeldahl technique as described in SM 4500-N_{org} B. Organic nitrogen compounds are digested in sulfuric acid in the presence of potassium sulfate and copper (II) sulfate catalyst. Amino nitrogen and free ammonia are converted to ammonium ion. A solution sodium hydroxide and sodium thiosulfate is added to the digestate, resulting in the conversion of all ammonium to ammonia. The ammonia is then distilled into a solution of boric acid that also contains methyl red and methylene blue indicators. At least 200 mL of distillate is collected, and then titrated with standardized 0.02 M sulfuric acid. One milliliter of acid neutralizes 280 μg total kjeldahl nitrogen (TKN).

Species can be measured for their organic nitrogen only by adding 25 mL of borate buffer, adjusting to pH 9.5 with 6 M NaOH, and distilling away 300 mL of the sample. The distilled fraction can then be collected and analyzed for ammonia nitrogen by the titration method described above, and also in SM 4500-NH_3 C.

Spikes are carried out by adding known concentrations of ammonium chloride solution to samples before digestion is begun. Duplicate samples and DI blanks are carried through the digestion and distillation processes.

Phosphorus

Reactive phosphorus is determined spectrophotometrically using either the Vanadomolybdophosphoric Acid (VM) Colorimetric Method (SM 4500-P C) or the Ascorbic Acid Colorimetric Method (SM 4500-P E) depending on the sensitivity destired. The ion chromatographic method may also be employed (retention time = 10 minutes).

Samples are measured for total phosphorus by first digesting an aliquot (50 mL) in a mixture of sulfuric acid and sodium persulfate for up to 2 hours or until the solution has a final volume of 10 mL. The sample is diluted to 50 mL and analyzed by the colorimetric technique. Samples are measured for ortho-phosphate by carrying the sample through the colorimetric technique without preliminary digestion.

The VM colorimetric technique is carried out as follows. Fifty milliliters of sample in an Erlenmeyer flask are pH-adjusted (<10) if necessary by addition of one drop of phenolphthalein indicator solution, and addition of 1:1 HCl until the solution becomes clear. If the sample is excessively colored, 200 mg of activated charcoal is added and the flask is swirled for 5 minutes. The charcoal is then removed by filtration.

A measured quantity of sample (35 mL or less) is transferred to a 50-mL volumetric flask. Ten milliliters of vanadate-molybdate reagent is added to the flask, and the contents are diluted to the mark. The solution is mixed, and allowed to develop for 10 minutes. The absorbance of the solution is then measured at 470 nm in a 1-cm quartz cell.

Five standards between 0.3 and 20 ppm are analyzed along with a reagent blank Samples are randomly spiked with appropriate amounts of potassium phosphate that has been prepared from solid that has been dried at 104^{o} for at least two hours. Duplicate samples are processed identically to provide an experimental duplicate.

The ascorbic acid techique is carried out by first acidifying the sample with the aid of phenophthalein indicator to a clear end point. An 8-mL aliquot of combined developing reagent consisting of ascorbic acid, ammonium molybdate, potassium antimonyl tartrate and sulfuric acid is added to the sample and allowed to react for at least 10 minutes. The blue color developed is measured using a UV/visible spectrometer set at 880 nm and the absorbance is related to concentration via Beer's Law.

pH

A three-point calibration using commercially prepared buffers of pH 4, 7, and 10 will be performed on all field and laboratory meters prior to any determinations. A 50 mL aliquot of each buffer solution is used to calibrate the pH meter with all pH readings for the buffers being within +/- 0.05 pH units of their values for analyses to proceed. A best fit line is determined from the buffer pHs and used to calibrate the pH meter internally.

The calibration and sample reading will be recorded in the field and laboratory records. In the laboratory precision by duplication will be performed on a daily basis.

Samples are unpreserved for this analysis and therefore must be analyzed within twenty-four hours following collection. Each sample is brought to room temperature and stirred gently on a magnetic stirrer during analysis.

Silica

Molybdate-unreactive silica is determined spectrophotometrically using the Molybdosilicate Method (SM 4500-Si D). Samples known to have dissolved silica can be reacted with ammonium molybdate to form molybosilicic acid, which has an intense yellow color. Molybdophosphates may form in samples that also contain phosphates, but this interference is destroyed with the addition of oxalic acid. The sample's absorbance at 410 nm can then be correlated linearly to silica concentration.

Fifty milliliters of sample are added to a flask, followed quickly by 1.0 mL of 1:1 hydrochloric acid and 2.0 mL ammonium molybdate reagent. After mixing, and 5-10 minutes of standing, 2.0 mL of oxalic acid (7.5 grams in 100 mL distilled water) is added

to the sample. After two minutes of color development (but before 15 minutes), an aliquot of sample is added to a 1-cm cuvette and the absorbance at 410 nm is recorded using a UV-visible spectrometer. The absorbance correlates with silica concentration according to Beer's law in a linear fashion.

Five standards between 0 and 30 ppm are analyzed. The 0 ppm standard serves as a reagent blank to assure that no silicates are leached from the glassware if glass is used. Samples are randomly spiked with appropriate amounts of silica external standard solution which is purchased from a vendor. Duplicate samples are processed identically to provide an experimental duplicate.

Sodium

Atomic emission spectrophotometry is used to analyze for sodium. Analysis takes place at 589 nm with at least six standards, typically 10, 20, 30, 40 ,50 and 100 ug/L used to calibrate the spectrophotometer daily. The standards are prepared by serially diluting a 1000 ppm stock solution of sodium chloride. The stock solution is purchased from a vendor and is accompanied by a certificate verifying the concentration to within +/- 1 percent. Following the analysis of the standards, the correlation coefficient for the linear curve is calculated by the instrument. The coefficient for the curve must be 0.99 % before analyses are to proceed. All samples are analyzed in duplicate with a statistical analysis of the data including mean, standard deviation, and RSD being reported by the instrument. Blanks, spikes, duplicates, and reference samples are used to assess quality control with reference samples being replaced quarterly.

Sulfates

High level sulfate concentration (> 1 mg/L) is determined by a turbidimetric method that relates the turbidity formed by barium sulfate precipitation to the dissolved sulfates in the sample. Dissolved sulfate is precipitated by adding barium chloride and acetic acid to a sample aliquot and measuring the resulting turbidity. One hundred milliliters of sample are measured into a 250 mL Erlenmeyer flask using a graduated cylinder. Twenty milliliters of a buffer solution (30 g $MgCl_2 \cdot 6H_2O$, 5 g $CH_3COONa \cdot 3H_2O$, 1.0 g KNO_3, 0.111 g Na_2SO_4, and 20 mL 99% acetic acid diluted to 1 liter with deionized water) are added with stirring. A scoop of $BaCl_2$ crystals is added. After stirring for 60 +\- 2 seconds the sample is transferred to an absorption cell and the turbidity is determined on a Hach Ratio Turbidimeter, model 18900. .

A stock solution of 0.1479 g anhydrous Na_2SO_4 diluted to one liter with deionized water is prepared for sulfate analysis. Alternatively, a commercially purchcased 1000 mg/L sodium sulfate solution may be used. From either stock, a series of five standards, 1.0, 5.0, 10.0, 20.0, and 40.0 mg/L as SO_4 are prepared and analyzed using the turbidimetric procedure. A standard analytical curve of turbidity verses barium sulfate concentration is made and used for sample analysis. The sample turbidities are converted to $BaSO_4$ by using the standard curve, and the original sulfate concentration is calculated as shown.

$$\text{mg/L } SO_4^{2-} = \left(\frac{\text{mg } BaSO_4 \text{ X } 411.6}{\text{mL sample}}\right)$$

Sulfates from 0.05 to 100 mg/L are also analyzed using the same ion chromatographic procedure as for nitrate and chloride. The sulfate peak has a retention time of about 12 minutes.

Quality control requirements for sulfates includes analyzing blanks, duplicates, spikes, and reference samples. A blank is analyzed each day sample analyses are performed. By averaging the blank values obtained over the course of a year a detection limit of 1.0 mg/L was determined for the turbidimetric method. A purchased reference sample of known concentration and ninety-five percent confidence interval is used for internal quality control. No sample sulfate analysis is performed until analysis of the reference sample is within the 95 % confidence limits supplied by the manufacturer. One duplicate and spike sample are analyzed for every ten samples analyzed; with a minimum of one duplicate and spike analysis being done anytime sulfate is analyzed.

ORGANIC PARAMETERS

Assimilable Organic Carbon (AOC)

Pure cultures of *Pseudomonas* strain P17 and *Spirillum* strain NOX are grown to a maximum density in a batch culture of pasteurized water sample. The density of the viable cells is then converted into AOC concentration by comparison to an empirically-derived yield factor. The yield factor for strain P17 is 4.1×10^6 CFU/mL and the yield factor for strain NOX is 1.2×10^7 CFU/mL.

Prior to sample collection, working stock cultures of P17 and NOX strains must be prepared. A loop of pure stock culture is aseptically transferred into 100 mL of a 2 ppm solution of sodium acetate. The mixture is allowed to incubate for 3 days at 25 ± 1 ^oC. Separate mixtures are prepared for each strain. Prior to incubation, each working stock culture is plated on R2A plates and is incubated together with the working stock culture. Separate dilutions are prepared for plating. Each culture is plated in duplicate. The cell density on the R2A plates as determined after three days will determine the dilution factor for the inoculation of the water samples.

Water samples are collected in carbon-free bottles. If suspended solids are present, these solids are removed by filtration. The pH of the water sample is adjusted to between 7 and 8 with phosphate buffer (pH = 7). The samples are then pasteurized at 70^oC for a period of 30 minutes. Samples with no residual chlorine are pasteurized immediately after collection, and are inoculated within 24 hours of sampling. Samples with residual chlorine are pasteurized within 24 hours of collection, and can be stored at 4^oC for up to two weeks before inoculation.

The dilution factor for each strain is determined by the results of the R2A plates, and strives to achieve a cell density of 1×10^4 CFU/mL, which takes into consideration the inoculation volume (0.1 mL) and the final volume (40.1 mL) after inoculation. A

working stock solution is prepared by dilution, using mineral salts buffer as a diluent. This dilution is used to inoculate the pasteurized water sample.

An aliquot (40 mL) of the pasteurized water is transferred into a sterile vial. The vial is capped with a teflon-coated silicone septum and screw-cap. Sodium thiosulfate (0.05 mL of a 10% solution) is injected into chlorinated sample vials using a step-pettor and a syringe with needle. An aliquot of working stock culture (0.1 mL) is added into each sample vial. All vials are then incubated at 25 $\pm$ 1 ^{o}C for 3 days.

Water samples shoud be inoculated with each strain separately, in duplicate. In parallel, a blank control (mineral salts buffer) and a yield control (0.1 ppm sodium acetate) are also inoculated separately with each strain. All vials are plated on R2A plates after the third day. Different dilutions of each inoculated vial are prepared and plated in duplicate. All plates are incubated at 25 $\pm$ 1 ^{o}C for 3 days. The cell density of all plates is determined after 3 days.

Quality control of the bioassay is assessed by comparison of the cell density and the AOC values to the following values:

Blank control = 2.20×10^4 CFU/mL
0.003-0.035 ppm AOC

Yield controls = 1×10^5 CFU/mL for P17
0.1 $\pm$ 0.01 ppm AOC

2 x 105 CFU/mL for NOX
0.1 $\pm$ 0.01 ppm AOC

Biologically Degradable Organic Carbon (BDOC)

Water samples are incubated with sand that has been colonized by bacteria. Incubation of water samples are carried out at 20 $\pm$ 2 ^{o}C, in the dark, in an enviroment that has been rendered free of organic carbon contamination. Water samples are aerated with organic-free air during incubation. NPDOC concentration is measured daily from the beginning of the test by the UV-persulfate oxidation technique described below. The assay is carried out when the NPDOC levels have reached their minimum values. The minimum NPDOC value, which corresponds to the non-biodegradable NPDOC, is commonly reached after a 5 to 7 day incubation period. BDOC is then calculated and reported as the difference between the initial and minimum NPDOC values.

Prior to sample collection, the bioactive sand to be used as inoculum is prepared and pre-treated. The sand is acquired from a sand filter of a water treatment plant that does not employ a pre-chlorination stage, i.e does not pre-disinfect with chlorine. An alternate source of such a sand would be a freshwater fish tank. The sand must be washed several times with dechlorinated tap water, followed by several more washings with deionized water. These rinsings are carried out until the NPDOC levels in the wash water are equal to or less than the NPDOC levels of the deionized water itself ($\leq$ 0.2 ppm). Once this NPDOC level is achieved, the experiment may begin.

Water samples are collected in carbon-free bottles and inoculated within 24 hours of collection. If suspended solids are present, these are removed by filtration. Residual

chlorine is quenched with an aliquot of 10% sodium thiosulfate prior to inoculation. The pH of the sampel is adjusted to between 7 and 8 with phosphate buffer (pH = 7).

An aliquot of sand (100 $\pm$ 10 grams) is weighed into a 500-mL Erlenmeyer flask to which 300 mL of water sample is added. Each sample is prepared in duplicate. The mixture is aerated with air, delivered by an aquarium pump, throughout the experiment. The air is first passed through two deionized water scrubbers, then into the water sample itself. The aerated samples are then incubated for 5 to 7 days. Duplicate NPDOC analyses are conducted on each sample daily. The experiment is continued, and NPDOC is monitored, until two days after the minimum NPDOC level is reached.

An activity control (AC) and an inhibition control (IC) are run in parallel with the water samples. The activity control contains 300 mL of solution containing 2 ppm sodium acetate instead of water sample. The inhibition control contains 300 mL of water sample to which 3 mL of 200 ppm sodium acetate has been added.

Quality control is assessed by a few different calculations. Spikes and recoveries are not possible to assess with this technique, however, duplicate BDOC measurements should possess an RSD value of less than 30%. The bioassay can be assessed for validity by use of the following suggested levels for the controls:

$BDOC_{AC} = 2.0 \pm 0.4$ ppm
$BDOC_{IC} = BDOC_{sample} + BDOC_{AC} \pm 20\%$
(all BDOC values are reported as ppm C)

DBP Formation Potential

Chlorine Dosing

The measurement of trihalomethanes and haloacetic acids encompasses the organic parameters for which formation potential will be determined during this project. Formation potential is evaluated by pretreating a sample in such a manner that strict control over pH, temperature, chlorine dose and the length of reaction time is observed. In this project formation potential will be evaluated using a chlorine dose that will provide a 0.5 to 2.0 mg/L residual after 48 hours at constant temperature. Unpreserved four liter samples are taken in large amber jugs and transported to the laboratory on the day of collection. A sample volume of one to one and a half liters is taken from the four liter jugs, placed in a beaker and stirred for approximately four hours to rid the sample of sulfides which have a high affinity for chlorine. An appropriate volume or dose of chlorine stock solution is added in order to leave a target chlorine residual of 0.5 to 2.0 mg/L at the end of a forty-eight hour reaction period, under which the pH and temperature conditions are controlled.

The chlorine dose is determined in relation to the NPDOC and other chlorine demanding materials in the sample and is typically constant by sample class. These chlorine doses are determined from chlorine dissipation studies for the various sample classes. The chlorine stock is standardized against 0.003 N ferrous ammonium sulfate solution each time chlorine dosing is performed to precisely determine the amount of chlorine to be added.

Immediately after dosing, the pH of the sample aliquot is adjusted to 7.6 by addition of 0.1 N hydrochloric acid or 0.1 N sodium hydroxide. The aliquot is then divided between bottles for THM, (60 mL), HAA (125 mL) and pH and chlorine residual (125 mL). These bottles will be sealed with a Teflon lined cap, no head space and placed in the dark in a 20 ^{O}C incubator for forty-eight hours. The sample size, original pH, concentration of the stock chlorine solution, volume of chlorine stock solution used, date and time of dosing, pH after dosing, and time and date in which to quench the samples are recorded in the bench records.

After the prescribed reaction period is completed, the samples are removed from the incubator and the chlorine residual and pH are measured and recorded on the bench sheet that was created at the time of dosing. To quench the remaining chlorine residual, trihalomethane samples dosed with 10 or less milligrams per liter chlorine will receive 500 microliters of 0.4 M sodium thiosulfate, while those dosed with greater than ten are to be quenched with 1 milliliter. The HAA samples are quenched using 0.4 M ammonium chloride solution. The samples are then stored at four degree Celsius, and analyzed within two weeks. They are extracted and prepared for GC analysis in accordance with the respective DBP extraction protocol.

Gas Chromatographic Analysis

Gas chromatography (G.C.) is used for the analysis of THMs and HAA in the UCF Laboratory. During the course of this project a Hewlett-Packard gas chromatograph, model 5890, a Hewlett-Packard model 7673A autosampler and a Hewlett-Packard model 3396A integrator will be used to record the chromatograms and calculations. The Hewlett-Packard model 7673A autosampler is programmed to make two microliter injections. Methods including the temperature program, retention times, and compounds of interest are stored in the integrator memory. The integrator will perform the calculations for compound concentration once the calibration curve have been run and the peak heights for the known concentrations have been plugged into the integrator's memory The two methods differ on calibration type (THM is internal standard, HAA external), therefore the equation 1 is used for the HAA while the equation 2 is for the THMs.

Equation 1

$$C_s = \left(\frac{As \text{ X } Cst}{A_{st}}\right)$$

where:

A_S = peak area of sample
A_{st} = peak area of standard
C_{st} = concentration of standard (ug/L)
C_S = concentration of sample (ug/L)

Equation 2

$$C_s = \left(\frac{As \text{ X } Ci}{Ai}\right)$$

where:

A_S = peak area of sample
A_i = peak area of internal standard
C_i = concentration of internal standard (ug/L)
C_S = concentration of sample (ug/L)

The chromatograms and integrator analytical reports, GC autosampler sequences, and Dosing/Extraction Logs are retained for all analyses. The Dosing/Extraction Logs are kept in a composition notebook, and includes such information as the work order number, date of dosing, quenching, extraction, solvent used and EPA method. Method, position on autosampler, and peak areas are logged by the instrument on the chromatogram report generated by the software associated with the GC. The chromatograms and analytical reports are filed on the hard drive of the attached computer, and backed up on disk or on hard copy as often as needed.. The analytical records are to be retained in the laboratory for at least seven years. The specific temperature programs, columns, and pressures are detailed by method in Table 10 below.

Table 10

Summary of Gas Chromatographic Conditions

Method	**501.2**	**552**
G.C. Column	HP-6890 J & W DB-5 30M x 0.32 mm l micron film fused silica	HP-6890 J & W DB-1701 30 M x 0.32 mm 1 micron fused silica
Inj. Temp.	250	200
Det. Temp.	290	290
Inj. Vol.	2	2
Initial. Temp	60	50
Final Temp	210	250
Temperature Program	Hold 60, 3 min ramp 30°/min to 210, hold 2 min	Hold 50, 10 min ramp 10°/min to 250, hold 10 min.

All temperature are in degrees Celsius

Trihalomethanes

The USEPA method 501.2 (US EPA 1980) is applicable to the determination of the regulated trihalomethanes; chloroform, dichlorobromomethane, dibromochloromethane, and bromoform. The method used liquid-liquid extraction for quantitative sample concentration and analysis by a gas chromatograph with a linearized electron capture detector. Within seven days following the reaction period the THMs are extracted by pipetting ten milliliters of sample into a Pyrex screw top tube containing two milliliters of pesticide-grade hexane. (Pentane may be used alternatively, but hexane is preferred.) The vial is sealed with a Teflon-lined screw cap and shaken vigorously for two minutes. One half milliliter of extract (organic phase) is then transferred to a chromatographic sample vial. The vial is then crimped shut, labeled, and placed on the gas chromatograph autosampler for analysis.

A multiple standard calibration takes place each day that samples are analyzed. Standards are prepared by diluting a mixed stock solution of 200 mg/L of each of the four trihalomethane compounds purchased from Supelco Inc. Typically 10, 20 50, 100 and 200 ug/L standards are used for calibration. The settings for the gas chromatograph are contained in Table 10.

Quality control for THMs consists of analyzing laboratory reagent blanks, injections of the extraction solvent, duplicate and spiked samples. The laboratory reagent blank is an aliquot of deionized water that is treated exactly as a sample. One blank sample is analyzed per ten samples analyzed, with at least one blank analysis per day. Solvent is taken from the manufacturer's storage container, and injected without dilution into the gas chromatograph. Both the solvent and blank analyses are measures of background contamination that may have been present at the time of extraction and/or analysis. Sample analysis is not performed if the results of the solvent or blank analyses showed that analytes are present in the solvent or blank samples. If contamination is present, a new set of extractions are performed for the sample set . The duplicate and spiked samples are measures of precision and accuracy. Three duplicate and spike aliquots are taken from the same sample. Two of the aliquots are spiked by the addition of ten microliters of the 200 mg/L standard. The final concentration in the spiked aliquot was 20 ug/L. One of the spiked aliquots serves as the laboratory fortified sample matrix spike, while the other is referred to as the matrix spike duplicate. The recovery of the spiked analytes is determined after all three samples are extracted and analyzed:

The values obtained for the sample, the two spiked aliquots, spike amount, percent recovery, and the relative percent deviation between the two spiked samples are reported. The duplicate data is used to calculate the range, warning and control limits for each analyte; while the spike data is used to obtain the average recovery, lower and upper warning and control limits. The precision and accuracy data are presented in Shewart control chart form. A 0.5 ug/L detection limit has been found for this method

Haloacetic Acids

USEPA method 552 (US EPA 1990) will be used to determine haloacetic acids. The samples were liquid-liquid extracted, concentrated, derivatized, and analyzed on a gas chromatograph by electron capture detection.

A thirty (30) milliliter sample aliquot is transferred into a 40 milliliter vial following pH adjustment to < 2 by the addition of 3 mL of 1:1 sulfuric acid to the sample. The initial and final pHs are recorded on an Organic Extraction Log sheet to confirm that this step was taken. Three milliliters of high performance chromatography grade methyl-tert-butyl ether (MTBE) are added to the vial, followed by 3 mL of MTBE, then 3 grams of copper (II) sulfate pentahydrate, and then 12 grams of anhydrous sodium sulfate. The vials are briefly shaken to dissolve the salts.

Vials are then placed on a mechanical shaker, and shaken for 30 minutes. After shaking, the vials are allowed to settle for 5 minutes. After settling, exactly 2.0 mL of the MTBE layer are transferred to a 2-mL volumetric flask. Care is taken not to transfer any of the aqueous layer.

A clean stream of nitrogen gas is used to evaporate 0.3 mL from each 2-mL flask to make room for the addition of diazomethane and of standard in the case of spikes. Cold diazomethane (250 μL) is abudded to each flask. The flask is then diluted to the mark with MTBE, and allowed to stand for 30 minutes. A small amount (0.2 grams) of silica gel is added to the flask to remove unreacted diazomethane, and the flask is again allowed to sit for another 30 minutes. Sample (about 1.5-2 mL) is then transferred to a vial for GC analysis.

The gas chromatographic settings for HAA analysis are listed in Table 10. The system undergoes an external multipoint calibration using 5, 10, 20, 50, 100, and 200 ug/L combined standards. Any sample that exceeds the value of the most concentrated standard is diluted. Sample values could be read directly from the integrator output, and are calculated using the equation cited in page 41.

A solvent blank is analyzed daily. One laboratory fortified blank, matrix spike and matrix spike duplicate is analyzed for every ten samples or a minimum of one per day when acid DBPs were analyzed. The solvent blank is an injection of undiluted solvent straight from the manufacturer's storage container, while the laboratory fortified blank is an one hundred milliliter aliquot of deionized water that is treated as if it was a sample. The two blanks are used to measure any background contamination that may have been present.

The matrix spike and spike duplicate are used as measures of accuracy and precision respectively. Three aliquots of a sample are taken. Two are spiked with one hundred microliters of a spiking solution that was: 20 mg/L-dibromoacetic acid, 20 mg/L-dichloroacetic acid, 20 mg/L-monobromoacetic acid, 20 mg/L-trichloroacetic acid, , 20 mg/L-monochloroacetic acid, and 20 mg/L-bromochloroacetic acid.

The samples are then extracted and analyzed by the 552 procedure. The unspiked sample concentration, spike concentration, matrix spike concentration and duplicate concentration, percent recoveries, and the relative standard deviation between the two spiked sample are reported. A detection limit of one microgram per liter for all analytes was observed.

NPDOC

NPDOC is measured using a Dohrmann Phoenix 8000 TOC analyzer. This instrument uses persulfate oxidation in an acidic environment to convert organic carbon to carbon dioxide in the presence of ultraviolet radiation. The carbon dioxide is measured by a non-dispersive infrared analyzer. The inorganic carbon species are converted to carbon dioxide and purged from solution before infrared analysis of the converted NPDOC.

The analyzer is equipped with an autosampler, and a Hewlett-Packard laser printer which produces hard copies of the analytical results. The analytical sequence consists of a gang valve which transfers a pre-set amount of sample (depending on concentration range) to the liquid sparger. The inorganic and purgeable organic carbon fractions are converted to CO_2; sparged out and vented to the atmosphere. The liquid that remains in the sparger now contains only the NPDOC fraction. A fixed volume of the sparged liquid is injected into the UV reactor. An aliquot of sodium persulfate solution is automatically injected into the reactor. The atmosphere in the reactor is oxygen-rich ensuring the complete oxidation of all organics. The CO_2 gas is then swept into the non-dispersive infra-red detector and measured. The detector is pre-set by the manufacturer so that a full scale deflection (1.0 v) corresponding to a measurement of 2500 ppm CO_2. Direct readings are attainable after calibrating the instrument with NPDOC standards.

The instrument is calibrated with a series of standards each day that analyses are performed. A 200 mg/L organic Carbon stock is prepared by dissolving 425 mg of potassium acid phthalate (KHP) that has been dried at 105 degrees Celsius overnight, in one liter of distilled DI water. When not in use the stock is stored at four degrees Celsius, and is discarded after one month. The stock in turn is used to prepare 1, 2.5, 5 and 10 mg/L working standards. A new reference sample, preparation instructions, actual value, and a ninety-five percent confidence interval for the sample are supplied quarterly by the vendor. No analyses are performed unless the reference sample results are within the confidence interval. Analyses of standard solutions are repeated after every tenth sample in order to ascertain that the calibration is maintained. A dilution and reanalysis is performed if a sample value exceeded 10 mg/L.

Deionized water is used as a blank in order to measure any background contamination. A blank is analyzed after calibration, at the beginning of sample analyses, and again after every tenth sample to monitor any carry over that may occur between samples. Also the system is flushed with deionized water after every sample analysis to prevent cross contamination. The blank determinations are also used for calculating the analytical system's detection limit. The blank values over the course of a year were totaled and averaged. Typical NPDOC levels in the laboratory blanks (i.e. in freshly produced distilled deionized water) ranges from 20 to 300 ppb NPDOC.

In addition to the standards, reference check samples, and blanks; duplicate and spike analyses are performed at the rate of ten percent or a minimum of one each per day that sample analyses take place. The duplicate analyses are then statistically accessed for range, control and warning limits as a measure of precision. The spike results are used to determine average percent recovery, and lower and upper warning and control limits. Both sets of statistical data were maintained in a Shewart control chart. A mean % RSD of 4 with a standard deviation of 4% and an accuracy mean of 98 +/- 7 % recovery are the most recent analytical targets.

Samples are stored at four degrees Celsius until analysis, which will occur within seven days after sampling. An aliquot of at least ten milliliters is poured into a fifty milliliter screw cap test tube that is then topped with a septum cap that the syringe of the sample loop could pierce. Three one milliliter injections are made from each sample aliquot. The NPDOC measurement for each injection, an average, and the standard deviation for the three injections are printed on a hard copy by the Thinkjet printer. The average value is then recorded in the laboratory bound bench records; and reported as the NPDOC value for the sample. The position on the autosampler, login number, and dilution factor if applicable, are also noted in the laboratory bench records. Both the bench records and the hard copy printouts are retained as part of the laboratory's records.

Pesticides

The pesticides are described as group A: simazine, atrazine, bentazone, diuron, DNOC, dinoseb and group B: pirimicarb, metamitron, metribuzin, metalaxyl, MCPA, mecoprop and vinchlozolin. Analytical methods used in this project for pesticide analyses will follow procedures outlined by KIWA for pesticide analysis. That procedure is summarized as follows.

All sample containers, volumetric or otherwise, should be glass. Glassware is washed first with soap and water, and is then rinsed three times with HPLC-grade acetone followed by three more rinses with HPLC-grade petroleum ether. Glassware is then blown dry with a stream of high purity nitrogen gas for a few minutes, or allowed to air-dry for at least 30 minutes. No odor of ether should be detectable after drying.

Aliquots of feed samples are syringe-filtered with Spartan 30/B membranes fitted by Luer lock onto a glass 20-mL syringe. All samples are acidified with 3:10 reagent-graded phosphoric acid to a pH of 2.3 $\pm$ 0.05. Aliquots of acidified sample are then analyzed by HPLC at wavelengths 230 and 270 nm.

The solvent system consists of acetonitrile and dilute phosphoric acid (1.2 mL acid per liter of ultrapure water). All solvents are HPLC grade or better. The following gradient system (Table 11) should be used for the chromatographic analysis.

Table 11

Pump scheme for HPLC pesticide analysis

Step	Duration (min)	Flow (mL/min)	% Acetonitrile
0	5	0.7	10
1	2	0.7	10
2	40	0.7	80
3	2	0.7	100
4	6	1.0	100
5	2	0.7	10
6	15	0.7	10

High purity helium gas should be applied to both solvent reservoirs at about 1 atm pressure to minimize retention time drift over the course of an analysis. Solvent reservoirs should be glass-lined.

The HPLC method is based on High Performance Liquid Chromatography (HPLC) with eluent programming followed by UV-absorbance detection. (Noij and Brandt 1995). The University of Central Florida has procured a Perkin Elmer LC 235C High Performance Liquid Chromatograph and mastered the analytical technique KIWA has developed for pesticide analysis. The methodology for these analytes was supplied by KIWA. Multiple standard calibrations of the analytical instrument will be done on a daily basis when pesticide analyses are conducted. Reference samples for these compounds with the exception of atrazine and simazine was supplied through KIWA's laboratories. The analytical column is a silica-based ODS-2 column procured from Canadian Applied Sciences.

A 10-mL aqueous sample is passed over a pre-concentration column (hereafter, "precolumn") filled with a porous polymer based sorbent ("PLRP"), incorporated in a rotary switching valve. After concentration, the valve is switched and the precolumn is in-line with the analytical column. The analytes are desorbed by the eluent and carried to the analytical column where the constituents are separated. Consecutive detection is by UV-absorbance at 230 and 270 nm, or by recording the entire UV-spectrum using a Photo Diode Array detector.

AGGREGATE PARAMETERS

Color

The presence of colored metal complexes, humics and other substances is assessed by measuring the "color" of a sample. Color is measured at ESEI using the platinum -cobalt/spectrophotometric variety of the Visual Comparison Method (SM 2120 B). One standard unit of color is defined as that amount of color produced by 1 ppm platinum as chloroplatinate ion. Potassium chloroplatinate (K_2PtCl_6) standard is prepared by dissolving 1.246 grams of reagent grade (not commercial) K_2PtCl_6 and 1.00 gram of cobaltous chloride hexahydrate ($CoCl_2 \cdot 6H_20$) in water with 100 mL concentrated HCl, and diluting to 1 L in a volumetric flask. This solution yields a stock standard of 500 color units. At least three working standards (1, 5, 10, 25, and/or 50 units are suggested) are prepared by diluting the 500 unit stock solution in deionized water. (Note: The best quality standards are prepared in RO/NF treated water.) The samples are adjusted with the aid of a pH meter to a pH of 7.6. Absorbances of samples and standards are then measured using a Hach DR/4000 UV/visible spectrometer set at 455 nm. Duplicate samples are prepared for at least 10% of samples.

Conductivity

A conductance bridge (YSI Model 32 or equivalent) fitted with a dip cell (YSI Model 3402 or equivalent) is used to measure conductance of a solution. The cell constant is first determined by measuring the conductance of a 0.01M solution of

potassium chloride. This solution has a well-established conductivity of 1412 μmho/cm. Taking this value into account, the cell constant, C, in cm^{-1}, is determined by the following equation:

$$C = 0.001412 * R_{KCl} * [1 + 0.019(T - 25)]$$

where R_{KCl} is the average resistance of 3 aliquots of 0.01 M potassium chloride, in ohms, and T is the temperature in degrees Celcius. The cell constant has a typical value of 0.1 cm^{-1} but must be measured and validated daily. Further performance checks on the cell include measuring conductances of a series of potassium chloride solutions (0.01M - 0.2 M) and observing a linear response in conductance measurements.

Once the cell constant is known, sample conductances are measured directly using the dip cell, by immersing the entire cell beneath the sample liquid level and recording the conductance from the meter while the sample is being continuously stirred. Care is taken to note the range (mmho/cm or μmho/cm, etc) that the meter is set upon, and to assign correct conductance units to the readings. Conductance is read directly from the instrument, and used with the above-determined cell constant to calculate conductivity (k) as follows.

$$k\ (\mu mho/cm) = 1{,}000{,}000 * C * (\text{conductance in mhos})/(1 + [0.019(T - 25)])$$

Values typically range from 50 to 1500 μmho/cm.

Oxidation-Reduction Potential (ORP)

A Corning Redox Combo RJ double-junction electrode attached to a Corning Model 440 pH meter is used to measure ORP in accordance with SM 2580 B. This probe is a combination/double junction electrode consisting of a silver/silver chloride junction and a platinum wire junction. Saturated potassium chloride is used as a fill solution for the silver junction. The readout is obtained through the pH meter set in the millivolt mode, and is capable of measuring between -2000 and +2000 mV accurately.

Quality control consists of duplicate and blank measurements.

Particle Counts

Suspended particles are measured on a Hiac-Royco 8000A digital 8-channel particle counter equipped with a 3000A sampler and a thermal printer. A known volume of sample is aspirated into the instrument at a fixed rate (60 mL/min). The Micro-Count-5 sensor detects particles from 0.5 to 350 microns by means of a light-scattering signal. Each particle passing through the sensor generates a electronic pulse that is amplified and conditioned by the circuitry of the unit. The effect is comparable to casting an electronic "shadow" on the sensor by causing a fluctuation in the pulse emanating from the 50mW laser diode in the sensor, which allows the unit to "measure" the size and quantity of particles that pass through it.

The instrument 8 channels or "bins" for particle size selection, which can be specified by the user to detect particles within the above-specified range. Typically, sizes

of 0.5 and 2 microns are of interest, but any value from 0.5 to 350 microns can be selected. Duplicate readings within 10% at either 0.5 or 2 microns constitute acceptable precision for ESEI purposes. The technique measures an aggregate property for which no accuracy test has yet been developed.

Solids

Matter, both organic and inorganic, suspended in water is collectively referred to as "solids". Total dissolved solids (SM 2540 C) and total suspended solids (SM 2540 D), add together to give total solids (2540 B).

Total Dissolved Solids (TDS)

In this procedure, a measured volume of sample is filtered through a pre-washed (three times with organic free distilled water) glass fiber filter disk. The filtrate is added to a porcelain evaporating dish that has been washed, dried in an oven at 180 $\pm$ 2 ^{o}C, and has been cooled to constant weight. The sample is then dried at 180^{o}C for at least one hour. The sample is then removed from the oven, cooled to room temperature in a desiccator, and weighed until a constant weight is reached. Constant weight is defined as a weight loss of less than 4% between weighings or of 0.5 mg, whichever is less. Duplicate aliquots are filtered, dried and weighed to determine precision.

Total Suspended Solids (TSS)

The sample is filtered as in the TDS procedure above, but in this case, after a measured volume of sample is filtered, the residue on the filter paper is recovered and dried to constant weight. The filter paper is transferred to a pre-weighed steel planchet or a watch glass and placed in an oven at 103-105 ^{o}C, and dried to constant weight (at least one hour). The sample is then cooled to room temperature in a desiccator. After cooling, the sample is weighed. The drying/cooling/desiccating/weighing cycle is repeated until a constant weight is achieved, or until weight loss upon drying is less than 0.5 mg or 4% of previous weight (whichever is less). Alternatively, total solids can be determined as described below on one aliquot of sample, and TDS can be determined on another aliquot, as above. The difference of these two determinations gives TSS. This method circumvents the problem of loss of sample due to embedding in the filter disk, and the like.

Total Solids (TS)

This procedure is the same as that for TDS, except that sample drying takes place at 103-105 ^{o}C. The weight gain of the porcelain dish upon drying is reported as total solids in this case.

Turbidity

The nephelometric method (SM 2130 B) is the selected method for measuring turbidity in samples. A nephelometer measures the intensity of light scattered from a sample at a right angle with respect to the incident light beam. ESEI uses a Hach Ratio Turbidimeter (Model 18900 or 2100N are available) fitted with a tungsten filament source. The instrument is left on continuously and its calibration is checked daily with Gelex® turbidity standards of 200, 20 and 2 NTU. If the readouts vary from these known values, the instrument is re-calibrated with formazin primary turbidity standard. The primary standards (1.8, 18, and 180 NTU) are prepared by dilution of an external stock solution of 4000 NTU (purchased from Hach Company) with distilled water. This primary stock solution is stable for an excess of a year. Duplicate samples are measured and the precision is noted for quality control.

UV-Absorbing Constituents (UV-254)

This parameter is often considered a preliminary assessment of amount of dissolved UV-absorbing organic species present, and is carried in accordance with Standard Methods protocol (SM 5910). A filter assembly and disk should be selected and pre-washed with 50 mL of distilled water that has been rendered organic-free by passing through a granular-activated charcoal filter. This filter assembly consists of a 70-mm glass fiber filter (Whatman 934 AH or equivalent) mounted in a glass filter funnel with a PTFE support plate. The filter assembly and disk should be pre-washed with 50 mL of distilled water that has been rendered organic-free by passing through a granular-activated charcoal filter.

Samples are prefiltered using the above assembly. The filtrate is collected in a clean glass beaker. An appropriate spectrophotometric quartz cell (usually 5-cm; 10-cm if no absorbance is observed using the 5-cm cell) is rinsed with organic-free distilled deionized water, and then again with sample. The cell is then filled with sample, inserted into the spectrophotometer, and the absorbance is read at 253.7 nm. Duplicate samples are processed, and their results compared for precision of technique.

MICROBIOLOGICAL PARAMETERS

Coliforms, Fecal (SM 9222 A-D. Membrane Filter Procedure given here)

Dehydrate M-FC medium is prepared according to the manufacturer's instructions. The medium should include 10 g Tryptose, 5 g Proteose peptone, 3 g yeast extract, 5 g sodium chloride, 12.5 g lactose, 1.5 g bile salts mixture, 0.1 g aniline blue, and 15.0 g agar (optional). All substituents are dissolved in 1 liter of reagent-grade water containing 10 mL of 1% rosolic acid in 0.2 N NaOH.

The mixture is heated to boiling, then promptly removed from heat, and allowed to cool to below 50^{o}C. The mixture is not to be sterilized in an autoclave. Aliquots (5-7 mLs each) are delivered by pipet into 50x12 mm petri plates and allowed to solidify. The final pH of the medium should be 7.4 $\pm$ 0.2. Finished medium is stored at 4-8^{o}C.

Fifty milliliters of sample (or a sample size that will yield a count between 20 and 60) is filtered through a membrane filter mounted in a seamless filtration unit that has

been sterilized by UV irradiation or immersion in boiling water for at least two minutes. After sample is filtered, three aliquots of 20-30 mL of sterile water are filtered through the same membrane.

A sterile absorbent pad is placed in a sterile culture dish. M-FC medium (1.8-2 mL) is added carefully by pipet. The filter through which sample was passed above, is placed aseptically onto this pad. The dish is covered and incubated (without inversion) for 1.5-2 hours at 45 $\pm$ 0.2^{o}C. Care is taken not to incubate longer than 24 hours. Fecal coliforms (blue colored cultures) are counted as soon as possible after 24-hour incubation using an illuminated, magifying (10-15x) binocular wide-field microscope.

Count density is calculated as the quotient of the number of verified FC colonies over the total bacterial colonies counted, multiplied by 100. The Coliform colonies per 100 mL sample is calculated by multiplying the number of coliform colonies by 100, and dividing by the total volume (mL) of sample.

Quality control for Coliform count is assessed by culturing samples in duplicate, as well as by taking counts using sterile water as a medium (blank), and by running nutrient (reagent) blanks and control samples.

All media, glassware and materials involved in the analysis are sterile, and are used under sterile conditions. An aseptic technique was performed using a Class II Biosafety cabinet during the analysis. Positive and negative controls were used in every analysis.

The positive control consists of 100 mL of sterile distilled water spiked with 1.0 x 10^{5} CFU/mL of coliform strain of E. Coli. This sample is used for both HTC and TC. Results within 2 standard deviations (within the 95% confidence level) were considered acceptable.

The negative control consists of 100 mL of sterile distilled water. This verifies the sterility of glassware, materials and media used in the analysis.

Heterotrophic Plate Count

The scope of this test is to estimate the number of living heterotrophic bacteria in a given water medium. Stock cultures are prepared, and diluted with a calibrated volumetric pipetter using disposable tips in such as fashion so as to yield an estimated count of 30 to 300. Most potable waters require between 0.1 and 1 mL of undiluted sample.

Sterile, solid agar (either R2A or NWRI agar) is melted in boiling water or by exposure to steam in a partially closed container. Melted agar is maintained at a temperature of 44 to 46^{o}C, until used. Unused portions are discarded after three hours, and are not resterilized or re-used.

Melted agar (10-12 mL) is carefully poured into plates or tubes kept warm in a warm water bath. Mixing of the poured medium with the sample is conducted carefully to avoid spillage of sample or agar. No more than 20 minutes should be allowed to elapse before all melted medium is poured.

Care is taken when dispensing samples with pipets to not allow pipet tips to drag across agar media or against sides or lips of containers. Sterile pipet tips are used with each new dispensation. Pipet tips should not be submerged more than 2.5 cm into a given medium. Samples or dilutions are delivered at a 45-degree angle into a Petri dish

uncovered by only a sufficient amount to allow entry of the pipet tip. Exposure to open air is kept to a minimum.

Samples are incubated at 25 $\pm$ 1^{o}C for a period of 5 to 7 days. Humidity within the incubator is maintained to avoid sample loss due to evaporation during incubation. A pan of sterile water placed in the bottom of the incubator serves this purpose.

Plates are counted using a colony counter after the incubation period. The number of colony-forming-units per milliliter of sample (CFU/mL) are reported along with all experimental conditions and method used. These conditions include temperature, time duration of incubation, plating method used, and type of agar medium. This and any other relevant information is included in the log.

Quality control occurs at several points during the procedure. Blanks of medium and of dilution water are poured onto control plates and carried throughout the procedure. Additional blanks prepared with different pipets or glassware can be used to diagnose contamination sources (glassware, etc.)

OTHER CONSIDERATIONS

NOM Stock

Natural organic material (NOM) will be used as an additive in the laboratory investigations. Two sources of NOM will be used. The first and primary NOM source will be NOM concentrated by RO or EDR treatment of a highly organic natural water. Ion-Exchange, acid and/or antiscalent addition pretreatment of the organic feed water may be required to avoid scaling within the membrane. NOM can be concentrated by membrane processes by continually passing the concentrate through the membrane and cleaning the membrane intermittently. The NOM will be used to determine the effect of organics on the mass transfer of pesticides and DBPFP precursors in the laboratory phase. Commercially available humic acids can be used as a NOM source but have been criticized as being to different from NOM. Limited work will be done to compare the mass transfer and DBPFP of NOM and commercially available humic acids. However NOM can and will be concentrated using RO or EDR.

Single Cell Units

Single cell units will be used during the laboratory phase of the project to determine the operating characteristics of given films. These units differ from the bench scale units in that they are lower flow units and are usually operated at a recovery of less than 1 %, and they use flat sheet membranes as opposed to spiral wound or hollow fine fiber elements as in bench or pilot scale. The same membrane characteristics can be determined with single test units as with bench or pilot scale membranes. However membrane characteristics determined from single cell units using flat sheet membranes can be used to differentiate among membrane films but are not considered to provide accurate means of estimating performance of field or practical membrane units. Laboratory data generated from the operation of single cell units will be recorded and maintained in a laboratory log during the course of this project.

Bench Top Units

Bench top membrane units (BTMU) will be used during this project. The BMTUs will be used following the laboratory phase to determine the effects of varying operational characteristics and chemical feed parameters on mass transfer. The BTMU will be monitored much the same as any single stage membrane process in that the water quality, flow and pressure will be measured during operation. The BTMU will receive one feed stream and provide two output streams which will be a permeate stream and a concentrate stream. The BMTU will operate much like a normal pilot plant or a full scale plant in that there is partial recovery and a spiral wound or hollow fiber element will be used. The BTMU elements will typically have surface area of 2 to 4 square feet and produce approximately 10 to 20 gallons per day if operated continuously. Recovery, pressure gradients, flux mass transfer coefficients and other parameters common to membrane operation will be measured for determining the operating characteristics of a

given membrane and model development. Operational data for all laboratory BMTU units will be recorded and maintained in a log during the course of the project.

DATA MANAGEMENT

Data Reduction and Validation

Data reduction and validation will take place according to the analytical methods employed. Under no circumstances will the standard operating procedures, calculations, and techniques stated in the methods be altered during the course of this investigation. Data that is subject to interpretation requiring the expertise of experienced personnel (i. e. interpreting chromatograms) will be dealt with only by qualified analysts. All data will be subject to a quality assurance quality control review before final reporting. In order to process data in a timely manner the raw data, calculations, quality control results, and final values for parameters are reported to laboratory manager/quality assurance officer, for review and approval as soon as they are generated. As mentioned in several of the procedural sections all raw data, instrument log books, extraction records, and bench notebooks will be kept on file in the laboratory for at least seven years.

Data Collection and Storage

When all the parameters for a sample have been tested and validated, a report is generated for the sample or sample set. The report is referenced using the chain of custody number that the sample or sample set was assigned upon receipt at the laboratory. The values and units for the parameters are typed on a computer form, along with the other identifying information about the sample set such as date sampled, sample site identification number. In addition to the final results a quality control report for the precision and accuracy data that was generated along with the sample set values will be made. Both paper and computer disk copies of the full report are kept. Once generated the report is sent to the laboratory manager/quality assurance officer for a final review and approval. The paper copies are filed according to the work order numbers and issued to all parties involved with data interpretation.

REFERENCES

APHA, AWWA, and WEF (American Public Health Association, American Water Works Association and Water Environment Federation). 1998. Standard Methods for the Examination of Water and Wastewater. 20th ed. Washington, D.C.: APHA.

Noij, T. H. M. and A. Brandt. 1995 HPLC with on-line solid phase extraction for the trace analysis of polar pesticides. In *Analysis of Pesticides in Ground and Surface Water II*, Springer, Heidelberg, Berlin.

Taylor, J.K. 1988. Quality Assurance of Chemical Measurements. Chelsea, MI: Lewis Publishers, Inc.

U.S. Environmental Protection Agency. 1980. Analysis of trihalomethanes in drinking water by liquid-liquid extraction. 40 CFR Part 141, Appendix C, Part II.

U.S. Environmental Protection Agency. 1990. *Methods for the Determination of Oganic Compounds in Drinking Water. Supplement 1*. EPA 600/4-90-020.