SEQUOIA NATIONAL PARK
ACID DEPOSITION/ECOSYSTEM STUDIES
WATER AND METEOROLOGY SAMPLING PROTOCOL

Original December 1983

Revised December 1986

Introduction

The purpose of this protocol is to provide the guidelines necessary to assure the consistent collection methodology and quality control according to scientifically accepted procedures and analytical techniques for each type of sampling carried out.

During the design of this study, it became clear that different agencies and principal investigators often follow different procedures when collecting similar data. It was impossible to consolidate these different methods without some compromise.

Dr. Robert Stottlemyer is credited for firmly installing in us the belief that "one of the most difficult aspects to fully appreciate in the conduct of field research is the need for consistent procedures."

Contents

I. Water Analysis

A. Stream Sampling (NPS)

1. Overview: The purpose of stream sample collection is to determine chemistry of stream output from the study sites. Stream samples will be collected biweekly from each site, with more frequent collections during spring snow melt and selected precipitation events. For each collection, stream flow data is necessary to relate sample chemistry to output volume. Stream gauging methods are described in Section III. Due to inaccuracies of measuring field pH and our proximity to the laboratory, stream pH will be measured at the lab under controlled conditions. When periodic field pH measurements are taken for quality control checks, samples will be analyzed for field pH with a Markson Model 95 pH meter with YSI 701 thermister and Gam Rad pH electrode. In all cases, temperature will be measured in the field and subsamples filtered (.45 u membrane filters) into LPE bottles for MTU and NPS lab analysis. An additional 250 ml bottle of unfiltered sample will be collected for alkalinity and conductivity analysis. When field conditions such as bad weather do not permit field analysis, pH and filtering will be done at the NPS lab within six hours of collection. Samples are transported in the dark and chilled enroute to the NPS lab. Samples are refrigerated (4o C) in the lab and one chilled 30 ml subsample will be mailed to MTU within 48 hours of collection for cation and anion analysis. Filtered samples will be analyzed for NH4 (Appendix A) and PO4 (Appendix B). Portions of each filtered sample will be archived for later silica analysis (refrigeration) and quality control tests (frozen). Lab pH (Altex Model 3500 pH meter and Beckman phI 40 with Beckman #39835 combination probe), alkalinity (Appendix C) and conductivity (Beckman Model RC-16C with YSI 3403 K=1.0 probe (samples > 50 umbos) or YSI 3402 k=.10 (samples < 50 umhos)) are measured on unfiltered water at the NPS lab within 24 hours of collection.

2. Field Equipment:
- 1 250 ml acid washed LPE bottle
- 3 60 ml acid washed LPE bottles
- 1 30 ml acid washed LPE bottle
- 1 50 or 140cc syringe, filter holder and .45u membrane filters (Gelman GA-6)
- 1 Markson Model 95 pH meter w/YSI 701 thermistor and Gam Rad pH electrode (or other pH probes as selected)
- 1 250 ml squirt bottle w/DI water
- 1 field notebook, permanent pen, label tape
- 1 liter bottle in snow conditions

Bottles should be prelabeled at NPS lab with site name, sample number, date and subsample letter. Subsample letters will be as follows:

A = MTU sample
B = NPS chemistry: NH4/PO4
C = archive, re-runs
D = SiO2 analysis
NF = unfiltered for pH, conductivity, alkalinity

Sample numbers are given in sequence from field notebook.

3. Field Methods

1. Measure or estimate flow stage (discharge) by reading from the flume and stream staff gauges. Record site, time and flow rate in notebook. (See Section III). All samples should be collected at mid-depth and mid-flow of the stream.

2. When periodic field pH measurements are necessary, determine pH with Markson meter. To calibrate the pH meter: 1) Insert probe and thermistor in 7 buffer after first rinsing the probes with DI water. Turn control to TEMP to read temperature of buffer. 2) Dial the temperature control knob to the temperature of the buffer solution. 3) Switch to ATC function and use the calibrate knob to adjust the pH reading to 7 or pH shown in instructions corresponding to the temperature. 4) Remove probes and rinse thoroughly with DI water. After rinsing, place the probes in the 4 buffer solution and adjust the slope control on the back of the meter until the meter reads 4 when in the ATC mode. The control knob should be on TEMP whenever the probe is removed from a solution and/or rinsed. Once the pH meter is calibrated rinse the probes extremely well by soaking in several beakerfulls of DI water and intermittently swirling and squirting the probes. To measure a sample rinse a 60 ml LPE bottle three times with stream water, then fill. Insert electrode and thermistor, swirl for three minutes, let the meter reading stabilize, and then replace the sample water for a final reading. Let the sample stabilize and read pH after 3 minutes, extend the period if not stable to the nearest 0.1 pH unit. Switch to TEMP and record stream temperature and pH in notebook.

3. If field conditions permit filtering, assemble the filter holder with a .45 u membrane filter. Rinse a portion of water through the syringe and about 25 mls of water through the filter. Rinse the 60 and 30 ml sample bottles with filtered water three times, then fill with filtered water. Filters may need to be replaced during this process if particles in the water block the filter and make it hard to squeeze the syringe.

4. Rinse the 250 ml bottle 3 times with unfiltered stream water and then fill with unfiltered water.

5. If an acceptable field portable conductivity meter becomes available in the future this measurement will be taken at the site.

6. Store samples in the dark and in a cooler if possible while returning to lab. Rinse and store the pH meter probes.

4. Lab Handling:

1. Immediately refrigerate all water samples (4 ^{o}C).

2. If samples were not filtered then do so as soon as possible at the lab. Conductivity and lab pH measurements should be made immediately upon return also.

3. Unfiltered sample will be run for conductivity (see Beckman manual for instructions) and alkalinity. (Methods in appendix).

4. One 60 ml filtered sample will be used for PO4 and NH4 analysis (Methods in appendix).

5. The 30 ml subsample will be packed in a Lil Oscar cooler with 2 units of blue ice and mailed to MTU within 48 hours of collection via Express Mail. Conductivity of the sample should be written on the label. Address of MTU:

Great Lakes Resources Study Unit
Department of Biological Sciences
Michigan Tech. University
Houghton, Michigan 49931
Attn: Stottlemyer

6. Freeze 20 ml of one 60 ml filtered sample in a labeled "Whirl Pack Bag" for archiving. The remaining filtered water may be used for splits or reruns as may be needed.

7. The extra 60 ml filtered sample (bottle with subsample letter "D") is refrigerated for silica analysis by UC Santa Barbara personnel

8. Labels for all sample bottles and archived samples will include site, sample number, date and subsample letter. Samples sent to MTU also include the words "Sequoia National Park."

B. Stream Sampling (USGS)

1. Overview: In conjunction with the Parks' acid precipitation research program, the US Geological Survey has selected Emerald Lake as a study site for a long term watershed trends research program. The program includes stream gauging and chemical analysis of Emerald Lake outflow.

Park Service personnel will conduct biweekly to monthly sampling of Emerald Lake stream outflow and mail samples to the USGS Central Laboratory in Arvada, CO for analysis. The yearly sampling schedule will be as follows:

a. March through July-biweekly sampling with one replicate each month.
b. August through September-biweekly sampling
c. October through February-monthly sampling

2. Field equipment

Bottles
1 glass labeled LCO113
1 brown 250 ml LPE labeled FC
2 250 ml LPE labeled FU and RU.
1 500 ml POLY w/red cap labeled FA

Filters
.45 silver filter (USGS)
.45 membrane filter, NPS (Gelman GA-6)
.1 membrane filter, 135 mm (USGS)

Filter Holders
stainless steel filter holder
47 mm Nuclepore filter holder
135 mm Nuclepore filter holder

Geopump
Rubber tubing
Electric cord
Battery, fully charged

Marking tape
Marking pen
Tweezers
DI squeeze bottle w/DI water
Notebook
Gloves - surgical

Nitric Acid ampules - 1 packed in plastic container for safe transport

Syringe - 1 140 cc

Some items may be at the Pear Lake cabin and some may not be. Check each before heading out to sample.

3. Field Methods:

1. Determine pH as in Section A. Record pH and water temperature, and air temperature.

2. To set up the 135 mm filter holder, place the .1 u filter between the fabric screens and clamp tightly. Take care to keep the fabric screens placed in the same direction on the same side of the holder all the time. Changing the arrangement of the screens will affect the sample. Attach the 12 volt battery to the pump and thread the tubing through the peristaltic pump. Place the intake end of the tubing in the stream or in a 1 liter 3 X rinsed bottle of stream water. Attach the outflow end to the filter holder. (Note - water can be prefiltered through a .45 u membrane filter before filtering through .1 u filter). Rinse the filter with about 5 mls of water. Using the .1 u filter rinse three times and fill - FU, FC, FA - Fill FU with 100 mls, FC with 15 mls, and FA with 250 mls of filtered sample. Add one ampule of HNO3 to FA and cap. Keep chilled. Wear rubber gloves when adding acid (.1 u filter used for all samples as of 1/85 and FAB deleted as of 4/85).

3. The .45 u silver filter is used in the stainless steel filter holder with the glass LC113 bottle. Rinse water through the filter and rinse LC113 bottle three times and then fill to brim and cap. Keep cool to 4o C.

4. Rinse RU three times with unfiltered stream water and fill to brim, cap and store chilled.

4. Handling:

Store in cooler until return to NPS lab. Mail the samples in the round blue coolers packed w/blue ice and packing material. Fill out lab data form, enclose form in a zip lock bag and mail via express mail to:

Denver Laboratory
USGS Water Quality Laboratory
5293 Ward Road
Arvada, CO 80002

Send a xerox of the lab form to:

Dave Leighton
U.S. Geological Survey
Federal Building Room W 2235
2800 Cottage Way
Sacramento, CA 95825

He is also our contact to obtain new supplies for the sampling.

C. Precipitation

Rain will be collected as event and/or bulk precipitation at or near each study site. Event collections will be made at the NADP station at Giant Forest and at Ash Mountain and Emerald Lake by the Aerochemetrics sampler installed by the California Air Resources Board (CARB). Bulk collection of rain will be made in open Lewis collectors at all three sites which are sampled every Tuesday. Bulk collection of snow will be made with a combination of Lewis collectors, large LPE containers and snow cores at or near the Log Meadow site by the NPS. UCSB will be responsible for more detailed snow measurements at Emerald Lake under a contract with the State Air Resources Board.

Bulk collectors will be cleaned and rinsed each week on Tuesday regardless of whether precipitation occurs. A second Lewis collector has been placed at the Ash Mountain site 4/85 and will only be collected and rinsed if precipitation has occurred within the "Tuesday to Tuesday" sampling period. These samples will be labeled as "Lewis-Open", coded as a Bulk sample, and should be noted in the field book as to the last sampling date. (Example: Lewis open since 860809)

"Snow cans" are 208 liter (55 gallon) LPE containers (with acid washed plastic liners) used as snow event or bulk collectors. Snow pack cores are used to determine snow pack chemistry. The sampling device is a 5 cm diameter, 75 cm long PVC tube with aluminum extension poles. Snow cores will be stored in acid washed plastic bags or LPE bottles, transported to the lab, and thawed for filtering and analysis within 24 hours of collection.

All subsamples will be transported in the dark, in a cooler if possible. In general, precipitation samples, including snow once melted, will be treated and analyzed like stream samples. In the event there is less than 250 ml of sample, priorities of analysis will be scheduled according to Table 1.

Table 1. Rain Sample Priority Uses

1. Unfiltered
   a. pH - 30 ml
   b. conductance - 30 ml
   c. 200 ml sent to El Monte lab (CARB samples only)

2. Filtered
   a. Cations and Anions - 30 ml
      (Send to MTU for analysis)
   b. Nutrients (NH4, 20 ml; PO4, 40 ml)
      (SEKI)

1. Lewis Bulk Collector

a. Field Equipment: 250 ml acid washed LPE sample bottle, 500 ml squirt bottle with DDW, Whatman 541 filter, field notebook, permanent pen and label tape.

b. Field Methods:

1. Remove precipitation collection container. Record date, time, location and total volume at nearby rain gauges.

2. Subsample 250 ml into sample bottle after rinsing 3 times with sample (or all precipitation if less than 250 ml), label and record sample number, date, type, location, and observations as necessary (ie. insects, disturbances, unusual activity in area, etc.)

3. Remove old Whatman 541 filter, squirt down Lewis collector with 200 ml or more DI water and replace with a clean and washed container and a new filter.

4. Store samples in the dark, in cooler if possible, and transport to lab.

5. On returning to the lab acid wash collection container and funnels and rinse well with DI water. Cover container opening with parafilm and store in lab.

2. Snow Cans

a. Field Equipment: 2 250 ml acid washed LPE sample bottles, field notebook, permanent pen, label, tape, PVC snow corer. Snow can with replacement liner or liner alone.

b. Field Methods:

1. A snow bucket with a clean plastic liner will be set in place at the NADP site weekly. The liner itself may be replaced alone if that is more feasible.

2. To take a sample, stir the can contents thoroughly with a clean PVC snow corer and subsample into two 250 ml bottles (treated as splits). Record date, time, sample type and location in notebook and on sample label. If the sample is too icy to get an appropriate subsample, return the entire sample to the lab, bring to room temperature, then subsample.

3. Store samples in the dark, in cooler if possible, to transport to lab, then treat as other NPS precipitation samples.

3. Snow Pack Cores

a. Field Equipment: PVC snow corer, acid washed and covered w/plastic or parafilm, plus extension poles, zip lock bags, large size, or 2 liter LPE bottles - acid washed. Field notebook, permanent pen and label tape.

b. Field Methods:

1. Push snow corer through the snow several times to rinse it out.

2. In the general area of the snow course take a core through the snow pack, adding extension poles as the hole gets deeper. Push the corer through the snow until it seems to have filled it, up about 75 cm down, lift up the corer and snow and carefully tap out the snow into an acid washed zip lock bag. One cores goes into each bag. Label the bag with a number and the depth of the snow pack it contains. Alternately, cores may be taken only of the most recent snowfall by sampling of plastic sheets.

3. Keep samples frozen as long as possible.

4. Lab handling for precipitation samples:

Lab handling for precipitation samples is basically the same as stream samples, with a few changes.

a. Chill liquid samples until used. Keep snow samples frozen until they are to be analyzed, then slowly melt to room temperature then in the zip lock bag or LPE bottle. Measure the volume of the thawed snow before filtering for subsamples.

b. Take pH and conductivity of the melted samples in the lab.

c. Filter samples with a .45 u membrane filter into a 30 ml LPE bottle for shipment to MTU, a 60 ml bottle for NPS processing and enough extra for 20-30 mls into a "whirlpack bag" for frozen archival. No sample is needed for silica analysis or alkalinity.

d. Mail the MTU sample. NH4 and PO4 will be run on filtered sample within 24 hours.

e. On occasion extra subsamples may be kept and acidified with a .12 ml Ultrex Nitric Acid and stored in the dark for later metal analysis.

5. National Acid Deposition Program and National Trends Network (NADP/NTN)

a. Overview: The Sequoia NADP/NTN site at Giant Forest has been in operation since July 1980. From then, until September 1984, operation of the site was the responsibility of the Resources Management Division. In October 1984 the Research office assumed the responsibility as an integral part of the acid deposition research project. At the site is an Aerochemetrics rain event collector and a Belfort weighing rain gauge. They are powered by AC current. The sampling buckets are collected weekly on Tuesday and mailed to the NADP Central Analytical Laboratory (CAL) for analysis. Field measurements of pH and conductivity are made at the NPS lab. The NADP/NTN protocol is rigidly adhered to. Data from the site is stored on a computer file at the Research office.

b. Field Equipment: The collector and rain gauge are located below the Lower Kaweah area next to the road to the sewage treatment plant. Maintenance procedures for equipment are explained in the NADP Site Operation Instruction Manual; a copy is located in the green lab file.

The new buckets are stored in the shed behind the Research Center. Each new bucket should be dated as received and used in chronological order.

For each sampling trip bring:
1 new bucket
1 data sheet
1 rain gauge chart
masking tape

CAL will send notices when they want the dry side buckets changed or quality assurance samples submitted.

c. Field Methods: The NADP/NTN Site Operation Instruction Manual and Field Observer Instruction Manual detail specific methods for the collection of the buckets, lab procedures and data sheet completion. These manuals must be read by all individuals prior to collecting and handling NADP/NTN samples.

d. Lab Handling: Follow procedures as described in the above manual. Any sample of the 20 ml aliquot remaining after lab work should be mailed to MTU for analysis in an acid washed test tube kept in the cabinet with the NADP check samples. The sample is given an NPS number from the field notebook and coded as an event rain type.

e. Any major problems should be directed to the Central Analytical Lab (CAL) and to any of the appropriate personnel.

1. Jackie Lockard-217-333-9234-for electrode/meter information.
2. Scott Dossett-217-333-0249-for any site information, both field and lab.
3. Sheri Uber-217-333-3936-for conductance and pH measurements.
4. Clarence Dunbar-217-333-5593-for site supplies and shipping information.

7. California Air Resources Board (CARB)

a. Overview: As part of the statewide atmospheric deposition research program the California Air Resources Board has located three sampling sites (Aerochemetric samplers) within the Parks. The first, installed in August, 1983, is near the Ash Mountain Park Headquarters. The second was installed in July, 1984 at the inlet of Emerald Lake. The third was installed July, 1985 at the Giant Forest Lower Kaweah site.
The Ash Mountain site is powered by an AC line from the maintenance building and a Belfort rain gauge was installed June, 1985. The Emerald Lake site is operated only during

snow-free months, usually June to November. It is battery powered with a combination of solar panels and batteries. A Belfort rain gauge used at this site. The Giant Forest site is powered by AC line installed at Lower Kaweah in July, 1986. Precipitation amounts are measured by the NADP Belfort. As part of the CARB quality assurance program an Aerochemetric sampler was co-located at the Giant Forest site in February, 1986.
Samples are collected weekly on Tuesday from all sites. In 1985, CARB began event sampling during the summer months, approximately June through October. Events are defined as any precipitation occurring within a 24 hour period (9A.M.-9A.M.). Weekly sampling would resume for the winter.

b. Field Equipment:
Emerald Lake Site: Sampling bottle from CARB, 500 or 1000 ml graduated cylinder (or appropriate sized scale), 2 liters DI water, Belfort rain chart, NPS 250 ml bottle, chemwipe tissues.

Ash Mountain Site: Clean CARB wet side bucket in black box, DI water, chemwipe tissue.

c. Methods: The Air Resources Board Site Instruction Manual is in folder in the NPS lab. It has specific instructions for sample collection and lab procedures which are to be closely followed. Some noteworthy points are:

1) Remember to wipe down the sensor mechanism and the interior plastic seal of the sampler with DI water and chemwipes each collection day.
2) The Ash Mountain bucket should be weighed on the triple beam balance to determine volume as described in the instruction manual. The Emerald sample must be measured in a graduate cylinder until a suitable scale is found to use at the site. Rinse the graduate thoroughly with DI water before measuring the sample volume and cover after use.
3) Empty the bucket inside the Belfort gauge at Ash Mountain and Emerald Lake and wind the clock with the silver handle beneath the drum every week before replacing the chart.
4) Every week data sheets and Belfort charts, will be mailed to the CARB El Monte lab whether or not precipitation has occurred.

d. Lab Handling: As mentioned above, lab procedures are defined in the CARB manual. (Updated Jan 1986) Additionally, when sufficient sample is available, aliquots will be sent to MTU and analysis for ammonia and phosphate done at the NPS

lab. When this is done the sample will be assigned a sequential number from the NPS fieldbook in addition to the CARB site number.

e. Any questions or comments can be directed to the following CARB personnel:
1. Daniel Tackett-supply requests, equipment, 916-324-6699
2. Alice Westerinen-quality assurance/quality control 916-324-6191
3. King Yu-lab analysis, 818-575-6968

7. Precipitation Volume

a. Overview: Monitoring of precipitation volume occurs at two levels - between study sites and within each site. At Elk Creek and near the Log Meadow study site a Campbell Weather Station with Belfort weighing rain gauge outputs rain accumulation on an hourly and daily basis. At the NADP station at Giant Forest a Belfort rain gauge with a one week strip chart is operating. Rain accumulation is also measured at the NOAA weather stations at Lodgepole and Ash Mountain.

Within each study site a series of paired True Check plastic rain gauges are distributed across the elevational gradient of the site to determine site-specific variation in rainfall. A minimum of three stations, at the bottom, mid section and top of each study site, have been established. Other gauges are set in other places in the watersheds. The rain gauges are checked biweekly (summer rainfall, overall inches). If no precipitation has occurred during the previous two weeks the gauges should still be checked to clean out insects and debris.

b. Field Equipment: Squirt water bottle, bottle brush, and notebook.

c. Field Methods: Record station number and precipitation amount. Empty both chambers of the rain gauge and brush with the bottle brush to remove bugs. Periodically the rain gauges need to be taken to the Research Center and washed with detergent.

d. Data storage: Record the data in the appropriate file in the office.

8. Snow Quantity (Emerald Lake)

a. Overview: University of California, Santa Barbara scientists are conducting a snow hydrology and chemistry study in the Emerald Lake Basin. Consequently, the NPS will conduct only a moderate level of snow sampling at that site.

A snow course of five points near the lake outflow will be sampled for water equivalence during the winter at the same time the State Water Surveys are done. This is during the last week of the months of January, February, and March. Sampling will be done with the Mt. Rose samples and the techniques used by the State Snow Survey followed. Complete instructions for snow sampling as done by the California Cooperative Snow Survey should be reviewed prior to field sampling trips to the lake.

b. Field Equipment: Mt. Rose Snow Sampler, Data Sheets for snow sampling, silicone spray.

c. Field Methods: The site of the survey area is the level area west of the USGS tower. A series of 5 snow cores are taken along a westerly transect at four meter intervals. At each sampling site:

1) Assemble the snow corer sections in proper order to exceed the expected depth of the snow. Before connecting the individual sections spray the threads with silicone. Spray the inside of the corer well with silicone also.
2) Suspend the scale so it hangs vertically, a ski pole strap works well. Weigh the tube and handle in the cradle hanging from the scale, record the value in "weight of empty tube".
3) Drive the corer through the snowpack or as deep as possible into the snow. Ice layers can block the corer and then the corer will need to be weighed and emptied before reaching the bottom then reinserted in the core hole. Weigh the core and record in "Weight of Tube and Core". If several cores are necessary, add up the weights.
4) For each core record the total snow depth and each core depth from the scale on the side of the tube.
5) Empty the sampler by turning it upside down and tapping lightly against a ski. Compacted snow may have to be prodded out with a small knife. In wet or very cold snow the sampler may need to be sprayed with silicone frequently to prevent ice up.
6) The sampler is disassembled by using the pin spanners inserted in the holes at the end of each section and turning opposite of each other. Take care not to strip the threads as the aluminum is very soft.

d. Data Storage: The water content and density percent of the snow can be determined back at the office. A Lotus 1-2-3 file is on disk for snow survey data and does the computations. Water content is the difference between the empty tube weight and the tube and core weight.

D. Lab Analysis techniques/procedures

1. Acid washing of bottles and lab equipment

a. Overview:

Lab equipment and sampling containers should be thoroughly cleansed of contaminants so that no interference from the equipment affects analysis. Handling methods vary between the various pieces of equipment and are detailed below. Personal safety while cleaning equipment is important. Gloves and goggles should be worn when using dilute acid solutions and all work using concentrated acids is to be done under the fume hood with the blower on. Used HCL and the first DI rinse must be placed in the HCL Hazardous Waste container (See Hazardous Waste Management Plan for details).

b. Methods:

Nalgene LPE bottles: LPE containers need to be acid washed after each use. A 1:10 solution of concentrated HCL is stored in marked bottles to be used for acid washing and dated after use.

1. Rinse bottles with DI water.
2. Add 1:10 acid solution to about 1/5 the bottle volume.
3. Let the bottles lay on their sides, turning occasionally, for at least 1 hour and preferably overnight.
4. Rinse with DI water at least five times, emptying the first rinse into the hazard waste container for HCL.
5. The conductivity of the final rinse water should be compared to the DI water to check that the acid is fully rinsed from the bottle. All Lewis collector buckets and a minimum of one third of the bottles being rinsed must be checked. If five rinses do not cleanse the bottle, keep rinsing until conductivity matches or comes within 0.5 us/cm of the DI water.

Lab Glassware:

Glassware which is used with HCL, such as for alkalinity, should be rinsed well with DI water. Graduated cylinders and volumetric flasks should be rinsed with 1:10 HCL and rinsed many times (8-10 with DI water). Before using the glassware to mix standards for NH4 or PO4 rinse with DDW (deionized, distilled water). Glassware can be difficult to rinse clean of acid and unusual pH or conductivity values should be noted and glassware rinsed before rechecking values. Rinsed glassware should be covered with lab film and stored in the upper cabinet.

Microburettes:

As they are used only with a HCL solution the microburettes do not need to be acid washed but left with HCl in the reservoir and tip, then completely emptied and refilled before next use.

Plastic Test Tubes:

The test tubes used for NH4 have a small amount of HCL solution in them while stored. They need to be rinsed five times with DI. After the analysis NH4 tubes should be rinsed with DI and about 1-2 mls of 1:10 HCL left in them.

PO4 tubes need to be rinsed with DI before and after use. The phosphate analysis is a digestion process which removes all the phosphate from the tube therefore DI rinsing is sufficient.

Zip Lock Bags:

Zip lock bags for snow core collections need to be acid washed with the same procedures as LPE bottles. A squeeze bottle works well for squirting acid down the sides of the plastic bag. Rinse with DI water at least 5 times and seal.

2. Quality Control:

The best lab check on washing quality is to compare conductivities of rinse water and DI water. Unusual pH values should be inspected for bottle contamination.

The anion analysis from Michigan Tech should be examined for unusual Cl values and these samples compared with lab data on pH and conductivity. These samples can then be flagged as suspect.

Older bottles may not rinse clean even after repeated rinses. In such cases, the bottles (or other unit) will be eliminated and replaced.

3. Filter Equipment:

Rinse well with DI water before and after use. Before filtering a sample, run several refills of sample water through the syringe and about 30 mls. of sample through the filter system. Acid wash the filter holders and syringes after each use and store in clean plastic bags.

4. Equipment storage:

1. Each size bottle and other lab equipment has an assigned area. The shelf under the fume hood sink can be used to store dirty labware until washed. The cabinet to the right of the fume hood has LPE bottles for acid rain sampling. The top shelf is for acid washed bottles ready for field use. Bottom shelf has acid washed CARB and USGS bottles.

2. The upper shelf in the refrigerator is for reagents only. The exception may be very large sample bottles which do not fit on the other shelves.

3. Rotate clean LPE bottles forward as they are taken from the shelf, so their use is evenly distributed.

E. Quality Assurance/Quality Control

1. Overview

This temporary QA/QC protocol will be established and sent out for critical review prior to finalizing. Major portion of this temporary protocol have been adapted form Kirchmer (1983) and Wilhour (1983). As a starting point, we feel it necessary to define the terms to be used throughout the protocol.

2. Definitions of Terms

Accuracy: the total error of a result (from the true value) where accuracy represents the combined random and systematic errors of results and is said to improve as the total error decreases (Kirchmer 1983).

Bias: systematic error in water analysis due to unrepresentative sampling, instability of samples between sampling and analysis, interference effects, biased calibration, a biased blank correction, and for inability to determine all forms of the determined (that which is to be determined) (Kirchmer 1983).

Blank Solution: a solution that contains everything in the sample solution except the analyte (O'Haver 1976, Kirchmer 1983)

Control Chart: a graphic display of individual analytical results, where measured values (ie. concentration found for standard solution in mb/1) are plotted on a chart in which mean + 2 standard deviation defines the "warning limits" and mean + 3 standard deviation defines the "action limits" (APHA 1981, Kirchmer 1983).

Detection limit: the lowest concentration of deteminand that the analytical process can reliably detect (Kirchmer 1983)

Precision: the degree of mutual agreement among individual measurements made under prescribed conditions with a single test procedure (EPA 1979).

Quality Assurance (QA): the orderly application of procedures to reduce errors during sampling and analysis to improve precision (APHA et al. 1981, Wilhour 1983).

Quality Control (QC): the application of procedures to ensure the accuracy of results during sampling and analysis (Wilhour 1983).

Recovery: the difference between the analytical results of spiking compound and multiplied by 100 to convert to percentage (Kirchmer 1983).

Standard solution: natural water with a known amount of an element of compound (APHA 1981).

The purpose of this protocol is to outline our present QA/QC program for field sampling, laboratory analysis, data entry and data analysis for lake, stream and precipitation samples.

3. Field Sampling

Field QA/QC will be maintained through sampling standardization, sample preservation and replication, instrument calibration and field log books.

Standardization

A standardized approach for field sampling incorporates consistent sampling procedures such as:

- -consistent preparation for field sampling including checklist of equipment and supplies required for sampling (eg. as outlined in the Water Analysis Protocol).
- -standardized procedures for sample collection, filtration, treatment and storage (e.g. as outlined in the Water Analysis Protocol).
- -routine procedures for shipping samples to the different laboratories.
- -back-up equipment for each sampling trip.

Preservation and Replication

Estimates of variability or uncertainty in sampling can be evaluated by:

- -Archiving samples; all samples will be archived (this includes refrigerated and frozen samples).
- -Replicating samples; one of every ten samples "will be treated as a true replicate including each step in field sampling as called for by the Water Analysis Protocol (ie. recalibrating meters, separate filters and bottles etc.).

- -Splitting samples, one of every fifteen samples will be split prior to laboratory analysis.

Instrument Calibration

- -All field instruments will be calibrated at each collection site prior to sampling and at least twice daily in the laboratory.
- -Records of each calibration will be kept in the lab/field notebooks.

Field (or lab) Log Books

Field logs will be maintained that identify, as a minimum, the following:

-Date, time and location
-Sampling team
-Calibration data
-Sample data (see notebook "stamp" for a complete list)
-Problems, unusual conditions, etc.
-Ideas to improve sampling efficiency, accuracy or precision
-Other observations that may assist in interpreting the water chemistry data

4. Laboratory Analysis

Laboratory QA and QC must be sensitive to the accuracy and precision at each step (see Kirchmer 1983) in the analytical process. In general, this means to:

-Define the determinand, limit of detection and accuracy required.
-Choose analytical methods with satisfactory small sources of bias and adequate precision. New methods will not be used unless they can be calibrated to the previous technique. When suitable methods are not available, improved methods will be developed.
-Ensure that the chosen methods are completely and unambiguously specified and that they will be followed as far as possible by all laboratories.
-Estimates the standard deviation of analytical results and, if necessary, improve the precision until the target value is achieved. Ensure that standard solutions used by all laboratories are in satisfactory agreement.
-Establish a control chart and regularly analyze solutions of known concentrations to ensure that the precision remains adequate.
-Estimate the bias of each laboratory and, if necessary, improve until the target value is achieved.

More specifically, the following steps will be taken to ensure within-lab and between-lab accuracy and precision. This includes precisely following established and accepted standard analytical methods by trained personnel in the following:

-lab preparation; calibration of equipment following manufacturers' recommendations, cleaning of equipment and supplies (ie. acid-washing bottles, glassware, etc.), inventory of supplies needed/used etc.
-preparation/testing of standard solutions, chemicals (ASC Reagent Grade) reagents and deionized-distilled water; mix standards, reagents, and blanks according to standard analytical procedures; label storage devices with contents , storage location, date, shelf life, and prepares initials; test all solutions, reagents chemical and deionized-distilled water as called for by "Standard Methods" (APHA et al 1981) including quality control charts.
-use of standard methods for water chemistry analysis; following step by step procedures outlined in Standard Methods (APHA et al. 1981) or other established accepted analytical methods.
-analysis of replicate and splits (10-15% of the total samples) as outlined by Standard Methods (APHA et al. 1981).
-use of inter-lab crosschecks (including participation by all laboratories in the EPA "Audit Program", USGS/NADP audit and CARB inter-lab crosschecks.

5. Data Entry

Data base entries also will receive rigorous QA/QC so the aberrant and/or erroneous values can be removed or modified. These procedures will include:

-Data storage on hard copy and computer disks in similar format to field/lab notebooks.
-Screening field/lab notebooks, hard copy, and computer data files for errors (ie. edit checks).
-Systematic entry of data from one format to another (ie. field notebook to hardcopy and hardcopy to computer file.)
-Consistent use of units for each variable
-Adequate training of personnel in data entry procedures including use of the computer.
-Flags on questionable or suspect data

A data management protocol has been developed in a separate document.

6. Data Analysis

Preliminary data analysis will identify potential errors through graphic displays and descriptive statistics. Specific procedures such as:

-frequency distribution,
-scatter diagrams (and control charts),
-ionic balance control charts,

can quickly identify outliers requiring additional investigation.

F. Data Recording and Storage

1. Overview:

Water analysis data will generally be in three forms: NPS field /lab notebook form, MTU ion summary data sheets, and USGS summary data sheets. The NPS field/lab notebook and MTU ion data will be combined on large "Water Chemistry Summary" sheets (hard copy) and then entered in the IBM d-BaseIII data file name "Waterchem." The USGS summary data will be entered on the IBM d-BaseIII data file name "USGS". Basic programs "NH4PO4" and "Alka" are used to compute chemical and alkalinity figures from raw lab data.

2. Field Data Book = 4 1/2" X 7" "write in the rain" notebooks are used for field notes. A rubber stamp, kept at the lab, is used to print a data form in the field notebook for each sample before going into the field. As much as possible keep all information pertaining to an individual sample on the sample page, with the exception of spectrophotometer readings which can all be together for a particular run.

3. Specific details for data storage can be found in the Data Management Plan.

II. DRY DEPOSITION

A. National Oceanic and Atmospheric Administration (NOAA)

1. Overview: In July, 1986 an intergrated air chemistry and meteorological monitoring station was established near the Wolverton ski area in Sequoia National Park. The system is designed to provide information necessary to deduce dry deposition fluxes of suflur dioxide, nitric acid vapor, and submicron particulate material. The National Park Service is maintaining this station in conjunction with the National Oceanic Atmospheric Administration and the Air Turbulence and Diffusion Division (NOAA/ATDD). Personnel from the Research and Resource Management Divisions are currently operating the station.

2. Methods: Each Tuesday a new cassette tape and stacked filter unit is installed and meteorological instruments are checked. For each sampling trip the following items are necessary:

1 new cassette tape
1 prepared stacked filter unit
2 sets of climbing gear
1 cruiser vest
1 500 ml squeeze bottle w/DI water
1 250 ml squeeze bottle w/methanol
chemwipes
1 new data sheet/pencil
4 AA batteries and tape head cleaner (as necessary)
end caps for leak tests

All the supplies are kept at the NPS water lab.

3. Lab handling: Three copies of the data sheets should be made with the original sent with the cassette tape to:

J.D. Womack
P.O. Box E
NOAA/ADTL
Oak Ridge, TN 37831

The second copy will be mailed with the filter unit to the same address as above. The third copy of the data sheet will be put in the NPS file at the water lab. Any site or equipment questions can be answered by contacting:

Ray P. Hosker or Jim D. Womack
P.O. Box E, 456 S. Illinois Ave.
Oak Ridge, TN 37831
(615) 576-1233; FTS 626-1233

Before 12/86 all used filter units were sent to Ed Drake, USGS Water Resources Division, 6481B Peachtree Industrial Blvd., Doraville, GA 30340

III. STREAM GAUGING

A. Flumes

Determination of the volume and timing of stream flow in the study drainages is necessary to calculate nutrient transport through the ecosystem. Stream gauging at each of the sites has had to be tailored to the unique conditions of the drainage. The gauging system at Emerald Lake was installed by the USGS and is operated and maintained by that agency. It consists of a fluid gauge and a Stevens recorder powered by a solar panel, housed in a 24 foot tower structure adjacent to the lake. The USGS estimates outflow by calibrating lake level with stream discharge (measured

approximately 6 times per year with a pygmy meter).

At the mid elevation site a Parshall flume and Stevens recorder operate at Log Creek and at Tharps Creek. Charts are changed on a monthly basis and the data is typed into a computer file which calculates and graphs a hydrograph.

An H-Flume was installed at Lower Chamise Creek in January, 1984 and at Upper Chamise Creek in February, 1986. Both flumes contain Stevens Type F stream recorders which are checked monthly during the summer and bi-weekly during the winter.

Gauges at the streams will be calibrated against Pygmy meter flow estimates or volumetrically to check their accuracy. Routine servicing of the equipment and the area directly surrounding the flumes and adequate winterization should ensure fairly continuous recording of flow data.

Methods:

Changing Stevens recorder chart

Field Equipment:

Felt tip pen, new chart (#F7, Leupold & Stevens, Inc.), six D cell alkaline batteries.

1. Unlock the stilling well and open the top.

2. Check the height of the staff gauge in the flume with the felt pelt arrow the ending point of the water line. Note date and time off and write the staff flume gauge level on the sheet.

3. The set screw at the rear base of the drum holder turns about a full turn to release the drum. Remove the drum and the bands from around the chart and take off the chart. Replace with a new chart, fitting the notch in the chart to the pin on the drum. Replace the drum and rotate it until the pen tip lines up with the correct staff gauge level on the "depth in feet" side of the chart at the key. Double check the location of the pen in relation to the staff gauge depth reading. Note any problems or special conditions on the chart.

4. Change batteries in clocks every 3 -5 months.

5. Periodically shovel out the streambed in front of the flume.

6. Winterizing the flumes. Add 1 pint of salad oil to each stilling well in November when temperatures start to drop. Fit the plywood cover over the top of the flume.

7. See Appendix E for flume chart analysis.

IV. WEATHER STATIONS

a. Overview: Campbell Scientific Inc. meteorological stations (with CR-21 micrologger) are now located near the low elevation (Elk Creek; installed April 1983), and mid-elevation (Log Meadow - MEWSS; installed November 1983) and high elevation (Emerald lake; installed November 1984) sites. The stations gather a variety of meteorological data, but generally include hourly data on accumulated precipitation, soil temperature, solar radiation, air temperature, relative humidity and wind speed and direction (Table 2). At midnight, the stations compile data collected in the previous 24 hour period and compute appropriate maximum and minimum values as well as accumulated precipitation. Sensors are calibrated, cleansed and/or replaced following manufacturers suggested maintenance schedule. This data is stored on a SM64 storage module which should be changed once a month at Elk Creek, MEWSS, and Emerald Lake weather stations. Two 2-week storage modules (Model SM16) are available for backup purposes. Data is off loaded to an IBM Personal Computer at the Park Research Office and is stored on a hard drive Bernoulli Cartridge, with one cartridge designated for each site. A program has been developed by Donald Herman, UCLA to divide the data and organize it into a more efficient form for summarization and analysis. (See Appendix D for weather station retrieval and storage)
The Emerald Lake weather station has been operated in conjunction with a University of California, Santa Barbara, snow hydrology project. Recording devices (CR21 Campbell MicroLogger and Omnidata EasyLogger) are shared to maximize efficiency given different sensor location.

Additional weather station data (daily precipitation amount and max/min temperatures) are also available from U.S. Weather Station located at Ash Mountain and Lodgepole.

b. Field Equipment: Storage Module (SM-64 for Elk Creek MEWSS and Emerald Lake), medium sized flat head screwdriver, 8-foot folding ladder (MEWSS), SK5-77 key (MEWSS) or USGS Tower key (Emerald), notebook and pen.

C. Field Methods

1. For MEWSS only - locate 8 foot step ladder approximately 30 meters south of weather station. Unlock chain and set up ladder at weather station. Unlock micrologger box and remove bar in front of side plate on micrologger box.

2. Open the CR-21 micrologger box by unscrewing the four screws on the side plate with the flat head screwdriver. Rubber grommets in each of the screw holes on the side plate will eliminate unscrewing the screws all the way out.

3. Pull out and downward on the sideplate to gain access to the CR-21 micrologger and the storage module. Side plate is hinged so will not fall completely off. The storage module is attached to the sideplate with one screw. Undo this screw.

4. Unplug the blue cord from the storage module.

5. Remove storage module from the side plate.

6. Place the new initialized storage module in the side plate slots (making sure all switches are down), plug in the blue cord and tighten the screw holding the storage module in place.

7. For Elk Creek only:
At this point check the rain gauge bucket for precipitation.
   A. Take the top cover off the Belfort rain gauge by twisting and pulling up.
   B. Take the rain bucket out and pour out any water.
   C. Place the rain bucket back inside the Belfort making sure the copper tube is placed in its slot.
   D. Put the top cover back on the gauge.
   E. Zero out the weight of the rain bucket on the CR21 micrologger
      - by entering * 4 A A A until 13: is shown
      - press 0 A
      - press * 6 1 A and record weight of empty bucket
      - press * 4 A A A until 13: shows again and enter the negative of the bucket weight. For example a bucket weight of 3.45 would be offset by entering
        * (to clear entry)
        C (to change sign)
        3
        D (to enter a decimal point)
        4
        5
      - check how close this comes to zero by entering

* 6 1 A . It should be close to zero, if not, minor adjustments to the buckets weight offset can be entered in the * 4 mode.

F. Be sure to enter * 0 before closing up the unit.

8. For the MEWSS station only:
At this point check the Belfort rain/snow gauge bucket for precipitation depth. If the bucket is full or nearly full it must be emptied. Bucket holds 788 mm of liquid. To empty the bucket and zero the CR-21 micrologger:
- open the outside panel at the bottom of the rain gauge. Inside there is a small diameter tube with a petcock on it. By turning the petcock, water inside the gauge will be emptied.
- once the gauge is empty close the petcock and the side panel. Take the correct precautions for ice up depending on the time of year. This involves adding 4 quarts ethylene glycol antifreeze, 6 quarts alcohol, and 1/5 quart of 30 weight motor oil before winter.
- zero out the weight of the rain bucket using the following procedures:
    - enter * 6 1 A and record this value
    - enter * 4 and wait until the display changes to 04:
    - enter A A A or until 13: is displayed
    - press # to clear present entry
    - enter the negative of the value earlier recorded and press A to enter
    - to check enter * 6 1 A and the display should be close to zero

9. Enter * 0 before closing the case.
10. Reattach side plate to CR-21 micrologger box with the four screws and tighten. Lock up the CR-21 and lock up the the ladder.

Table 2. Meteorological equipment at Elk Creek, Log Meadow (MEWSS) and Emerald Lake.

Sensor	Data Type	E.C.	L.M.	E.L.	Model/Type
Accumulated Precipitation (mm)	Hourly Accu. Daily Total	X	X		Belfort 5-780 Universal Recording Rain Gauge(EC) Belfort 6071 High Capacity(LM)
Solar Radiation (kw/m2)	Hourly Mean Daily Total & Mean	X	X	X	Li-Cor L12005(EC&LM) Li-cor L12005 and LI1905B(PAR) (EM)
Soil Temperature (Celsius)	Hourly Mean Daily Min/Max	X	X	X	Campbell #102
Air Temperature (Celsius)	Hourly Mean Daily Min/Max	X	X	X	Fenwal Electronics UUT51J1 Thermister(EC&LM) Campbell #101
Relative Humidity (percent)	Hourly Mean Daily Min/Max	X	X	X	Phys-Chemical Model PCRC-11 Fenwall Electronics UUT-5171 Thermister
Wind Speed (m/s)	Hourly Mean Daily Max	X	X	X	Met-One 014A
Wind Direction (degrees)	Hourly Direction	X	X	X	Met-One 024A

V. LITERATURE CITED

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VI. APPENDIX

Appendix A

AMMONIA DETERMINATION (NH4+)

A phenol solution and a mixed reagent are added to 5 ml aliquots of blanks, standards and samples and absorbance values read on the spectrophotometer. Concentrations are calculated on the IBM PC after determining an F factor.

Precautions: Phenol is very toxic, handle with caution.
All glassware must be kept clean - acid wash and cover after each use.
No smoking or use of cleansers during analysis.
Old bleach gives uncertain results, don't use it.
Check dates on reagents with each use.

I. REAGENT AND STANDARD PREPARATION

1. Primary Standard - (usually plenty in refrigerator) Rinse a large acid washed beaker with DI water. On weighing paper measure out 0.661 grams of (NH42S04) and place in beaker. Measure in graduate cylinder 1000 ml of DI water and add to beaker. Store in labeled and dated Nalgene bottle and refrigerate. This primary standard is 10 uM NH4 and is diluted to a secondary standard of 10uM and 100uM during the analysis procedure.

2. Reagent A - Discard outdated reagent in the hazardous waste container for Ammonia Indophenol Method. Rinse bottle well into the hazardous waste container. Turn on electronic balance, let it warm up for 10-15 minutes. Get a clean beaker from the cabinet.

   a. Once the balance is warmed up, tare weighing paper and measure 0.040 g. nitroferricyanide dihydrate (also called sodium nitroprusside). Add into brown reagent bottle.

   b. Put on the respirator mask, gloves and goggles found in the bottom drawer below the scale. Adjust the mask to fit snugly. Measure out 3.5 g. of Phenol (from acid cabinet) into a weighing boat. Do not return excess Phenol to the jar, place in hazardous waste container. Keep jar capped during use. Rinse metal spoon into the hazardous waste container and wipe area around balance, placing chem-wipes and weigh paper into hazardous waste container and rinsing beaker several times into hazardous waste container. Carefully add to brown reagent bottle and add 100 ml of DI water.

c. Label and date reagent bottle, initial. Reagent is stable for one month.

3. Reagent B - Alkaline reagent

a. Measure 200 ml of DI water in a graduate cylinder and add to well rinsed brown reagent bottle.
b. Measure 20 g Sodium citrate and add to reagent bottle.
c. Measure 2 g of Sodium hydroxide and add to reagent bottle, mix to dissolve.
d. Label, date and initial. Reagent is stable indefinitely.

4. Reagent C - Sodium hypochlorite solution, "Clorox". Bleach loses strength with time, so buy new bleach bimonthly, or more frequently if it does not smell "bleach-like".

II. ANALYSIS PROCEDURES

1. The tubes labeled for NH4 are stored with a small amount of 10% HCl. Empty the acid into the HCl hazardous waste container rinse the tubes 5 times wach with DI water with the first rinse going into the hazardous waste container. The number of tubes needed for each analysis is 2 blanks + 6 standards + 2x the number of samples. Label the tube tops (use label tape) with the number of the water sample plus A or B, ex. 183A, 183B.

2. Prepare two secondary standard solution. In a freshly rinsed volumetric flask measure 100 ml of DI water. With the finnpipette with draw 0.1 ml of water. Add 0.1 ml of primary standard solution to the flask, cap and mix. This is a 10uM standard solution. In a second 100 ml volumetric flask withdraw 1.0 ml of DI water and add 1.0 ml of primary standard solution. This is a 100 uM standard.

3. In each of the 2 "blank" tubes finnipipette 5 ml of DI water. In each of 3 "standard" tubes finnipipette 5 ml of secondary standard. For each sample place 5 ml of filtered sample in 2 tubes labeled with #a, #B. Bottles can be "eye-balled" to 5 ml line on test tube.

4. From the refrigerator take out reagents A, B, and C in clean beaker. Check the dates of preparation, mix up fresh when outdated.

5. Mix 4 parts of reagent B with 1 part reagent C in a small, clean beaker. 0.20 ml of mixed reagent is required for each tube so multiply 0.2 X # of tubes to determine the quantity of the mixed reagent needed. Make enough for some extra.

6. Adjust the smallest finnpipette to 0.20 ml and use the smallest size tip. To each sample, blank and standard add 0.20 ml of reagent A. Mix at once on vortex mixer. Change tips and add 0.20 ml of the mixed reagent B/C and mix on vortex mixer.

7. Place the samples in the dark - usually the cabinet under the balance. The absorbance can be read 1 - 20 hours later, preferably at least 12 hours later.

8. Reading the absorbances - Turn on the spectrophotometer with the switch on the left rear of the machine and let it warm up 10 - 15 minutes. Set the nanometer reading to 630, using the wheel control on the right side panel. Using the 1 cm (small square) cuvette cells, place distilled water in three (or 2) cell and polish the outer clear surfaces of the cell. Handle only the frosted sides of the cells, and keep the clear sides scrupulously clean. Insert the cells into the holder and onto the carriage on the door of the spectrophotometer. Close the door and observe the readings for each of the cells. Adjust to .000 absorbance using the silver wheel control on the top of the machine. Polish the cuvette and rearrange cells until all read .000. Keep the cells in the same slots during the rest of the readings. Once the cells are zeroed the samples can be read. Keep one cell with DI water to zero the machine during the process. The other cells are used to read samples. With the largest finnpipette set to 3.25 sample can be placed in the cuvette without spilling it onto oneself. Start with the lightest colored sample and work towards the darkest. Zero the DI water then record the absorbance of the blanks, standards and samples in the lab notebook. For each sample also read the absorbance of a "color blank" I of the original filtered untreated water. Color blank for blanks and standards should be .000 - the distilled water.

Example -

Sample #	I(Color Blank)	ABS (Reading)
blank 1A	.000	.001
standard 1A	.000	.100
183 A	.002	.025

9. After reading the absorbances, all the solutions used in the analysis should be emptied into the hazardous waste container for ammonia. Close the container between uses. The first rinse of the tubes should also go into the hazardous waste container. Rinse again thoroughly and store tubes with a small amount - several mls - of 10% HCL.

III. CALCULATING THE NH4 CONCENTRATIONS

1. A BASIC program PO4NH4 runs on the IBM computer to calculate the NH4 concentration from absorbance values read from the spectrophotometer.

2. Turn on the computer. Turn on the printer. When the systems c:\> prompt appears type:

   d: (CR)
   cd chemistr (CR)

3. Next type basica to enter BASIC. Once BASIC comes up:
   press F3 (on the left side)
   type alka or po4nh4
   press F2

4. At the prompts type in the correct information - NH4 or PO4 for the proper test. enter the concentration of the standard: 10 for NH4 or 1 for PO4 (note: this may be changed if one is running a different concentration for the standard, if so enter the concentration of the standard used.). Enter the absorbance of B1, B2 - separate numbers with commas, enter the absorbance of the standards in the same way. Enter the date of the analysis.

5. At the prompt enter the sample number, color blank absorbance and sample absorbance from the fieldbook. When all samples have been entered type in Q,0, 0 or q,0,0.

6. If you need to enter more calculations enter y at the prompt.

7. Results are printed out and dated. Turn off the computer and printer when finished. Record results in the hardcopy summary and file the printout in the water file in the filing cabinet.

8. The formulas for the computation of the values in UM are:

9. Formulas for computation of NH4 values are:

$$F = \frac{10.0}{As - Ab}$$

where As = average absorbance of the standards
Ab = average absorbance of the blanks

NH_4 uM = F(sample absorbance - Ab - I)

I = color blank

$$PO_4 \text{ mEQ/1} = \frac{(uM)(charge)}{1000} \qquad charge = +1$$

PO_4 mg/1 = 31.66(mEq/1)

For more information see:

Melack - Analysis Procedures, green file in lab under UCSB
Standard Methods, page 351
Strickland and Parsons, page 87

Appendix B

PHOSPHATE DETERMINATION (PO4)

A mixed solution of four reagents is made up just prior to the analysis and added to 10 ml aliquots of blanks, standards, and samples. The absorbance values are read on the spectrophotometer and concentrations of PO4 are calculated after determining an F factor.

Precautions: Glassware must be clean - acid wash and cover between uses.
No use of cleansers during the analysis.
Check dates on reagents before every use.

I. REAGENT AND STANDARD PREPARATION

1. Primary Standard - (usually made up in refrigerator) Rinse a large acid washed beaker with DI water. On weighing paper measure out 0.174 g of K2HPO4. Place in beaker and measure 1000 ml of DI water from a graduated cylinder into the beaker. Once it is dissolved, store in a labeled and dated Nalgene bottle and refrigerate. The primary standard is 1 mm and is diluted to 1 uM during the analysis. This standard should be made up fresh annually.

2. Reagent A - Ammonium Molybdate solution
   a) Rinse the brown Nalgene bottle several times and empty the rinse water into the hazardous waste container for phosphate determination. Measure 200 ml DI water into the bottle from a graduated cylinder.
   b) Tare a weighing paper on the balance. Measure 6 g of ammonium molybdate (NH4)6Mo7O24.4H2O and add to the bottle and mix.. The solution is stable indefinitely. Label, date, and initial bottle.

3. Reagent B - 15% Sulfuric Acid Solution
   a) Rinse the brown Nalgene bottle, discarding rinse into the hazardous water container. Using a graduated cylinder measure 180 ml of DI water into the bottle.
   b) Concentrated H2SO4 is in the acid cabinet. Wear gloves and goggles and work under the fume hood with the fan on. Measure 28 ml of H2SO4 in a dry cylinder and pour into the Nalgene bottle. Invert gently to mix. Label, date, and initial the bottle. Solution is stable indefinitely.

4. Reagent C - Ascorbic Acid Solution
   a) Measure 50 ml of DI water from a graduated cylinder into a clean rinsed beaker.
   b) Tare weighing paper and measure 2.7 g ascorbic acid and add to the beaker. Swirl to dissolve.
   c) Store in 2 30 ml Nalgene bottles with date, contents and initials on the label. Freeze until ready for analysis. Just before use thaw one bottle in warm water and after use return to the freezer.

d) If frozen this reagent is stable for 6 months. If not frozen it is stable about one week.

5. Reagent D - Potassium-Antimony-Tartrate

a) Rinse a brown Nalgene bottle and discard the rinse water into the hazardous waste container.

b) Measure 200 ml of DI water into a freshly rinsed beaker from a graduated cylinder.

c) Tare weighing paper and weigh 0.272 g of potassium-antimony-tartrate. Add to the beaker and swirl to dissolve. If the crystals will not go into solution it may be necessary to warm the solution gently on the hot plate.

d) Pour into the brown Nalgene bottle, label with contents, date and initial. Stored in the refrigerator, the solution is stable for six months.

II. Analysis Procedures

1. From the test tube rack labeled PO4 count out the number of tubes needed for analysis - 2 blanks, 2 standards, and 2 X the number of samples. Rinse the tubes with DI water three times. Label the tops with the number of the sample plus A or B, ex. 176A and 176B.

2. Make up a secondary standard solution. In a freshly rinsed volumetric flask measure 100 ml of DI water. Set the smallest finnpipette to .1 ml and withdraw 0.1 ml of water from the volumetric flask. Add 0.1 ml of primary standard, cap and mix. This is a 1 uM standard solution.

3. In each of the 2 "standard" tubes pour 13 ml of secondary standard. In each of the 2 "blank" tubes pour 13 ml of DI water. For each sample pour 13 ml of filtered sample into 2 tubes with #A, #B.

4. Take reagent C from the freezer and thaw it out. From the refrigerator get reagents, A, B, and D. Check the dates of preparation and make up fresh reagent if necessary.

5. In a small beaker add in order: 2 parts reagent A, 5 parts reagent B, 2 parts reagent C, and 1 part reagent D. Below is a table of quantities.

REAGENT:	A	B	C	D	yields enough for
Qty.	2	5	2	1	7 tubes
in	4	10	4	2	15 tubes
mls.	6	15	6	3	23 tubes

6. To each blank, standard, and sample add 1.3 ml of mixed reagent with the finnipipette. Mix at once. Place in the dark - usually the cabinet under the balance. Read the absorbances after 10 minutes and within 2 hours.

7. Reading the absorbances - turn on the spectrophotometer with the switch on the left rear of the machine and let it warm up 10-15 minutes. Set the nanometer to 885 nm using the wheel control on the right panel. Rinse the two cylindrical 5 cm cuvettes, fill with DI water, and polish the flat surfaces with chemwipes until they are very clean. Insert the cells into the carriage tray and close the door. Observe the readings for each cell and adjust to .000 absorbance, using the silver wheel control on top of the spectrophotometer. Polish and rearrange the cells until both read .000. Keep the cells in the same slots during the rest of the analysis. One cell remains in the rear slot during the entire process to zero between samples. Empty the other cuvette and fill with sample; there won't be quite enough to fill the cell. Work from lightest to darkest if one can discern a color difference, usually they all look clear. Place the cell in the front slot and close the door. Adjust to .000 on the rear cell and push in the carriage to read the front cell. Record absorbance for blanks, standards and samples. For each sample also read a "color blank" I of the original filtered untreated water.

Color blanks of the blanks and standards should be .000, the distilled water.

Example - Sample	I(Color Blank)	ABS(Reading)
blank 1A	.000	.001
standard 1A	.000	.096
176A	.002	.043

8. After reading the absorbances, empty all the solutions used in the analysis in the phosphate hazardous waste container. the first rinse of the tubes and beakers should also go into the hazardous waste container. Rinse the tubes once more with DI water, cap and store.

9. See Appendix A "Calculating the NH4 concentrations" for procedures to calculate PO4 concentrations. The concentration of the standard is 1.

10. The formulas for the PO4 computations are:

$$F = \frac{1.0}{As-Ab}$$

where As = average absorbance of the standards
Ab = average absorbance of the blanks

PO4 um = F (sample absorbance - Ab - I)
I = color blank

$$PO4\ mEq/l = \frac{(um)(charge)}{1000} \qquad charge = -3$$

PO4 mg/l = 31.66 (mEq/l)

Appendix C

ALKALINITY - GRAN TITRATION PROCEDURE

NOTE: This procedure applies to samples with pH's above 4.5. If pH is below 4.5 an acidity titration can be done. (See acidity protocol).

1. Place 100 ml of sample in 150 ml plastic beaker.

2. Measure pH.

3. Add increments of 0.10 HCL* with micrometer buret and record pH after 2 minutes or when stable. Drop the pH to around 4.5 initially. About 5 readings should be taken between 4.5 and 3.5 Be sure to swirl sample sufficiently to mix aliquots of acid. Be sure to get points at 4.3, 4.1, 3.9, 3.7 pH.

4. 0.1 NHCL acid is mixed from Dilute It ampules of HCL found in the acid cabinet. Add some DI water to a freshly rinsed volumetric flask and add acid and water as instructed in the Dilute It box.

5. Read Talling, 1973, Freshwater Bio. 335-339 and FBA-Chemical Methods revised, pages 35-43.

   *From June 1983-Jan. 1984. 0.01 N HCL was used for alkalinity titrations of Emerald Lake samples. As of Feb. 1984 0.1 N HCl was used for all titrations. Samples are titrated to 3.3 but after February 1984 calculations were made using points between 4.5 and 3.7 after discussion with Melack and Sickman, UCSB. As of September 1984 all alkalinity values have been calculated using the same 4 pH points of 4.3, 4.1, 3.9, 3.7.

Calculating Alkalinity Values

1. Follow instructions for entering BASICA as in Appendix B. Once in BASICA, load ALKA by typing F3 ALKA (carriage return) then F2.

2. At the prompt enter volume of water and normality of titrant. For F3 values enter 4 (carriage return).

3. At the prompts enter the volume of titrant, carriage return and the pH value (carriage return).

   Enter the volume and pH for 4 points on the titration:
   pH 4.3
   4.1
   3.9
   3.7

Use the value nearest these points, for example 4.33
4.12
3.95
3.68

4. When entries are completed type Q (may want to use caplock key).

5. Record the alkalinity value and r value in the notebook.

6. A program which graphs the alkalinity curve, IBMTWOD, is also on the BASIC programs diskette. To use it one must be in Hercules BASIC.

Appendix D

Weather Station Data Retrieval and Storage

Storage modules from the field will be off-loaded onto an IBM Personal Computer and information stored on a floppy disk. Hard copies can be obtained when necessary.

TO RETRIEVE WEATHER STATION DATA

1. Connect storage module to RS232 interface and plug in the RS232 adapter to the wall. A total of four plugs should be connected.
2. All switches on the storage module should be down.
3. Switches on the RS232 shoud be on "transparent" and "data to terminal and modem".
4. Turn on the computers with the orange switch. When the computer boots up press the button over the D: drive to release the drive door and insert the proper cartridge for the site being offloaded, then close the door and reboot the system.
5. Change to D: drive by: D: (CR)
   Call up the proper subdirectory for the module that is being off-loaded. Type: cd elkweath (CR) for Elk Creek
   cd mewss (CR) for MEWSS
   cd em (CR) for Emerald Lake
6. Type: xtalk (CR)
7. Press Esc until Command?_____ appears.
8. Type speed 19 (or sp 19)
9. Press Esc
10. Type ca +
11. Turn up switches 1 and 2 on datalogger, and switch toggle on RS232 from transparent to SM unload.
12. Depress button on datalogger and data should begin to roll off onto the screen.
13. When finished, press Esc.
14. Type wr (space) filename, ex. elk005.85
    mewss029.86
    em156.87
15. After the data has been written on the weather cartridge press Esc and type Quit.
16. Data can be checked by entering the subdirectory and typing dir to see if the appropriate file exsists.

17. Back up the file - all the files are to be backed up on the Archive Weather Cartridge. Open the C: drive and insert the Archive cartridge, close the door and reboot the system with the diskette with DOS and IOMEGA in drive A:
    - copy file to Archive cartridge on c:, example:
      D:>copy d:\elkweath\elk123.86 c:\elkweath\elk123.86
    - check copy by doing a DIR of the subdirectory to see if it made it across
    - once copy is completed, remove the C: data cartridge by pressing the button on the top. Insert Systems Cartridge and pull down door.
    - reboot the system by Ctrl-Alt-Del
18. Initialize the storage module (erase all data) by pushing up switches 5 and 6 and all other switches down on the storage module and pressing in the "initialize" button. If done correctly a red light will show after 4-5 seconds. Then press switches 5 and 6 down again.(toggle on RS232 must be on transparent to initialize the logger)
19. Disconnect the RS232, adapter and storage module and store in the cabinet.

APPENDIX D.2.1

Dividing the Output Tables with MRCLEAN.BAS

Overview: The data set which is offloaded from the Campbell datalogger is in a format which mixes the three tables which are produced daily by the programming within the CR21. The MRCLEAN.BAS basic program can be run from within the site subdirectory to split the output into three tables with the extraneous data removed. The output is set up differently for each station so the format for running MRCLEAN varies slightly.

1. Turn on the computer with the proper site cartridge in drive D:. Enter the site subdirectory and go into basic by typing BASICA.
2. Put a blank formatted diskette into drive A: to receive the errata file (garbage data).
3. Type F3 MRCLEAN.
4. Follow the instructions carefully. As a protocol for naming the new files created by MRCLEAN, use e for elk data
m for mewss data
em for emerald data,
followed by 1,2 or 3 for the table number, and the julian date of the file being split, followed by .prn. Examples: e123886.prn
m205086.prn
em311886.prn
Output tables with more than 8 channels including table #, date and hour must be split into two lines. The following pages have examples for each site with the proper responses highlighted. At the print hardcopy? one would usually respond N, as hardcopy is only rarely needed.
5. The cleaned up files can then be incorporated into the daily tables which are in LOTUS or the hourly tables which are in DBASE. Instructions for these procedures are in Appendix D.2.2 and Appendix D.2.3

APPENDIX D.2.2

Creating Daily Tables from Tables 2 and 3 in Lotus

1. Enter the LOTUS program while on the C: drive and set the proper directory with the /FD command. If the proper directory does not come up at once, it often works to press ESC and then /FR or/FI. The listing of files in the D: subdirectory should be displayed.
2. To import the data into LOTUS, use /FIN and the filename of a .prn file. One would normally import tables 2 and 3. They can be aligned side by side with the same Julian date on the top line. One should then have the channel numbers in columns which alternate with the data. Use /WDC to eliminate the columns with channel numbers or the Julian date in table 3 (leave the Julian date in table 2). Save the file with some simple name, it is only a temporary file - /FS name R.
3. Call up the daily file for the year such as 1986T2 with /FR. Position the pointer to the bottom of the file in column A. Add the new data to the old file with /FCC. The data fields should line up below the proper columns.
4. It is necessary to survey the precipitation record as recorded by the Belfort by hand and compute the rainfall increments for each day. One can add a column to the right of the precipitation column and compute the rainfall per day. However, it is best to do this on a seperate file or at the end of the year. Any data which is incorportated as described above will be offset by one column if there are any extra columns in the data set. It is not a large problem but one would be aware of the importance of having the columns aligned properly at all times. There are printouts of past years in the file folders (green cabinet) which can serve as examples.
5. Save the new version of the file with /FSR.

APPENDIX D.2.3

Creating Hourly Tables with DBASE III

1. Hourly data as compiled by the CR21 is included in Table 1. Due to its large size, DBASE III was chosen to store this data. A header file is used to import the MRCLEAN file and then this data is appended to the yearly file. As it is appended to the larger file, the fields which begin with X, which are the channel numbers, are deleted. The file that remains contains the table number, julian day, and hour for each record. All the fields are character fields and would have to be converted to values to do mathematical calculations with the data, however logical operators such as greater than and less than do work on the character fields and can be used to manipulate records.

2. Enter DBASE on drive C: and set the defaul and path to the D: subdirectory you're working in. This is the basic procedure.

```
.USE TAB1
.APPEND FROM (FILENAME)ex.el25886.prn
.USE 86TAB1 (or correct filename)
.APPEND FROM TAB1
.USE TAB1
.ZAP (to empty it for use the next time)
```

3. Data may have to be manipulated with logical operators to delete undesired sections of files, such as overlapping dates. Data can be put in correct order of date if it is out of order by

```
.SORT ON DATE, HOUR TO (filename)
.COPY (filename) to 86TAB1 (or other name)
```

4. The desired fields can be printed out with the list to print command or the report form format if desired.

5. Note that the correct header format must be used for the different file sites, as the arrangement of data output fields varies from station to station. Hopefully problems can be avoided as the different stations all have unique cartridges.

APPENDIX E

Flume Chart Analysis and Ion Budge Analysis

Log Creek and Tharps Creek

a. Make a xerox copy of the lower portion of the flume chart.

b. Measure the total horizontal length of the pen line along the bottom line at the base of the chart.
ex: Log Creek, March 29, 1984-April 24, 1984 measures 7-13/16 inches, or 7.8125 inches.

c. Calculate the number of days that the pen recorded.
ex: Log Creek, March 29, 1984-April 24, 1984 is a 26 day interval (when counting days, count either the first day or the last day but not both, because the first and last dates add up to one day)

d. Calculate the number of horizontal inches per day.
ex: Log Creek, March 29, 1984-April 24, 1984:
7.8125/26 = 0.300"/day (Carry this out to thousandths)
0.300 x 16/16 = 4.87/16 or about 5/16 inches per day.

e. Measure and mark off days on bottom of xerox copy of chart with pencil.

f. Check waterchem data sheet or waterchem data notebook for sample dates. Mark sample dates with a solid red line. (Do not mark sample dates if Cation/Anion ratio is less than 0.8 or greater than 1.2, or if the sample had obvious contamination problems. For example, for Log Creek, March 13, 1984, sample #242 was replicated with sample #243, but sample 243 has an atypically high PO4 value. Thus sample 242 was selected even though it has a lower C/A ratio than its replicate. If replicates were taken, normally the replicate with the C/A reatio closest to 1.0 is selected.)

g. Determine the midpoint between sampling dates and mark with a dotted red line.

h. Calculate the total flow between dotted lines. The middle scale (million gallons per day flow) is used. Use a ruler to divide each horizontal interval on this scale into smaller intervals to measure the height of the pen line. Take the average height of the pen line in each minor time division. Write the height (carry to thousandths) in each minor time division block on the xerox copy.

Add heights for all minor time divisions between the dotted lines. Divide the sum by 10 times the number of inches per day (i.e. divide by 3 for the scale 0.3"/day). Multiply this value times the appropriate factor according to the flume width: Tharps Creek has a 3" flume, factor is 1/2; Log Creek has a 12" flume, factor is 2.
ex: Log Creek, April 4, 1984-April 17, 1984:
(7.732/3 x 2 = 5.1546667 million gallons

Convert to liters by multiplying times 3.7853:
(5.1546667 x (3.7853) = 19.511,960 million liters
= 19,511,960 liters TOTAL FLOW

i. Calculate the contributions to the ion budget. Multiply the ion concentration (microequivalents per liter, get this value from the waterchem data sheets) of the samply by the total volume of flow between the dotted lines.
ex: Log Creek, April 4, 1984-April 17, 1984, H+ contribution:
0.13 ueq/1 x 19,511,960 liters = 2,536,555 ueq of H+.

Continue for all major ions.

NOTE: Please keep a copy of all calculations in the folder with the charts. This way if there is a question or adjustment all of the figures are easily accessible.