QUALITY ASSURANCE PLAN

BIOGEOCHEMISTRY LABORATORY

Air, Water & Aquatic Environments Program
Rocky Mountain Research Station
U. S. Forest Service
U.S. Department of Agriculture

Derek Pierson
dpierson02@fs.fed.us
(970) 498-1017
240 W. Prospect
Fort Collins, CO 80526

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Acronyms / Abbreviations

AD	analytical duplicate
ASTM	American Society for Testing and Materials
AWAE	Air, Water, & Aquatic Environments Program
BB	bottle blank
CFR	Code of Federal
cm	centimeter
DIC	Dissolved Inorganic Carbon
DIW	deionized water
DL	detection limit
DOC	Dissolved Organic Carbon
DSOL	Dissolved Solids
EPA	Environmental Protection Agency
FD	field duplicate
FEF	Fraser Experimental Forest
HDPE	High Density Polyethylene
IC	Ion Chromatograph
L	Liter
MDL	minimum detection limit
µeq	microequivalent
µg	microgram
µm	micrometer
µS	microsiemen
mg	milligram

mL	milliliter
MDL	Method Detection Limit
ML	Minimum Level of Quantification
ng	nanogram
NIST	National Institute of Standards and Technology
NPS	National Park Service
PPE	Personal Protective Equipment
ppb	parts per billion
ppm	parts per million
psi	pounds per square inch
QA	Quality Assurance
QAP	Quality Assurance Plan
QC	Quality Control
QCCS	Quality Control Check Sample
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
SOP	Standard Operating Procedure
SRS	Standard Reference Sample
SSCS	Second Source Check Standard
SSED	Suspended Sediment
TDN	Total Dissolved Nitrogen
TDS	Total Dissolved Solids
TN	Total Nitrogen
TOC	Total Organic Carbon

TV (tv)	Transition Value
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
v/v	volume to volume ratio
w/w	weight to weight ratio

Water Analysis Laboratory
Quality Assurance Plan

1.0 Introduction

The Rocky Mountain Research Station AWAE Biogeochemistry Laboratory was established in the spring of 1988 to provide baseline data characterizing the water and snow chemistry at the Fraser Experimental Forest. The Biogeochemistry Lab specializes in the analysis of research samples originating from streams, standing water, precipitation and sub-surface water. Services conducted by the laboratory include sample analysis, filtration, preservation, and extraction. The Biogeochemistry Laboratory uses standard analytical procedures and practices that in specific cases have been altered to meet the analytical needs of multidisciplinary research.

The AWAE Biogeochemistry Laboratory Quality Assurance Plan (QAP) describes protocols and procedures used in the laboratory. This is a living document that will be updated and revised as new methods and procedures are implemented. Methods, detection limits and acceptance parameters are tabulated for all analytical procedures. Standard Operating Procedures (SOPs) are listed in the appendix, and are available as separate documents.

2.0 Project Organization and Personnel

Current staff consists of one full time chemist and four student interns. Personnel and their primary responsibilities include:

> Derek Pierson, Chemist and Lab Manager: Dionex IC, Waters IC, Alkalinity, pH, conductivity, QuikChem AutoAnalyzer, Shimadzu TOC, documentation, database management, staffing, quality assurance and reports.
>
> Student Interns: sample log-in, sample preparation, extractions, reagent preparation, sample storage and organization, cleaning of glassware and laboratory, general chemist support.

3.0 Quality Assurance Objectives

Quality Assurance (QA) Objectives for the AWAE Biogeochemistry Laboratory are outlined in Table 3.1. Project specific QA Objectives supersede those listed.

Table 3.1 Methods and Detection Limits

Analyte	Reference Method	Method Description	Minimum Detection Limit	Practical Quantitation Limit
pH	EPA 150.1	Mantech PC-Titrate	NA	0-14 pH units
Conductivity	EPA 120.1	Mantech PC-Titrate	0.2 µS/cm	1 µS/cm
Alkalinity	EPA 310.1	Mantech PC-Titrate	2 µeq/L	10 µeq/L
Anions Cl, F, NO3,NO2, SO4	EPA 300.0	Dionex ICS-3000 Ion Chromatograph	0.01 mg/L	0.05 mg/L
Cations Na, NH4, K, Mg, Ca	ASTM D6919-03	Waters 580 Ion Chromatograph	0.01 mg/L	0.08 mg/L
Bromide (Br) or phosphate (PO4-P)	EPA 300.0	Dionex ICS-3000 Ion Chromatograph	0.01 mg/L	0.05 mg/L
Total Nitrogen	ASTM D5176	Shimadzu TOC-V Combustion Analyzer	0.05 mg/L	0.2 mg/L
Total Carbon	EPA 415.1	Shimadzu TOC-V Combustion Analyzer	0.2 mg/L	0.6 mg/L
Total Organic Carbon	EPA 415.1	Shimadzu TOC-V Combustion Analyzer	0.2 mg/L	0.6 mg/L
Total Inorganic Carbon	EPA 415.1	Shimadzu TOC-V Combustion Analyzer	0.6 mg/L	2 mg/L
Ammonia - N & Nitrate-N	EPA 350.3		-	-
Ammonia - N	Lachat 12-107-06-2-A	Lachat QuikChem AutoAnalyzer FIA+ 8000 Series	0.05 mg/L	0.1 mg/L
Nitrate - N	Lachat 12-107-04-1-B		0.05 mg/L	0.1 mg/L

Revised:
December, 2015

4.0 Sample Containers and Glassware Preparation

This section details the protocols for washing sample aliquot bottles, general laboratory glassware and analysis specific vials/tubes. All laboratory preparation, filtering, and cleaning is done while wearing nitrile gloves and appropriate safety gear.

4.1 Sample Bottles

Remove tape labels and rinse bottles twice with DIW. Fill bottles with DIW and soak for 12-48 hours. Rinse bottles twice with DIW and place upside down on drying shelves. New bottles received the same wash treatment prior to use. Caps are rinsed along with bottles and placed on drying rack shelves. When dry, clean bottles are capped and stored for future use.

Bottle blanks are used bi-annually to verify the bottle washing procedure. Bottles are filled with DI and remain at sealed at room temperature for a period no less than 10 days. Analytical results of the bottle blanks samples should be lower than one standard deviation over the detection limit.

4.2 Glassware

Empty, remove tape and markings, and rinse five times with DIW. If residue is present, scrub with brush and repeat rinsing. Fill completely and soak overnight. Rinse glassware one more time prior to drying. Invert glassware and place on drying shelves with freshly lined absorbent matting. When dry, glassware is sealed with parafilm and stored in the proper cabinet for future use.

4.3 Filter Equipment

Thoroughly rinse each part individually with DIW before and after use, as well as between samples. Cover individual parts with Kim Wipe prior to storage in laboratory cabinet.

4.4 Carbon Analyzer Glassware

Rinse tubes and caps four times with DIW and soak in DIW overnight. Caps can then be covered and dried on drying shelves. Bake tubes in a muffle furnace at 550 ºC for no less than three hours. Allow tubes to cool overnight in the furnace. Tubes and lids are reassembled and stored in laboratory cabinet under a sealed layer of aluminum foil.

4.5 Ion Chromatography Vials and Glassware

All glassware and plastic containers used for ion chromatography eluent, reagent, and dilution purposes are rinses with DIW five times and allowed to soak overnight before a final DIW rinse. Items are to be dried upside down on drying racks.

Sample vials for the Waters IC arrive sterile from Globe Scientific and are not reused. Sample vials for the Dionex IC are re-used and are washed using the same procedure as all other ion chromatography glassware.

4.6 Plastic Falcon Tubes For pH, EC, and Alkalinity

Plastic 50 ml falcon tubes are rinsed with DIW and soaked overnight. Falcon tubes are then rinsed three times with DIW and placed upside down on drying racks.

4.7 Miscellaneous Glassware, Carboys, Plastic Containers, Etc.

In general, all vessels or containers should be rinsed 4+ times with DIW, soaked overnight, rinsed again, and placed upside down on drying shelves. All vessels or containers should be stored in enclosed areas protected from contaminants.

4.8 Laboratory Maintenance

Trace level analysis requires exceptional laboratory hygiene. See Appendix for regular laboratory cleaning and maintenance tasks.

5.0 Sample Custody, Preparation and Preservation

The accuracy of analytical data as a representation of true sample composition is dependent upon collection and treatment of samples before they arrive at the laboratory. Sampling techniques and procedures must be such that the sample does not deteriorate or become contaminated before it reaches the lab. Recommended protocols for field collection are located in the appendix.

5.1 Sample Custody

A sample log, and labeled sample containers, should be delivered to the lab as soon as possible following sample collection. Requested sample analyses should be discussed and agreed upon prior to sample delivery. Once at the laboratory, samples are entered into the tracking system. Sample condition, number of samples and date of receipt are recorded (see Sample Receipt and Tracking Form in the appendix). Before and after analysis, all samples will be stored below 4 ºC, or frozen if necessary.

Prior to analysis, samples are logged in to the electronic database and a project code is assigned (see Table 5.1) and samples are numbered consecutively within the code for each individual project.

5.2 Sample Storage

Samples are stored in the walk-in cold room (4ºC), or one of the laboratory freezers (-8 ºC) / refrigerators (4ºC). Storage temperatures are monitored daily through the use of thermometers or HOBO temperature sensors. Analyzed samples are held for one month after submission of final database or longer based on a preexisting agreement.

5.3 Sample Processing and Preservation

Samples requiring filtered aliquots should be filtered as soon as possible after collection to minimize biological and algal activity. Membrane filters (pore size 0.45 um) and glass-fiber filters (0.7 um) are most commonly used. The AWAE Biogeochemistry Lab uses hydrophilic Millipore Durapor PVDF membrane filters (FisherSci #HVLP-047-00) and Millipore borosilicate glass fiber filters (FisherSci #APFF-047-00). See Appendix for the RMRS lab filtering protocol. After filtering, both filtered and unfiltered samples should be stored in the dark at 4°C until delivery at the lab.

In general, the most reliable analytical results are obtained when samples are analyzed immediately after collection. This is rarely possible. The most commonly used sample preservation methods consist of addition of chemical preservatives. The AWAE Biogeochemistry Lab does not recommend chemical preservation of samples as it increases the potential for contamination and interferes with some analyses.

For intermediate and long term storage purposes we recommend freezing a filtered sample aliquot for most analyses; other aliquots should be kept cold and in the dark. See Table 5.2 for various analysis- specific preservation and hold time procedures used by the AWAE Biogeochemistry Lab.

Regardless of the preservation method, complete stability for every constituent is unattainable. Strict rules for preservation of water samples do not exist and effectiveness of most preservation methods are questionable for various analytes. Extensive studies have been published supporting preservation of water samples by freezing for many analytes. Whatever methods are used, they should be consistent across the life of the project and procedures should be well documented. The lab should be notified in advance of the preservation method used.

Table 5.2 Sample Hold Times

	Storage Temperature		
Analysis	**Filtered**	**Unfiltered**	**Hold Time***
Alkalinity	-----	4ºC	7 days
Ammonia-nitrogen*	-20ºC or 4ºC	-----	48 hours unless
Bromide	-20ºC or 4ºC	-----	28 days unless frozen
Calcium	-20ºC or 4ºC	4ºC	30 days unless frozen
Carbon, dissolved or total organic	-20ºC or 4ºC	4ºC	14 days unless frozen
Carbon, inorganic	4ºC	4ºC	72 hours
Chloride	-20ºC or 4ºC	-----	28 days unless frozen
Magnesium	-20ºC or 4ºC	4ºC	30 days unless frozen
Nitrate-nitrogen	-20ºC or 4ºC	-----	48 hours unless
Nitrogen, total dissolved or total	-20ºC or 4ºC	4ºC	28 days until digestion unless
Phosphate, ortho	-20ºC or 4ºC	4ºC	48 hours unless
Phophorous, total dissolved	-20ºC or 4ºC	4ºC	28 days until digestion unless
pH	-----	4ºC	7 days
Potassium	-20ºC or 4ºC	4ºC	30 days unless frozen
Silica	4ºC	-----	28 days
Sodium	-20ºC or 4ºC	4ºC	30 days unless frozen
Solids, Suspended	-----	4ºC	Filtered within 7 days
Specific conductance	-----	4ºC	7 days
Sulfate	-20ºC or 4ºC	-----	28 days unless frozen

5.4 Sample Tracking

Requested analyses are entered into the database at time of sample arrival. Sample analysis progress is tracked through data entry.

6.0 Calibration and Analytical Procedures

Standard Operating Procedures (SOPs) are available as individual documents for each analysis used by the AWAE Biogeochemistry Laboratory. A complete list of methods is found in Table 3.1 and general laboratory procedures are documented here. Additional methods may be developed upon request, and as new instrumentation is obtained.

Run logs are maintained for each instrument. They contain information such as analysis run details, samples analyzed, instrument maintenance, problematic symptoms, troubleshooting and response.

Descriptions of analytical procedures including instrument calibration are detailed in each analyte specific SOP. General laboratory procedures are outlined below.

6.1 Balance and Pipette Calibration

All laboratory balances are calibrated yearly. Pipette calibration is checked weekly by weight to within 1% of theoretical weight of aliquot volume.

6.2 Calibration Standard Preparation

Standards are prepared by serial dilution (if necessary) of standards purchased from vendors that provide traceability to National Institute of Standards and Technology (NIST) standards. Preparation of stock and working standards is recorded on worksheets (see example in appendix) and documented by the weight of standard added to a given flask before dilution to volume with DIW. The weight of standard dispensed must be within 2% of the expected value. All records of certification and standard preparation are kept on file.

6.3 General Calibration and Analysis Procedures

Generally, analytical instrumentation is calibrated at the beginning of each analysis set with three to six working standards. A second source check standard (SSCS) is analyzed after the calibration and after every 5-15 samples. For most analyses, the SSCS is followed by a blank. The SSCS is prepared from a source or lot different than that used for the calibration standards. Check standard recovery must be within 10 % of theoretical value, or within normal observed limits of variability, to accept the sample data preceding it. In addition to the SSCS, a detection limit standard and/or a bulk quality control check standard (QCCS) may be analyzed once at the beginning and end of each run. Approximately 5% of the samples analyzed are duplicated; duplicate values must be within 10% of the original value.

6.4 Minimum Detection Limits

The minimum (aka method) detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte (U.S. EPA, 40CFR136, App. B). The MDL is determined by repeated analysis of a standard solution approximately five times the concentration of the estimated detection limit. The standard sample used in determination of the MDL should complete all normal sample processing steps used in the analytical method. At least seven measurements are recommended for determining the MDL. The MDL is calculated as follow:

$$MDL = t*S$$

t = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom

S = standard deviation of the replicate analyses

7.0 Internal Quality Control Checks

Analytical instrumentation is calibrated using standard solutions of the analyte of interest. Calibration correlation should be greater than 0.995. For most analyses, drift is monitored with check standards throughout the analysis run. Check standards are from a source or lot other than that of the calibration standards. If drift outside 10% recovery is observed, the run is stopped and the instrument recalibrated, or the analysis is repeated. Samples beyond the last acceptable check standard are reanalyzed.

For most analyses, a bulk, surface water Quality Control Check Standard (QCCS) is analyzed twice each analysis run. Action is required for results outside three standard deviations of expected values, and may include recalibration and reanalysis, instrument maintenance and/or repair. Some analyte concentrations may change over time and this must be taken into account when determining appropriate response.

Sample duplicates are used to estimate precision. When sample volume allows, 5-10% of the samples are duplicated for every analysis. Field duplicates may be included upon request.

To estimate accuracy, the AWAE Biogeochemistry Lab participates in the United States Geological Survey (USGS) Standard Reference Surface Water test program and the National Water Research Institute's (NWRI) Environment Canada Proficiency Testing (PT) Program for analysis of test samples for nutrient and chemical constituents of natural waters. See summaries of recent results in the appendix.

Other quality checks performed during analysis may include blanks run throughout the analysis to monitor carry-over, detection limit standards, and filter and/or bottle blanks.

8.0 Calculation of Data Quality Indicators

Measurement Data Quality Objectives presented in Table 8.1 represent the 99 % confidence intervals about a single measurement. At lower concentrations, precision objectives are equivalent to the MDL, and based upon the standard deviation (*sd*) of a set of repeated measurements:

$$sd = \sqrt{\sum (x - \bar{x})^2 / (n - 1)}$$

where x is an individual measurement and $\bar{x}$ is the mean of the measurement set. For higher concentrations, the precision objectives are based on the percent relative standard deviation (*%RSD*).

$$\%RSD = \frac{sd}{x} * 100$$

This reduces the problems of unreasonable objectives for low or high analyte concentrations. Concentration ranges are specified to determine the concentration at which absolute or relative terms apply. The division between the ranges, the Transition Value (*tv*), is estimated by:

$$tv = \frac{\sqrt{\frac{sd}{2} * sd}}{RSD} - \frac{sd}{2}$$

where *RSD* = *%RSD*/100.

Table 8.1 Measurement Data Quality Objectives

Analyte	Minimum Detection Limit	Precision & Accuracy	Transition Value*
Alkalinity	2 ueq/L	± 4 ueq/L or ± 5 %	80 ueq/L
Ammonium	0.02 mg/L	± 0.015 mg/L or ± 10 %	0.15 mg/L
Bromide	0.01 mg/L	± 0.01 mg/L or ± 5 %	0.2 mg/L
Calcium	0.02 mg/L	± 0.02 mg/L or ± 5 %	0.4 mg/L
Carbon, Organic	0.30 mg/L	± 0.05 mg/L or ± 5 %	1 mg/L
Carbon, Inorganic	0.05 mg/L	± 0.1 mg/L or ± 10 %	1 mg/L
Chloride	0.01 mg/L	± 0.01 mg/L or ± 5 %	0.2 mg/L
Conductivity	0.4 µS/cm	± 1 µS/cm or ± 2 %	50 µS/cm
Magnesium	0.02 mg/L	± 0.02 mg/L or ± 5 %	0.4 mg/L
Nitrate/Nitrite	0.01 mg N/L	± 0.005 mg/L or ± 5 %	0.1 mg/L
Nitrogen, Total	0.01 mg N/L	± 0.01 mg/L or ± 5 %	0.2 mg/L
Ortho-Phosphorus	0.01 mg P/L	± 0.005 mg/L or ± 5 %	0.1 mg/L
pH	NA	± 0.1 pH unit	NA
Potassium	0.02 mg/L	± 0.03 mg/L or ± 5 %	0.6 mg/L
Sodium	0.01 mg/L	± 0.02 mg/L or ± 5 %	0.4 mg/L
Sulfate	0.01 mg S/L	± 0.01 mg/L or ± 5 %	0.2 mg/L
Suspended Sediment	2 mg/L	± 1 mg/L or ± 10 %	10 mg/L

** The value above which precision and bias are expressed in relative terms.*

To use difference instead of the standard deviation to evaluate precision, the difference between two measurements is used for the absolute term and the relative percent difference (*RPD*) is used for the relative term:

$$RPD = \frac{|x_1 - x_2|}{\overline{x}} * 10$$

9.0 Data Reduction, Validation and Reporting

Analytical results are collected in various formats, dependent upon the instrumentation output. All sample information, project data, billing, analytical results, quality control results and calibration statistics are entered and tracked through a database in Microsoft Excel and R. All QA and QC indicators are reviewed at time of analysis, and the analytical results are validated. The QA/QC is checked again before final submission of the database.

Analytical results, sample information and calibration summaries are sent electronically to the project PI in Excel and CSV formats. Unless other arrangements are made, investigators have three weeks to review the results and request reanalysis.

Validation of analytical results may include the following calculations:

- For projects requesting a complete analytical suite of anions, cations, pH and alkalinity, Ion Balance may be run to check for completeness and identify any outlying values. The balance may be skewed if there is an abundance of an ion not analyzed, but the balance check works well for most water samples.

$$Ion\ Balance = \frac{\sum anions}{\sum cations}$$

Where:

$\sum anions = HCO_3 + SO_4 + Cl + NO_3 + PO_4$

$\sum cations = H + Ca + Mg + K + Na + NH_4$

(All ion concentrations are in units of ueq/L)

- Total nitrogen concentration should be greater than the sum of ammonia

and nitrate/nitrite.

- Total phosphorus concentration should be greater than orthophosphorus.

- Total (unfiltered) results should be greater than dissolved (filtered) results. Data Quality Analysis Reports may be requested for detailed analysis of all indicators used by the Biogeochemistry Lab (fees apply).

10.0 Performance and System Audits

The AWAE Biogeochemistry Laboratory has participates in the USGS inter-laboratory comparison study for laboratory quality assurance testing semiannually. The program provides the laboratory with a Standard Reference Sample for precipitation. Accuracy of analytical results are ascertained based on performance in the program. See the appendix for a summary of recent results.

In 2014 the AWAE Biogeochemistry Laboratory began participating in Environment Canada's National Water Research Institute (NWRI) Proficiency Testing Program. The Biogeochemistry Lab participates annually in the Rain & Soft Waters Study. The advantage of this study is additional analysis accuracy and bias reporting due to the testing of a larger, more diverse sample set.

11.0 References

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12.0 Document Revision History

Original Document: March, 2014

Version: 1

Title: Quality Assurance Plan, AWAE Biogeochemistry Laboratory.

Author: Derek Pierson, Chemist/Lab Manager, AWAE Biogeochemistry Lab

Note: Originally adapted (with permission) from the Quality Assurance Plan for the Cooperative Chemical Analytical Laboratory at Oregon State University.

Edit Date:

New Version:

Purpose:

Appendix A – Water Sampling Protocol

- Streams should be sampled upstream from any man-made structure such as a bridge. Lakes are to be sampled at their outlet. Collect from the same sampling site for each repeated measure. Avoid disturbing the bottom as additional particulates may affect analysis.
- If temperature reading is required, leave the thermometer immersed for five minutes before reading. Avoid disturbing the bottom with the thermometer at the sample site.
- Label bottle with location (geographic area name and stream or lake name), date, time of day, water temperature and sampler's initials. Label bottle before immersion using a black permanent marker.
- Use plastic gloves when handling bottles during sampling. Bug repellents or sunscreen are particularly troublesome as contaminants. Once the gloves are on, be careful not to touch your skin, the ground, etc.
- Be sure to immerse the sample bottle completely, 10 cm (4 inches) deep, with mouth of bottle pointing upstream, so no water flows over your hand into the bottle. Remove the cap under water. Be sure the bottle does not get near the bottom of the stream where sediments can be disturbed. Fill bottle at least half full, replace cap loosely, remove from water and shake. Pour out rinse water downstream of sample point. Pour some rinse water over inside of cap. Do not touch bottle mouth or inside of cap. Partially fill the bottle, cap, shake, and rinse three times.
- Collect the sample on the fourth immersion. Use the same procedure as before but fill bottle completely. Be careful not to contaminate the sample with surface film, contact with human skin, breathing in/on the bottle or cap, etc. If necessary, squeeze the bottle slightly as the cap is tightened so no air remains in bottle. If stream is too shallow to immerse bottle fully, collect as much as possible, being very careful not to touch the bottom. Note depth on field notes.
- Collect "duplicate" sample if instructed. Generally, every 10th sample collected is duplicated. Sample sites chosen for duplicate sampling are selected at random among streams sampled. If a duplicate is required for your site, repeat procedures as with normal stream samples. The duplicate is the second when two samples are collected. Duplicates document repeatability of individual sample collections and reproducibility of laboratory results.
- One "field blank" sample should be taken to the field and remain unopened each sample day. Write sample study area, stream name, date, time of day, sampler's initials, and 'FB' on the bottle. Field blanks are necessary to quantify chemicals from non-sample sources such as water bottles, DI water, filter paper, handling procedures, etc. The extra bottle for the FB can be used for the sample in an emergency if the sample bottle is lost or contaminated.
- Place sample immediately in a Ziploc bag in a cooler after collection. Do not expose sample bottles to the sun. Fill out the field data sheet, noting any

unusual conditions such as wind or rain. Measure air temperature (shaded) and record. Keep gloves clean for next use. Rinse clean, dry, and transport gloves in a clean zip lock bag.

- Samples are filtered in the lab. Keep samples cool while transporting. Zip lock bags (double bagged) filled with snow work well if frozen icepacks are unavailable for transport from the field. Store at 4 C but do not freeze. Ship to the lab in a picnic cooler with frozen icepacks via FedEx or UPS overnight. Do not ship so the sample arrives on a weekend. If necessary, keep samples refrigerated for arrival weekdays. Hand delivery to the lab is preferred; or arrange for a contact to pick up the samples.

Ship or deliver samples to:

Derek Pierson
240 W. Prospect
Fort Collins, CO 80526
(970) 498 – 1017
dpierson02@fs.fed.us

Appendix B – Ion Chromatography Calibration Standard Table

Anions (mg/L)

Level	Conc.	F	Cl	NO3	PO4	SO4
2	DX.25	0.050	0.075	0.250	0.375	0.375
3	DX.5	0.100	0.150	0.500	0.750	0.750
4	DX1	0.200	0.300	1.000	1.500	1.500
5	DX2	0.400	0.600	2.000	3.000	3.000
6	DX3	0.600	0.900	3.000	4.500	4.500
7	DX4	0.800	1.200	4.000	6.000	6.000
8	DX5	1.000	1.500	5.000	7.500	7.500
9	DX10	2.000	3.000	10.000	15.000	15.000
10	DX20	4.000	6.000	20.000	30.000	30.000

Cations (mg/L)

Level	Conc.	Na	NH4	K	Mg	Ca
2	CDX.025	0.050	0.100	0.050	0.050	0.250
3	CDX.05	0.100	0.200	0.100	0.100	0.500
4	CDX.1	0.200	0.400	0.200	0.200	1.000
5	CDX.2	0.400	0.800	0.400	0.400	2.000
6	CDX.3	0.600	1.200	0.600	0.600	3.000
7	CDX.5	1.000	2.000	1.000	1.000	5.000
8	CDX1	2.000	4.000	2.000	2.000	10.000
9	CDX2	4.000	8.000	4.000	4.000	20.000
10	CDX4	8.000	16.000	8.000	8.000	40.000

Appendix C – Ion Chromatography Eluent Procedures

Waters Cation Eluent

1. Use the analytical balance to weigh out 0.0584 grams of EDTA and put this in the 2 Liter volumetric flask labeled Cation Eluent.
2. Add just under 2 Liters of deionized water, slightly below the red line, heat at 6 and stir on a stir plate until all of the EDTA is dissolved (about a couple hours). It will be very hot.
3. Add 378 µl of Ultrex® nitric acid (HNO_3). This can be done with the 10-100 µl adjustable pipet by adding 94.5 µl four times.
4. Rinse the inside of the volumetric flask with a little deionized water to make sure all of the acid gets mixed in.
5. Filter through a 0.2 µm filter to remove any undissolved EDTA

Waters and Dionex Anion Eluent

1. Use the analytical balance to weigh out 1.145 g of Sodium Carbonate (Na_2CO_3) and 0.101 g of Sodium Bicarbonate ($NaHCO_3$), and put both into a 4 liter carboy.
2. Add deionized water to the 4 liter mark on the carboy, tighten the lid (make sure to use a lid with a washer inside for a tight seal) and shake to dissolve the salts. The solution may need to sit for a while for the salts to completely dissolve.
3. Degas the eluent with helium gas for several minutes or let sit overnight.

Appendix D – Sampling Filtering Procedure

A. Introduction

Solutes present in surface waters are primarily derived from precipitation inputs and geochemical weathering. Because samples must be shipped out for chemical analysis, it is important that the original chemical composition remains unchanged before and during transport. Particulates in a sample can affect chemical results as well as clog lines of sensitive instrumentation. Biological activity in the sample can alter chemical composition. Therefore, it is important to filter samples as soon as possible post sampling to remove particulate materials, spores, and bacteria in sample water that might affect chemical analysis.

B. Equipment and Supplies

Equipment and supplies are located in the Water Lab.

Bottle(s) with sample

Absorbent Surface Liner Sheet (~20”x20”)

Millipore* Sterifil* 47mm Aseptic Vacuum Filter System (funnel, holder and receiver flask)

Gast* Pressure/Vacuum Pump or Nalgene* PVC Hand-Operated Vacuum Pump

Millipore* Durapore® Membrane Filters 0.45µm (IC Samples)

Millipore* Glass Fibre Prefilters 0.7µm (DOC Samples)

Clean forceps (blue) and tweezers

Deionized (DI) water for rinsing

Waste bucket

Clean 60-ml bottle(s) labeled with site name, date, temp., precip. Amt. or discharge, Sample ID#, etc. (copy all information from sample bottle)

C. Estimated Time To Complete Procedure

Allow approximately 5-10 minutes per sample, although filtering times may vary greatly depending on the amount of particulate matter in the sample.

D. Preparation

Washing

All pump apparati, except receiver flask, should be DI-washed after each use. This can be done in the sink in the Water Lab. To clean, triple rinse with DI water, soak in a bucket of DI for 24 hrs., triple rinse again, and air dry in a drying rack covered with a couple of Kimwipes. Conductivity of the rinse water should be < 2 µS cm-1.

Glass bottles must be triple rinsed in DI water and baked at 500°C for 5 hrs. The lids are washed as per above. These should be washed and baked in the RMRS Lab. They are stored empty, dry and capped in their original boxes and should be returned to the RMRS Lab in their original boxes when possible.

E. Procedures for filtering sample

Rinsing Pump

1. Rinse 250mL funnel and funnel holder with DI for ~3-5 sec. and place on clean surface (e.g. Kimwipe or on clean part of surface liner sheet)

Loading Filter

2. Using tweezers, remove blue papers over filter, throw away and carefully remove one filter (Durapore® 0.45µm or Glass Fibre 0.7µm) from box. Place filter paper on the holder. If filter is not centered, carefully adjust its position by pulling on edge with tweezers.

    Note:

    Millipore* Glass Fiber filters do not have any papers separating each filter. It is necessary to look carefully at each filter to make sure that you do not have more than one filter stuck together.

WARNING!

Be careful handling filters, as any contact of filter by forceps in any area except its extreme outer edge will result in contamination or damage to filter.

DO NOT breathe, sneeze, cough on or touch filter paper or any apparati that may come in contact with sample.

3. Screw filter holder onto funnel.

Filtering Sample

4. Place pre-labeled 60mL bottle in receiver flask using blue forceps. Make sure to place as little of the forceps tip into the bottle as possible to reduce the risk of contaminating the bottle or sample.

5. 2. Pour a few milliliters of sample into the funnel and pump through.

6. Remove 60mL bottle with filtrate using blue forceps. Replace lid, shake, remove lid and pour into waste bucket.

7. Repeat steps 1-3 three times before filling.

8. Pour 50mL into funnel for final sample.

   Note:

   If sample contains enough matter to clog the filter before the 60mL bottle is filled, it may be necessary to stop, change filter, and resume filtering. Remember to rinse the new filter with sample before beginning to fill bottle again.

9. Change filters between samples. Follow pump rinsing procedure as mentioned previously.

10. After all samples are filtered clean all equipment following the washing procedures described in section D above.

11. Store the 250mL samples and 60-mL filtered sample bottles in the refrigerator or in a cooler with a sufficient number of ice packs to keep the samples at ~40°F.