



**FIELD GUIDE FOR SURFACE WATER  
SAMPLE AND DATA COLLECTION**



**AIR PROGRAM  
USDA FOREST SERVICE**

June, 2001



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# FIELD GUIDE FOR SURFACE WATER SAMPLE AND DATA COLLECTION

## EXECUTIVE SUMMARY

The USDA-FS Air Program collects and analyzes surface water samples, primarily to inventory aquatic systems sensitive to atmospheric deposition and to determine whether effects of atmospheric deposition exist or may occur in the future. The quality of data collected can be assured by implementing a rigorous set of protocols covering all aspects of sampling, inspection and use of the data. Among the emphasis areas for a high-quality surface water sampling program are:

- Consistent methods among projects across different geographic areas
- Clear determination of individual program objectives guiding local protocols and selection of constituents
- Complete documentation of all field and lab methods
- Complete documentation of field conditions and other ancillary data
- Timely quality assurance of all data; through both current chemistry and comparisons to historical data
- Water sample archiving
- Easy to use and long-term data storage and retrieval capabilities
- Training for personnel in field sampling techniques and data QA, as well as field reviews of sampling techniques

## INTRODUCTION

In 1987 "Guidelines for measuring the physical, chemical, and biological condition of wilderness ecosystems" (Fox and others, 1987) was published and established a common set of protocols to facilitate inventory and monitoring in wilderness. These protocols were necessary to allow federal land managers and regulators to gather and use data in the administration of forestlands under laws including the Clean Air Act and the Wilderness Act. The need to determine whether significant changes have occurred requires data of known quality that can be compared with similar data over time and in different geographical areas. Scientifically defensible protocols are critical to this need. Because different programs may need different protocols the suggestions presented are directed to the needs of the USDA Forest Service (FS) Air Program. These suggestions may be appropriate to other programs or agencies as well but that must be determined based upon the needs of the other programs.

The 1987 guidelines cover broad categories of data collection, including: atmospheric environment, visibility, soils and geology, aquatic chemistry, aquatic biology, and plants. The need to update the information and protocols in these categories varies as techniques and understanding continue to advance at differing rates. The work presented here is an effort to supplement material originally presented in the category of aquatic chemistry. To fully update even this single category of data collection would be a large task and would duplicate published or ongoing work by scientists in universities and in agencies

such as the U.S. Environmental Protection Agency (USEPA), the U.S. Geological Survey (USGS), the National Park Service (NPS), the Bureau of Land Management (BLM), and others. Instead, the purpose here is to provide guidelines to FS personnel who design and implement routine synoptic and long-term monitoring of surface water chemistry to assess sensitivity to or effects of acidic deposition on these waters. The guidelines presented here may not be appropriate for every possible project. Particularly in multi-agency studies and studies with a significant enforcement responsibility approaches using more rigorous protocols may be necessary. It is hoped that these guidelines help foster an understanding of how to collect, process, analyze, interpret, and quality assure data that are necessary to the effective management of public lands. Just as there is need to update the 1987 guidelines, so too these guidelines should be viewed as one approach to address constantly changing needs with constantly changing technology. For those needing to consider alternative approaches a brief section of references to other study protocols is provided.

## **PURPOSE AND SCOPE**

This document discusses the supplies, instruments, and methods of collection that must be considered in the design and implementation of surface water sampling programs. Additional topics that facilitate the collection quality data collected are stepwise quality assurance (QA), thorough training and adaptability to changing conditions and requirements.

## **PROTOCOLS AS A LAND MANAGEMENT TOOL**

Land managers need to define the status of lands, determine whether or not present or proposed development within and off Forest lands is a real threat to Forest resources and Air Quality Related Values (AQRVs), and to demonstrate how resource condition has changed over time. Data of the highest quality are critical if the results of any of these land management actions are to be accepted by others in land management, the courts, the public, and science generally. Because land management agency decisions on mitigating the effects of development can easily result in costs to industry or the public on the order of hundreds of millions of dollars or more the data will be scrutinized by all involved parties. The protocols and data must be scientifically valid for conclusions based on them to be considered. Data collected under standardized protocols that have been reviewed by acknowledged experts in the field are far more defensible than data collected by untrained personnel using unknown, undocumented, or unsuitable protocols. Indeed, poor quality data may be useless or even counter productive.

Federal and state personnel making land management decisions must have confidence in the data quality and have an understanding of the degree of error associated with the data. For aquatic chemistry data, estimates of precision (how tightly the data cluster about the measured value) and accuracy (how the data are consistently shifted relative to the "true" value) are common measures of data quality that must be presented and must be defensible. Unfortunately, there may be too few samples for a given aquatic resource upon which to conduct the best estimation of error; however, by collecting data on several related systems using consistent protocols, it may be possible to pool data and allow a defensible estimate of errors.

Data collected for a specific purpose may be useful to others in the FS and elsewhere. To allow others to appropriately use such data, it is necessary to know the protocols that were used and the errors inherent in these protocols. It is particularly helpful in preparing regional or national assessments of resources to have data from all the contributors collected by protocols that not only are appropriate and well-documented but, as nearly as practical, identical.

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## BASIC HYDROLOGY OF THE STREAM/LAKE CONTINUUM

To effectively design or conduct a surface-water sampling program some knowledge of basic hydrology is needed. The chemistry of lakes and streams is largely a function of what surfaces and substances the inflowing water has contacted and for how long, and of some basic physics driven by sunlight and wind. Thus, selection of lakes and streams as monitoring sites needs to consider the hydrology of the system so that the chemistry can be interpreted in the proper context. If the site is to monitor the effects of acid rain or other atmospheric inputs on surface water, then the hydrology should minimize the possibility of processes that neutralize the atmospheric inputs. For example, many lakes and streams sensitive to acidification have a hydrology that allows minimal contact of precipitation with soil. In other regions, atmospheric inputs that flow through acidic organic soil zones or soil zones leached of reactive minerals are not neutralized before reaching lakes and streams. Although lakes and streams each can be classified into numerous categories, it can be useful to consider the systems in terms of how they fill and empty with water.

Some lakes, particularly chains of lakes in mountainous areas, may merely be wide spots in streams. These may completely refill with water in a matter of a day or so during periods of high discharge. Some streams in areas of flat topography may behave much like lakes, with stream flow even changing direction in response to changes in wind or tide. In the simplest sense, both lakes and streams are topographic depressions that fill with water; lakes generally have minimal topographic gradient between inflow and outflow whereas streams generally have measurable flow in only one (down gradient) direction. Water can enter lakes and streams by:

- 1) Direct precipitation onto the surface, thus having no opportunity to react with soil.
- 2) Rapid surface runoff from snowpack, exposed rock, or packed soil, especially during peak snowmelt or intense storms. Some reaction with the most surficial deposits is possible, thus introducing weathering products such as major cations and acid neutralizing capacity (ANC) and anything contributed by dryfall (dust and other atmospheric deposits between storms).
- 3) Shallow percolation through the soil zone that normally is not saturated. This allows more contribution of weathering products.
- 4) More or less continuous inflow of ground water that has had extensive contact with rock and soil. This allows considerable contribution of weathering products, i.e., constituents derived from the dissolution of soil or rock within the watershed such as  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{K}^{+}$ ,  $\text{Na}^{+}$ , and ANC.

Lakes and streams with factors that minimize the contribution of weathering products (and thus maximize the influence of atmospheric precipitation) have at least one of the following characteristics, perhaps several:

- 1) Large surface area of lake or stream to watershed area ratio.
- 2) Subject to periods of great inflow discharge from snowmelt, rain on snowmelt, intense thunderstorms, or hurricanes.
- 3) Little exposed soil in the watershed or, at least, near the lake or stream. Soil zones that do exist should be shallow.
- 4) Topographically perched relative to the local ground water, e.g., in topographic saddles, near places of rapid topographic drop-off or cliffs. This requires that an effective "seal" of clay or organic matter keep the lake from draining faster than it can be recharged by inflow. In such systems the local groundwater table is lower than the lake surface or the groundwater level is about the same elevation as that of the lake surface, thus providing little or no pressure difference to cause ground water to flow into the lake. Instead, the lake normally drains to ground water or there is insignificant contribution by ground water to the lake.



The discussion above centers around weathering products, which are important in determining sensitivity of lakes and streams to atmospheric deposition and some other sources of acid. Some types of bedrock, e.g. limestone and other sedimentary rocks with significant amounts of carbonate, weather readily and provide great protection against acid deposition. Other types of bedrock, e.g., granite and quartzite, weather slowly and often underlie areas that contain sensitive lakes and streams. Such systems also may be very sensitive to other inputs, such as nutrients from atmospheric deposition or land use disturbance. Not all projects will be concerned with these potential problems, but consideration of the hydrology of the system still will be critical in understanding how constituents can enter and leave the system.

Because water entering a lake or stream can have had differing contact with soil, rock, biota, and organic material these different sources of inflowing water can have greatly differing chemistry. Thus, the chemistry of the lake or stream may change greatly through time as one or another source of inflowing water dominates. The least variance occurs in systems that fill very slowly (slow flushing time lakes) or with the same type of water, e.g., only dilute water that rapidly runs off snow or rock, or only rather mineralized water that discharges from stable groundwater aquifers. Systems that can be dominated by atmospheric deposition during snowmelt or intense storms and by ground water during periods between storms can change between dilute and concentrated. Since the controlling changes in water source vary seasonally (snowmelt or dry period) or with weather (runoff or discharge) much of the variance can be explained by a plot of chemistry versus time (using Julian dates) or discharge, depending upon the site. Snowmelt dominated sites often show a strong correlation of chemistry versus discharge with minimum concentrations of cations and ANC at about maximum snowmelt and discharge. Because maximum snowmelt tends to occur at about the same time each year there is a sinusoidal pattern versus time .

Plots of chemistry versus time or discharge work well for major weathering products, i.e., constituents derived from the dissolution of soil or rock within the watershed such as  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{K}^{+}$ ,  $\text{Na}^{+}$ , and ANC. Constituents that are derived only from atmospheric deposition, such as (in some watersheds)  $\text{SO}_4^{-2}$ ,  $\text{NO}_3$ ,  $\text{Cl}^-$ , can be poorly correlated with Julian date and discharge and, thus, with major weathering products. It is useful to know which source each constituent has so that changes over time can be attributed to the correct source. If one is interested in the effects of atmospheric inputs of  $\text{SO}_4^{-2}$  then lake or stream systems having strong correlation of  $\text{SO}_4^{-2}$  with major weathering products are a poor choice for trend detection because in such systems the  $\text{SO}_4^{-2}$  likely comes from weathering as well as from atmospheric deposition.

Sites dominated by rainfall instead of snowmelt will have numerous periods of high and low concentration depending upon the frequency and intensity of rainfall runoff. Because intense storms are unlikely to repeat at the same dates each year plots of chemistry versus discharge are likely to be much more useful than plots against time (Julian date).

Sites that show regular patterns of chemistry versus time or discharge can be sampled much more efficiently than can sites having random relation with chemistry. The pattern characteristic of the site can indicate the conditions most likely to define the extremes of chemistry as well as average chemistry. It is precisely the need to define these extreme and average conditions that is the purpose of monitoring. Thus, sampling frequency and timing can be planned to coincide with extremes of chemistry, such as during snowmelt, if that is the purpose of the project. Especially when initiating a project, it is useful to use whatever surrogate data are available to estimate when extreme conditions may occur. Thus, if long term weather data are not available at the site, the

nearest long term station in similar terrain may provide an estimate of rainfall frequency and intensity, or of snowmelt. Similarly, long term chemistry data for other monitoring sites in the region can provide initial estimates of timing for extremes in chemistry. Sites such as those in the USGS Hydrologic BenchMark Network or similar long-term networks operated by the FS, NPS, BLM, and others can be used to learn what weather patterns commonly are observed in the region.

One major difference between most lakes and streams is thermal stratification. Stable layers of water may result in systems that aren't exposed to extensive mixing due to wind or streamflow. The upper layer, or epilimnion, is the warmer layer in summer because sunlight rapidly changes to heat in the shallow water. The epilimnion usually is well mixed by wind and is the area of greatest algal activity, therefore, available nutrients tend to be in small concentration here. Epilimnion samples are collected to represent this zone of most rapid biological activity.

Much colder water remains, sometimes throughout summer, at depth and is called the hypolimnion. It is in contact with sediment, where decomposition of organic matter releases nutrients and consumes oxygen.. In eutrophic, or "rich" lake,s the oxygen consumption can result in complete absence of oxygen in the hypolimnion. During such conditions the concentration of nutrients and some metals can be very high in the hypolimnion. In oligotrophic or "poor" lakes there may be little depletion of oxygen during summer and oxygen concentrations may even exceed those in the epilimnion because of higher solubility of oxygen at the lower temperature in the hypolimnion. Hypolimnion samples are collected to represent the extreme chemistry that can result in this zone, particularly during periods of low or zero dissolved oxygen.

The zone bridging the epilimnion and hypolimnion is the metalimnion or thermocline, where temperature changes fairly rapidly with depth. It is a zone of some interest because density rapidly changes and thin layers of detritus from dead plankton may float in this zone. However, because it normally is a small part of the lake and does not represent either extreme of chemistry it is rarely sampled. Also, because of the rapid changes with depth and time it is difficult to resample the same reference condition at different times, something easily done in epilimnion and hypolimnion samples.

In winter under ice cover, the upper layer of water is close to 0 degrees C due to its contact with the ice above. Slightly warmer water remains deeper since water is most dense at 4 degrees C. In lakes that are frozen most of the year, oxygen depletion may be more common in winter than in summer.

## **PRESENTATION OF EXISTING PROTOCOLS**

The FS Natural Resource Information System (NRIS) is the agency-wide repository for data, including historical aquatic data, project descriptions and protocols.

The project descriptions in the NRIS database were reviewed and projects having a significant surface water chemistry component were selected. Most of the protocol documents referenced in each project description were obtained directly from NRIS files as of September 2000. A few large documents (e.g., the USEPA lake and stream survey protocols) were obtained as published reports.

The protocol documents were reviewed and a template prepared to provide a uniform format for summarizing project protocols. Information in each protocol document was summarized in this new format. The summarized protocols were sent to each project for comment and revision. Any revisions made by the originating office were incorporated into the protocols presented here (Appendix 1).

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## PROTOCOL REQUIREMENTS

### *Bottles*

The bottles required for samples vary with the constituents to be sampled and the laboratory doing the analysis. Sometimes, several bottles will be required for each sample, with differing processing of each bottle required in the field or at the laboratory. The bottles used need to be non-reactive with the constituents measured from that bottle. Most constituents are collected in polyethylene bottles, but organic constituents such as pesticides typically are collected in glass bottles. The sample must be large enough for the laboratory to do any needed processing and analysis and have sufficient excess if a rerun of the archived sample is needed. Each bottle must have a waterproof label and all the information required by the laboratory must be written with waterproof ink. Because the needs of the laboratory must be considered it is advisable to obtain all bottles from the laboratory doing the analyses. The laboratory also may be able to supply appropriate labels with pre-printed data fields showing what information is required.

To minimize contamination of the sample by impurities in the bottle itself polyethylene bottles should be rinsed three times with deionized water, filled with deionized water, and allowed to stand for at least 48 hours. This service may be provided by the laboratory supplying the bottles. Bottles should be carried to the sampling site filled with deionized water from the laboratory. The deionized water then is emptied, in a manner so as not to mix the deionized water with the water to be sampled, immediately prior to sampling and the bottle and cap rinsed three times with sample. Then the sample is collected and the bottle capped. At all stages of sampling care should be taken not to contaminate the inside of the bottle or cap with fingerprints or soil and other impurities. Powder-free gloves should be worn to minimize contamination by the sampler's arm as the sample is collected. It requires only very small amounts of solids such as soil to overwhelm the chemistry of the water sample itself. For the analysis of trace metals acid cleaning of the polyethylene bottles is required; the laboratory providing the bottles should do this. These bottles and their caps are rinsed three times with sample before collecting the sample. These rinses are very effective in minimizing any carryover of contaminated water into the sample. For a common bottle size of about 125 ml it is unlikely that more than 1 ml of carryover would occur. If the bottle is rinsed with about 100 ml (allowing room for effective shaking) then the dilution of the contaminated carryover water is 1:100. If this water is emptied and again 1 ml of the now diluted contaminated water carries over then a second rinse would dilute it to 1:10,000 of the initial contamination level. A third rinse would dilute to 1:1,000,000 before any sample is collected.

Glass bottles used for organic analyses often are cleaned by heating in a furnace to burn off all traces of organic materials. These glass bottles do not need to contain deionized water nor do they require rinsing with sample before sample collection.

To assure that the bottles used are not contaminating the sample it is necessary to analyze samples of "blank" water that have been stored in the bottles for time periods comparable to the amount of time sample remains in the bottle before analysis. This is most conveniently done on each batch of bottles obtained from the manufacturer. Thus, it is most efficient if the laboratory supplying the bottles perform this quality assurance test. It is necessary to know the composition of the deionized water prior to being stored in the bottles and then analyze samples after storage in the bottles. The stored water should show constituents below the detection limit. If significant concentrations are found, the batch may need to be rejected or the bottles may need additional cleaning.

Bottles need to be protected from contamination during transport to and from the sampling site. It is

most convenient to keep the complete set of pre-labeled bottles for each site together in a sealed plastic bag. This minimizes the chance for dust to accumulate on the bottle and potentially contaminate the sample, as well as making all the required bottles readily available. If one or more bottles contain in them some remaining nitric acid from cleaning, such bottles should be packed separately to minimize the potential for cross contamination of nutrient samples by leaking from nitric acid washed bottles. If extensive vibration is expected, as is common during transport by packhorses, the lid may need to be taped to the bottle with a wrap of electrical tape; however, this poses additional problems in the laboratory and should only be done if necessary. If tape is used it should be wrapped so as to tighten, not loosen, the caps as the tape is applied.

Bottles need to be protected from excessive heat and excessive cold to minimize degradation of the sample. Excessive cold can freeze samples, which may rupture bottles or irreversibly precipitate out some constituents. Sunlight not only can heat the sample, but also encourage the growth of phytoplankton. The bottles filled with sample should be stored in the dark and just a few degrees above freezing. Thus, packing them with ice, cold packs, or snow, if it is handy, in an insulated cooler is best. Dry ice should not be used because it could freeze the sample. If an extended period without cooling is the only feasible option to store or transport samples, filtration of the samples at the site of collection and addition of preservatives such as nitric acid to some aliquots should be used to protect the integrity of the sample. Because of the difficulty in properly maintaining a large number of chilled samples while backpacking, the use of pack animals should be considered. In addition to allowing better maintenance of samples and faster return to the trailhead pack animals can improve the morale of sampling teams by allowing workers to bring items that will result in a more comfortable camp. The possible disadvantages of pack animals are beyond the scope of this work but will be common knowledge to anyone who has used them.

### *Filters*

Many samples require filtration either in the field or the laboratory. This filtration separates constituents dissolved in the water from detritus and other solids that may alter the chemistry of the sample before it can be analyzed. Filtration in the field adds the possibility of sample contamination if not done carefully. Program needs and the nature of the water being sampled determine whether the greater risk is from field filtration or from sample degradation before filtration at the laboratory. Samples containing large amounts of suspended solids or organic matter and samples analyzed for trace constituents (such as dissolved iron) are the most susceptible to degradation before filtration at the laboratory. If samples are filtered in the field it is possible to check for contamination by processing (filtering) deionized water of known composition at the same time to determine whether field filtration is associated with contamination.

As with bottles, each batch of filters must be checked to assure that they do not contaminate the samples. For the same reasons discussed for bottles, it is most efficient if the laboratory supply and quality assure any filters that are used for field filtration. As with bottles, care should be taken to avoid contamination of the filter and filter apparatus from fingerprints and soil. The filter and apparatus need to be rinsed well with either deionized water or sample prior to filling the sample bottles. Because filtering apparatus varies greatly in size it is impossible to give universal guidelines on the amount of rinse needed. Thus, it is most efficient if the laboratory specifies or provides any filtering apparatus and determines an appropriate rinse protocol for that apparatus. Filters commonly used are made of polycarbonate or are cellulose-based, e.g., cellulose acetate. The pore size of the filter is critical in determining what actually is analyzed in filtered samples. A pore size of 0.45 microns is commonly used for many constituents, .1 microns is used for many metals such as aluminum; however, smaller pore sizes may be needed for the analysis of some trace metals if colloidal material is present in significant

amounts. This is best determined by comparing a series of aliquots collected with filters of differing pore sizes, for example, 0.4 and 0.1 micron filters. This needs to be done only in studies that need the best estimates of dissolved trace metal concentrations.

### *Selection of Chemical and Physical Constituents*

Although it may be possible to conduct some programs, especially initial reconnaissance surveys, with only a few constituents determined on each sample, this rarely if ever is justified. Especially in programs where access to the lakes or streams is difficult and time consuming the analytical cost is negligible compared to the collection cost. Further, trying to analyze a minimum of constituents limits the possible uses of the data to later needs beyond those of the program conducting the initial sampling. Also, such minimalist approaches severely hamper the ability to properly quality assure the data and to interpret it. It is best in initial samples to over-analyze rather than under-analyze for constituents. If no data for a constituent have been collected then nothing is known about its importance; if initial data indicate it can be ignored, then future samples can drop that constituent except for occasional sampling to insure that the initial conclusion is still justified.

In addition to selection of constituents, it is important to insure that the analytical method used for each constituent is appropriate to the aquatic systems being sampled. The detection limit of the method needs to be well below the expected minimum concentrations for constituents expected to be present (some constituents may not be present at all but this absence may need to be documented). The precision of the method needs to be small relative to the concentration and to natural variations in concentration expected to occur. As part of the program planning, the justification of each method selected should be discussed. As data are collected, this discussion of methods should be revisited and either confirmed or a more suitable method selected.

### *Standard Surface Water Constituents*

Constituents to be determined are best considered as packages or analytical suites. The most basic suite includes all those constituents that have the greatest concentrations and that together exert many chemical controls on the nature of the water. This core group is called the major ions and common field measurements and includes:

- 1) Major cations -  $H^+$  (from pH),  $Ca^{+2}$ ,  $Mg^{+2}$ ,  $K^+$ ,  $Na^+$ ,  $NH_4^+$ .  $H^+$  and pH are important because of direct toxicity to aquatic organisms and they affect the solubility of toxic metals. The ions  $Ca^{+2}$ ,  $Mg^{+2}$ ,  $K^+$ ,  $Na^+$  are important indicators of how the rock and soil in the watershed react with water.
- 2) Major anions – Acid neutralizing capacity (ANC),  $SO_4^{-2}$ ,  $NO_3^-$ ,  $Cl^-$ . ANC is an important measure of the lake or stream's ability to neutralize acid; if its concentration is near 0 then additional acid can easily affect pH and produce toxic conditions. The ions  $SO_4^{-2}$  and  $NO_3^-$  are common indicators of acid from manmade or natural sources.  $Cl^-$  is very useful in estimating the amount of evapo-transpiration in some watersheds.
- 3) Common field measurements -  
Water temperature, pH, and specific conductance  
Dissolved oxygen  
Secchi disk depth (if sampling from a boat) in a lake  
Water level and, if applicable, discharge

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### *Additional Surface Water Constituents*

Depending on the stated program objectives, many additional constituents can be added to the major ion/common field measurements suite. Common additions are:

- 1) Additional nutrients - total P, soluble reactive P, total N. Nutrients are important in studies involved with the productivity of fisheries and with oxygen depletion. Point sources of nutrients, such as sewage outfalls, and non-point sources, such as intensive grazing near waterways, can greatly affect water chemistry, algal productivity, and the viability of aquatic organisms.
- 2) Additional inorganic chemistry - dissolved Al, large suites of other dissolved trace metals. Increased solubility of trace metals at low pH can cause toxic concentrations. Low pH commonly is a result of acid precipitation in watersheds of unreactive geology or of acid mine drainage.
- 3) Organic chemistry - Total organic carbon (TOC), dissolved organic carbon (DOC), various suites of pesticides and other organic toxins. TOC and DOC affect the toxicity of some trace metals, such as Al. Pesticides and organic toxins may be deposited by atmospheric deposition or runoff from treated lands.
- 4) Basic aquatic biology - phytoplankton, zooplankton, macroinvertebrates, fishery. Each type of organism interacts with water chemistry and may be an indicator of adverse chemistry not initially detected by sampling only chemistry. These organisms frequently are considered AQRVs or to have economic importance, such as fisheries.
- 5) Bacteria - total and fecal coliform, fecal strep. These organisms are used as indicators of contamination from sewage, grazing, or general soil contamination.

It is beyond the scope of this work to provide advice on which of these to add and on how to conduct all such possible sampling. If local expertise is not sufficient to decide whether to add these, then experts in aquatic chemistry should be consulted regarding program objectives and what they may require. Although some of these constituents require little or no change in sampling protocol, others do. It is much more difficult to quality assure some of these additional constituents than the core group recommended above. Additionally some field measurements are prone to problems with equipment and personnel training, and therefore the utility of these measurements should be considered against the difficulty of collecting them.

### *Selection of Sampling Site*

The sampling site needs to be safe, accessible, easily located by others using field descriptions, and representative of that part of the lake or stream of interest. In both lakes and streams the site should have good hydrologic connection with the main mass of water, i.e., circulation should not be impeded by excessive vegetation, shallow water depth, or be in a restricted embayment. The presence of tributaries needs to be considered so that adequate mixing is assured if sampling downstream of a tributary. Some measurement of specific conductance across a stream or in the vicinity of a lake inflow can determine whether mixing is complete.

If possible, lakes should be sampled away from shore by boat. If otherwise suitable, the deepest part of the lake is preferable. After determining the sampling location it should be marked with a permanent buoy, coordinates determined by GPS, or triangulated from easily recognized landmarks and these should be noted in any instructions to future sampling teams. If sampling by boat is not feasible then a shore location such as a rocky point located on the main body of the lake may be suitable. Lake outflows also may be suitable for sampling if the lake normally has significant discharge; otherwise, the outflow may not have good circulation with the lake.

Sampling locations in streams, including inflows and outflows of lakes, should be in areas of significant flow and little possible effect from tributaries, stagnant flow areas, or point sources and structures that may introduce their own chemistry. If safe, the sampler should wade to mid-stream in a well-mixed section of small streams. If available, a bridge or a boat can provide access to mid-stream areas of larger streams. If it is unsafe or not practical to sample at mid-stream then an area of unrestricted flow that can be sampled from shore should be used.

### *Observations*

In addition to field measurements, described below, the person sampling should note a variety of things that can be observed. For example, are insects, fish or amphibians observed. If so, information on approximate numbers, size, and type might be valuable later in determining whether changes have occurred in the biotic community. Certainly, any observation of dead biota should be noted, as this may indicate recent harmful changes in chemistry or physical conditions such as lack of oxygen, toxic agents, etc. Indications of recent high stage flow should be indicated. Land use and disturbances such as camps, livestock, and evidence of recent timber harvest or mining need to be recorded. Photographs of the sampling site, lake, and watershed provide valuable information in understanding the system.

### *Weather*

Weather can affect surface water chemistry. Wind and the amount of solar radiation are very important to the stratification of water and chemistry in lakes. Rain and snowmelt are important to the chemistry of streams. Air temperature and atmospheric pressure can indicate whether conditions are stable or a storm has recently occurred or is about to develop. It takes only a few minutes to record basic conditions, i.e.: Percent cloud cover, approximate wind speed and direction, whether storms are or have recently occurred, the status of snowmelt (if applicable), air temperature, and atmospheric pressure.

### *Dissolved Oxygen Measurement*

Dissolved oxygen (D.O.) can only be measured in the field. It is an important measurement because there are minimum D.O. requirements for aquatic vertebrates such as fish and amphibians, and the presence or absence of D.O. is a major influence on the solubility of constituents such as trace metals. Dissolved oxygen can be added to the water from the atmosphere or from photosynthesis by phytoplankton, macrophytes, and periphyton. Dissolved oxygen can be removed from the water to the atmosphere or by respiration and by decay processes in the water or the sediments. The ability of the water to contain D.O. is determined by its temperature, salinity, and the atmospheric pressure, with the solubility of D.O. decreasing with increasing temperature, increasing salinity, and with decreasing atmospheric pressure. Tables of solubility as a function of these variables are available (Wilde and others, 1998-1999). In lakes the D.O. normally differs from the surface to the bottom and profiles of D.O. are done if samples are collected from a boat. For calibration and maintenance see Appendix 2.

### *Water Temperature Measurement*

Water temperature can only be measured in the field. Water temperature is important as a measure of habitat conditions for organisms and is an excellent index to compare samples among different years. Because of annual differences in weather the water temperature often is a better indicator of the annual hydrologic cycle than is the calendar date. Water temperature should be measured at all sites when collecting water samples. Either thermometers or thermistors may be used; either must be calibrated at

two temperatures. Typically, an ice/water mix is used to determine what the reading is at 0 degrees C and a reading from a certified thermometer is compared to the one being calibrated at some higher temperature, e.g., 20 or 25 degrees C. The calibration data are recorded and presented in the project's annual quality assurance report. Thermistors have become standard and offer a low cost but easily readable and precise measurement. Sufficient time needs to be allowed for equilibration with the water by placing the thermometer or thermistor in the water for several minutes before reading. The reading should be taken with the thermometer or thermistor still in the water because the reading can change quickly once the probe is exposed to air. In lakes the temperature normally differs from the surface to the bottom and profiles of temperature are done if samples are collected from a boat.

## PH

The pH of water, especially in very dilute systems, can be difficult to determine accurately unless sampling personnel are carefully trained. Thus, pH of samples collected during initial inventories may be better measured in the laboratory. Because the pH can change between collection and analysis in the laboratory it is useful to have trained personnel make at least some field measurements for comparison to verify that the laboratory measurements differ little from field values. Both measurements are useful and at least one of the two is necessary. The pH is an important control on solubility of many trace elements and also may have biological effects itself. The meter must be digital and capable of reading to the nearest 0.01 pH unit. Other types of pH monitors are not acceptable because there is a high likelihood of erroneous measurement. The electrode typically is a combination (reference and pH indicating electrodes together) and should be suitable for measuring even low ionic-strength water. Calibration requires the use of two buffers that bracket the expected pH, commonly 4.00 and 7.00 buffers. Some electrodes that calibrate well with buffers, which are very concentrated solutions, fail to accurately measure pH in dilute water. The dilute acid standard used for National Acid Deposition Program (NADP) calibration can be used to verify the proper function of the electrode.

Dilute acid standards also can be prepared by precision dilution of acid references, e.g., a 0.02 N acid used to titrate ANC can be diluted 1:1,000 with deionized water to produce a dilute solution that should have a pH of 4.70. The measured pH should be within 0.2 pH units of the dilute acid standard value, otherwise, the electrode probably is not suitable. Electrodes may have to be replaced seasonally or at least yearly. Cross contamination of solutions between buffers, dilute acid standards, and sample can cause large errors. Deionized water is used to rinse the electrode between each step and separate plastic beakers labeled for each buffer, dilute acid standard, deionized water, and sample should be used but only for their labeled purpose. Color-coded buffers can help avoid confusion and cross contamination during calibration. For dilute water it is helpful to use a stepwise equilibration of the calibrated electrode to the sample to minimize effects of previous solutions; a soak in sample for 5 minutes each for two aliquots, followed by three aliquots that are each measured after 1 minute of equilibration is a useful approach in dilute water. All three of the final readings should be recorded, as should all the calibration steps and both the pre-calibration readings in the buffers and the reading in the dilute acid standard. These measures can indicate how stable the instrument is as well as whether the electrode is functioning properly.

### *Specific Conductance*

The specific conductance can be measured at the laboratory but at least some field measurements should be taken for comparison (particularly for inventory sampling) to verify that the laboratory measurements differ little from field values. Specific conductance is critical in quality assuring most major



ion analyses. Specific conductance often is so highly correlated with each major ion's concentration that it can be used cost effectively to approximate those concentrations in between actual analyses. Because of these uses and because of the simplicity of the measurement it should be measured on all samples.

In initial sampling within a region, specific conductance can be used to assign sites to likely concentrations of major ions. In regions of generally low specific conductance, the sites with lowest specific conductance **LIKELY** have the lowest ANC. In sites highly impacted by acid mine drainage, the sites with lowest specific conductance **MAY** have the lowest concentrations of acid. In either case, specific conductance is not a substitute for definitive data. It merely is a first approximation of major-ion chemistry that can be used to select sites for more detailed analysis.

### *Secchi Disk Depth*

The Secchi Disk depth measurement is performed from a boat in water deep enough to exceed the visibility limitations of the water. The disks come in differing sizes and may be black and white, all white, or mirror finish. Measurements are subject to individual eyesight problems, glare on the water, waves, etc. so notes on who is measuring and how are important. For consistency, it is best to measure on the shady side of the boat to minimize glare and to not wear sunglasses. A calibrated chain is attached to the disk and the disk lowered until it disappears, and the depth recorded. The disk is slowly raised until it reappears and that depth recorded. The average of the two depths is the single value normally entered as the Secchi Disk depth. If the disk can be lowered to the bottom and still be visible this should be noted, e.g., "Secchi Disk depth greater than maximum depth."

### *Water Level and Discharge*

Surface water chemistry can change in response to changes in the inflow of water, on timescales from less than a day to over an entire season. In lakes the water level can be a convenient measure of whether the sample is being collected during a period of generally normal, dry or wet conditions. The water level can be measured and continuously recorded by instruments that monitor a float assembly or pressure transducer, or just when samples are collected. It is important that a constant reference elevation is available so that all measurements are relative to the same reference; this could be a permanently mounted staff gage (a weatherproof "yardstick" used especially for this purpose) or a spike or other convenient point from which a metal tape can be dropped to the water surface. In wilderness, where permanent installations are not permitted, it may be necessary to use an inconspicuous chisel mark on a rock surface. It is helpful if a few backup references can be located in areas unlikely to be disturbed by visitors or extreme flows and surveyed relative to the normal reference point in case it needs to be re-established. Without such backup references it may be impossible to relate new data to older data.

The inflows and outflows of lakes can be measured for changes in level as can lakes, preferably in a straight stream section that has a natural or man-made control (place where the flow drops relatively rapidly over a stable lip or other change in topography). Changes in water level upstream of a control correspond directly to the discharge. Discharge can be measured directly with meters that measure water velocity at a number of points in the stream cross-section. Velocity times the area of the individual segments of the cross-section gives the discharge in each segment and the sum of the velocity-area products for all segments is the discharge at that cross-section. If meters are not practical or available, using objects drifting unimpeded in areas of typical velocity and timing how long it takes to travel a measured distance can approximate the velocity. If depth is sufficient, a neutrally buoyant object that won't be affected by wind (such as an orange or full soda can) may be suitable. A graph of water level

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versus discharge can be prepared for each site and used to estimate flow when there is insufficient time to do a discharge measurement.

## SAMPLING PERSONNEL

### *Designated Samplers*

Offices that conduct water sampling on a routine basis can benefit from having a core group of personnel highly trained in sample collection. Such personnel produce the most reliable data and can be cost-effective because of their familiarity with the needs of sample collection. Especially if the more difficult aspects of sample collection are needed, e.g., field pH, trace metals, and calibration of complex instruments, it may save time to have someone who is most qualified rather than someone who happens to be available but has little or no formal training.

### *Volunteers and Contract Samplers*

The use of non-agency personnel, such as volunteers or those hired on contract to collect samples at a nearby site, should be considered as a supplement to many sampling programs. Contract samplers typically are people who live or work near a system being sampled and who are hired to collect samples under the guidance of agency personnel. Sometimes, interested individuals from outdoor organizations or those who work for state or federal agencies may volunteer to collect some samples. Contract samplers may be more likely to collect high-frequency samples or to sample during periods of rapid runoff than are routine personnel because they are on-site or nearby. Although there is some additional cost it often may be minimal compared to mobilizing agency personnel if great distances are involved. The main disadvantage is the need to stay in contact to learn of problems as they develop and the need to assure that samples are collected safely and properly. If observer-collected samples are used only to supplement routine samples it is easier to quality assure the observer samples.

## SAMPLING METHODS

There are many acceptable methods of collecting water samples. Some, such as flow integrated stream samples, are complex and beyond the scope of this work; studies needing such sampling should consult appropriate references, e.g. Wilde and others (1999). Samples likely to be collected in most studies can be described as follows:

### *Grab/Hand Samples*

The most common samples, especially in reconnaissance or synoptic studies, are collected from or near shore. Once a sampling site has been selected (see Selection of Sampling Site), bottles should be assembled and necessary information added to the labels to unambiguously identify the sample. If the bottles contain deionized water, this should be discarded away from the shore so it does not disturb the sampling site. The field notebook or form should be filled in so the sample can be linked to field data and observations. A sample field form is shown in Appendix 3. Field notebooks are very helpful at sites used for long-term monitoring to provide easy access to historical information on site characteristics and field data collected during previous years.

Avoiding disturbance that can affect the water being sampled is especially important. For grab samples the most likely disturbances are stirring up sediment or surface debris into the water column; each can contribute significant amounts of chemicals to the analytical results. Falling in not only is a major disturbance of sediment and sampler but can pose safety problems; thus, selection of a stable place to wade or shore location to reach from is critical. Otherwise suitable sampling sites often are slippery because of water, ice, algae, or mud and unstable substrate such as loose boulders or poorly supported logs. Particularly if the sampler tries to use both hands for handling bottles while leaning over the water sudden loss of balance can occur. The sample should not be collected where the sampler has, if needed, waded or, if unfortunate, fallen. If the sampler is holding the bottles in hand then powder free gloves can minimize contamination from sweat, etc. Laboratory gloves generally cover to the wrist, but longer gauntlet style gloves cover to the elbow and should be used if the sample is collected by hand at depth greater than a few inches. In addition to salts in sweat, common contaminants are sunscreen and insect repellent. All of these potential contaminants can be minimized by rinsing the hands and arms before collection, at a site far enough away that the sampling site itself is not contaminated by the rinsing.

Bottles are individually uncapped, partially filled with sample, capped and shaken, and the rinse water discarded away from where the samples are to be collected, e.g., onshore, downstream, or where the sampler has waded. Three rinses for each bottle are needed unless protocols otherwise indicate (e.g. TOC samples, might not be rinsed). The bottles then are individually filled completely and capped. Especially at sites where surface films contain significant pollen, insect casings, or organic film the bottle should be capped until below the surface and then uncapped to fill. If possible, the cap should be replaced before raising the bottle back through the surface.

Sampling depth needs to be consistent and documented. It often is impractical and unsafe to collect samples deeper than about 1 foot without mechanical devices of some kind. See "point sampling" discussion below.

### *Shallow Samples*

If the site is very shallow, which may be the case for many small streams and the outflow of lakes, it may not be possible to sample that deep. Very shallow streams and seeps may require creative approaches to collecting samples without disturbing sediment. Creating a small dam that allows water to drop into the bottle may be necessary. Pipettes, syringes, or even plastic basters used for cooking can be cleaned and used to transfer sample to the bottle in extreme cases.

### *Pole Samples*

An alternative to collecting grab samples literally by hand is the use of a bottle attached to a jointed pole made of non-contaminating material such as smooth fiberglass or painted aluminum. The pole may be one that serves other purposes, e.g., ski poles or avalanche probes. This approach is safer than leaning over the water surface or wading. Also, this approach allows the sample to be collected farther from shore and at greater depth than can be done by hand. This approach is not suitable for streams with significant velocity because of excessive drag from the assembly. The bottle can be one larger than the sample bottles and used to rinse or fill them. Alternatively, the sample bottles themselves can be directly attached to the pole. Because of buoyancy and leverage it may be impractical to use a bottle larger than about 500 ml capacity and a pole longer than about 4 m. The bottle can be attached to the bottom of the pole with stainless steel hose clamps or laboratory 3-finger style bottle clamps. To minimize the possibility of contamination with surface debris or floating slush, and to allow collection at a

specific depth, the bottle can be plugged with a non-contaminating silicone stopper attached to a line that the sampler pulls when the bottle is at the proper depth. The depth can be estimated or can be measured with a simple float and line attached to the pole near the bottle. Care must be taken to avoid introducing soil, etc. on the pole; it should be soaked prior to use in an area away from the sampling site.

### *Point (Depth) Samples*

Point samples are those collected at a single depth. This may be needed to sample specific layers within a lake, for example, the hypolimnion, or to insure that samples are reproducibly collected from a protocol-specified depth. Van Dorn and Kemmerer bottles are the most common point samplers for lakes. The Van Dorn bottle has some advantage in allowing better circulation of water through the sample bottle. In either case the bottle is difficult to keep clean unless it is kept in a plastic bag between sites. At the site it should be soaked in the lake, from shore is acceptable. At the buoy or otherwise located sample site the bottle should be raised and lowered several times just below the surface to further rinse the bottle. The bottle then is lowered to the desired depth and triggered, usually with a weight that slides down the line holding the bottle. When sampling near the bottom of the lake care should be taken not to touch the bottom, as this will disturb sediment that could contaminate the sample. Sample depth is commonly a meter or so beneath the surface and a similar distance above the bottom. Because of the drag of long lengths of rope and the sampler, both Van Dorn and Kemmerer bottles are prone to sampling at shallower depths than indicated by the length of the rope. If the boat is drifting due to current or wind deeper samples may be in error for depth. In lakes, this can be avoided by anchoring or tying to a buoy. These samplers also tend to plane while being lowered, so allowing the rope to straighten before triggering the bottle can help minimize this error.

Pumps and tubing sometimes are used to collect point samples from lakes and streams, or to integrate samples from lakes. Primary concerns with these devices are keeping the tubing clean (it is impossible to thoroughly clean the inside of bacterial growth), generally by storing filled with deionized water and in a plastic bag; and avoiding disturbance of sediment. The tubing can easily block with slush during freezing conditions. Tubing does offer the ability to collect an integrated sample of the water column of lakes by lowering the tubing, at a constant rate of travel and pumping, to near bottom and back to the surface. This allows proper integration of the sample without knowing how long it takes to fully pump out the water in the tubing, which would be a problem if merely lowering the tubing..

### *Auto Samples*

Autosamplers may be used, particularly at intensively studied sites or at sites where the effects of storm water are studied or where episodic acidification is a concern. Bottles are handled much as bottles used for other sampling. The inlet must be secured to prevent damage during periods of high discharge in streams. The inlet should be located sufficiently above the bottom so as to avoid disturbing sediment but deep enough that it will not be exposed if water level drops. Duplicate samples collected by hand are used to assure that the autosampler collects representative samples.

Autosamplers have advantages over similar grab samples in that they can be programmed to collect samples with many options. For example, they can collect discrete (1 sample per bottle) or integrated (several samples per bottle) samples. Also, they can be activated at regular time intervals, such as daily, or triggered by a rise in stage or the onset of rain - as indicated by signals from a tipping bucket rain-gage. In defining the variance of systems during storms they are more likely to provide data than are grab samples because they are always at the site, no matter the time of day or the weather. The main

disadvantages of autosamplers are difficulty of operation during freezing conditions and the need to have trained personnel to troubleshoot the more complex arrays that may use a variety of weather and hydrologic inputs to control sampling. Proper installation of autosamplers requires a level and stable surface located above the highest water level expected and securing of the sampler by rocks, guy wire, or rebar, etc. to insure that the sampler is not disturbed by melting snowpack, wind, and rising water.

## SAMPLE HANDLING

Sample collection removes the sample from an environment operating at approximately steady state. The counteracting physical and biological influences that maintain surfacewater chemistry fairly constant from day-to-day no longer are in balance within the sample bottle. There are rapid changes in temperature and, perhaps, dissolved oxygen concentration. Without sunlight algae cease to grow whereas zooplankton continue to eat algae and to excrete. Bacteria may thrive on dead algae and the zooplankton excretions. Thus, nutrient concentrations may rapidly change. Trace metals may move from the dissolved state to being adsorbed to bottle walls or being taken up by bacteria. Regarding how rapidly the chemistry may change the sample can be thought of as a dilute soup; the same changes that can cause such a soup to spoil happen to water samples and at comparable rates. The sampler should arrange to have samples analyzed before this "spoilage" can occur.

Immediate analysis is impractical in most field situations except for the common field measurements, such as water temperature, pH, specific conductance, and dissolved oxygen. Chilling immediately after collection to a few degrees above freezing and rapid shipment to the laboratory are the most effective approach if field processing, such as filtering and the addition of preservatives, is impractical. The samples must not freeze because this can break the bottle or cause irreversible precipitation of some constituents, such as dissolved orthophosphate. Holding times before analysis vary among constituents. Morrison (1991) lists holding times between 48 hours (color) and 6 months (major cations and Al). For constituents needed by many programs, 7 days is a practical limit (nitrate and laboratory pH) as long as the samples are kept chilled until analysis is conducted.

## ANCILLARY DATA

Lakes and streams selected for monitoring often are picked to represent the most sensitive component in the area. Because much time and resources are invested in these systems it is easy to forget that they only represent that extreme condition for a particular project. Often, the most important use of monitoring data is for needs that develop later in programs completely different from the one that initiated site selection and monitoring. Thus, at least some effort should be devoted to supplementing the data set by sampling other systems, particularly those located nearby that can be sampled with little additional manpower cost. In addition to broadening the usefulness of the monitoring program such additional sampling may provide great benefits to understanding the main sampling sites.

### *Adjacent Surface Waters*

Other surface water systems nearby can provide information on how generally applicable the data at the main site are. For example, if the main site is a small lake, nearby potholes and streams likely will react differently to runoff from storms or snowmelt. These differences give some idea of how different routing of flow and the materials it contacts occur in the main sampling system as well as in the ancillary systems. It may be useful to sample a much larger lake that has a slower flushing time. Also, this

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approach can be extended to monitoring a few systems that are readily accessible compared to the main site, thereby affording an opportunity to sample during periods when the main site may not be accessible. To the extent that any of the sites operate similarly it greatly improves the statistical validity of conclusions reached for the main site.

### *Atmospheric Deposition*

Because surface water starts out as atmospheric precipitation or as ground water, some monitoring of these systems is critical to understanding the variables controlling surface water chemistry. If possible, atmospheric deposition should be sampled near the lake or stream being monitored, preferably within its watershed. If precipitation sampling is not possible, the nearest monitoring sites maintained by the National Atmospheric Deposition Program/National Trends Network or similar monitoring may be useful in approximating the atmospheric inputs to the watershed. In areas where snowpack is maintained without melting throughout much of the year direct sampling of the snowpack may be a cost-effective method of measuring atmospheric inputs.

### *Ground Water*

Programs designed to monitor surface water chemistry should consider inclusion of some groundwater chemistry. Although drilling of wells is impractical in many study areas, existing wells and natural springs or seeps can be sampled to provide a measure of groundwater chemistry. Because surface water chemistry normally is dependent on some interaction with ground water, knowledge of groundwater chemistry can be used to estimate how much ground water mixes with precipitation to produce the observed lake or stream chemistry, especially if concentrations of constituents in ground water are much larger than in the surface water.

### *Isotopes*

Although the subject of this work is chemistry, a very useful supplement to most watershed chemistry projects is the use of isotopes. Much progress has been made in adapting isotopic techniques to watershed studies, even in inaccessible watersheds located within designated wilderness. It is beyond the scope of this work to discuss how to apply isotopes other than to say what they can add to a chemistry study. Stable isotopes, those not subject to radioactive decay, naturally occur and can provide unambiguous tags on some sources of elements. For example, sulfate from atmospheric emissions sources may differ greatly in isotopic composition from sulfate derived by weathering of bedrock and soil. Thus, it may be possible to apportion how much of the sulfate in a lake or stream is from natural and manmade sources.

Radioisotopes, those that decay to produce other elements, may occur naturally or be introduced as a result of previous nuclear testing. They primarily provide a means of estimating how long it takes for various elements or water to move through a watershed.

The main advantage of isotopic techniques in chemical studies is to possibly provide answers to complex questions rather quickly and cheaply. They do not work in all systems or for all possible questions in any given system. When they do work, the answers they provide may otherwise only have been available in intensively studied systems with large commitments of instrumentation, sampling, and manpower.

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## DATA QUALITY ASSURANCE

### *Long Term Monitoring*

Quality assurance of data is greatly facilitated if a site has been sampled many times before. At a site fairly stable relationships among constituents and with variables such as discharge and season exist and can be used to decide whether new data are suspect. At each site some relationships will be more reliable than others and the quality assurance should be tailored to what works at that site. Suspect data require that the sample be rerun analytically and/or the data flagged in the database.

A stepwise approach to quality assurance of new data makes it possible to minimize the number of constituents that must be rerun. Because such stepwise approaches for each constituent of each sample necessarily generate many graphs and tables, it is very helpful to have it done in electronic format. This also allows rapid update of the useable database as more samples are collected.

The first step in quality assurance of a new analysis can be a comparison of:

- 1) Charge balance between cations and anions. The charge of anions and cations is determined by summing the concentration (in equivalents) times the valence of each ion and can be provided by the laboratory. Basic physics require that the sum of positive and negative charges be zero. Deviations from zero come from random or systematic error in one or more constituents or an incomplete analysis that neglects some significant constituent.
- 2) Calculated and measured specific conductance. Specific conductance can be easily and accurately determined. A fraction of the specific conductance of the sample is contributed by each ion; this contribution can be calculated from the concentration and the "limiting equivalent conductance" a fundamental characteristic of each ion. By summing the calculated contribution from each ion a calculated specific conductance of the sample is determined. Deviation between the calculated and measured specific conductance can indicate whether one or more constituent concentrations are in error, thereby leading to error in the calculated specific conductance. If the calculated value is greater than the measured value some constituent(s) likely err on the high side. If the calculated value is less than the measured value some constituent(s) likely err on the low side or the analysis neglects some constituent that contributes to specific conductance. Guidelines to the application of charge balance and specific conductance calculations to quality assurance are in Appendix 4.

If this first step comparison indicates potential errors the nature of the error can be narrowed. If the specific conductance comparison indicates an error on the high side then the larger of the cation and anion charges is the one more likely in error. If the specific conductance comparison indicates an error on the low side then the smaller of the cation and anion charges is the one more likely in error. Plots of the two calculated charges versus whatever parameters correlate best at the site also can be examined to determine which charge seems to be an outlier. This tells which ions need to be examined as potential outliers, i.e., an anion or a cation.

If, for example, the error is likely a cation with a high side error then each of the major cations can be plotted versus time (Julian date), specific conductance, discharge, or whatever independent variable best correlates with these ions. At least one outlier in the high side direction should be apparent and the sample rerun for that constituent.

In performing these basic quality assurance tests it should be kept in mind that the measured specific conductance may be in error. This is very easily measured and should be rerun if there is any doubt about its accuracy. If a plot of all major ions, both cations and anions, shows outliers in the same

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direction versus measured specific conductance it likely is the specific conductance measurement that is in error.

### *Synoptic (Inventory) Samples*

Although synoptic samples may have few or no historic samples to use for quality assurance it may be possible to do similar stepwise quality assurance of each analysis. Samples from lakes or streams draining terrain similar in geology, elevation, vegetation, etc. may be combined in the plots described above and one or more clusters of relationships may be apparent. These can be used to determine which constituent likely is in error; although, the apparent outliers are more subject to real differences among the sites.

### *Cross Comparison and Sample Archive*

In any sampling program historical data will sometimes be questioned for accuracy. Changes in methodology for sampling and analysis can cause systematic differences in the data that complicate detection of trends. Before any change in methodology is adopted it is important to collect and analyze duplicate samples by the old and new methods. A sufficient number of comparisons to cover the normal range of values and to provide a valid statistical comparison is needed.

Even when care is used in adopting changes in methodology, questions can develop as to the validity of older data or it may be desired to analyze for constituents not originally determined. Archived samples often can determine whether the older data are valid or to expand the constituents determined as new project needs develop. Archives representing the range of values for chemistry can be collected as duplicate samples to be used only for archive purposes or remaining portions of routine samples can be used. Although archive samples necessarily violate holding time requirements for routine samples many constituents may be effectively preserved for an indefinite period. Changes can be minimized by techniques including:

- 1) Filtering the sample.
- 2) Minimizing headspace in the bottle.
- 3) Keeping the samples chilled and in the dark.

Because archived samples require a commitment of time, space, and attention it is desirable and efficient to have a centralized sample archive. A more limited local archive also can be maintained.

### *Responsibility for QA*

Basic quality assurance of data, as discussed above, can be done locally by the office collecting the samples and/or centrally; also, it can be done internally or contracted. Depending upon the expertise and time available it can be done well, poorly, or not at all in any of these choices. The most important decision to make in planning for quality assurance is to assure that someone qualified does it and does it soon after samples have been analyzed. It is almost useless to determine that data are suspect only after the laboratory has discarded the samples; at best, the data only can be deleted or flagged in the data base. To assure that the quality assurance plan is adequate there should be a formal report submitted of what has been done to quality assure data and what is planned for future data. It is critical that whoever reviews and approves the quality assurance report have the proper background and commitment to provide a critical review. Because data may be used for interpretation or in litigation, either immediately or much later after all project personnel have changed, the reports should be archived. Preferably, the reports should be available for review from the same data administrators who provide



the data for public or internal use. Occasional review of the quality assurance process by qualified professionals from outside the agency can help assure that generally accepted approaches are used.

## OTHER NEEDS

### *Training and Field Review*

- 1) There is need for a routine training program in sample collection and processing. Most training, if done at all, seems to be word-of-mouth from present field personnel to new personnel. This does not provide for the level of assurance needed if data go to court. All training should be permanently documented in case this is needed in litigation.
- 2) There is need for field reviews on a regular basis to determine compliance with protocols and effectiveness of training and instructions.

### *Additional Laboratory Responsibilities*

The great majority of projects reviewed here use the Forest & Range Experiment Station Lab in Ft. Collins, Colorado. Thus, it may be especially cost-effective for some needed additions to quality assurance and procurement of field supplies, etc. to be done from this centralized facility. Some examples are:

- 1) Labels - The lab should provide pre-printed, waterproof labels with required data fields to be provided for routine monitoring sites. Since routine sites will have recurring samples it would be easy to standardize labels for each site. By providing the data fields, the lab can help assure that all the information they need to properly identify the sample is provided. The lab could add any unique number they desire for each set to make sure bottle sets are unambiguously separated.
- 2) QA of Supplies - The laboratory is the logical place to most efficiently obtain and perform any needed QA on new lots of bottles, filters and "blank" or reference water samples.
- 3) Sample Archive - There are potential benefits from establishing a sample archive. Such a facility would archive subsamples representing a range of sites nationally. As methods change such archived samples could help resolve questions on method comparability. Also, archived samples could be analyzed for additional constituents as program needs change, if needed. Such a facility is best centralized and the lab seems a likely choice to do this.
- 4) Use of Historical Data in QA of New Data - It would be very helpful to have a site-specific custom approach to initial QA provided by the lab along with the new analytical data as sample analyses are transmitted to the originating office, e.g., provide historical plots of data with an overlay of new data. This would greatly facilitate QA of the data. Much of it could be automated. Collaboration with the NRIS group would be helpful here.

### *Other Suggestions:*

- 1) The data repository (NRIS) is a logical repository for quality assurance documentation. Such doc-

umentation needs to be archived for use in later data interpretation, litigation, etc. Also, someone needs to be appointed to review quality assurance documents, which should be submitted by each project annually.

- 2) There is need for collaboration with researchers inside/outside FS to be sure the latest techniques are being used and that data are being used to fullest. This could be helped by having a position or contract to promote such collaboration for forests that don't have the professional contacts.

## FURTHER READING

This work provides basic guidelines to routine sampling of surface water. There are many alternative approaches, some of which are preferable in certain applications. Some funding sources may require the use of different methods. It is beyond the scope of this work to summarize all approaches to sampling and all that is known about the processes controlling surface water chemistry in all systems. The following references are not light reading, but can be very helpful in gaining a fuller understanding of sampling options and of watershed chemistry. These references contain reference to thousands of other reports for the truly obsessed.

Morrison (1991) provides a description of six regional sampling projects. It discusses sampling, processing, preservation, and analytical protocols. Guidelines are presented for quality assurance decisions on whether data are acceptable, e.g., what level of agreement is required in charge-balance comparisons and in measured versus calculated specific conductance.

The National Field Manual for the Collection of Water-Quality Data presents thorough discussion of protocols for: selection and cleaning of sampling equipment (Wilde and others, 1998-1999); collection of samples by more-complex methods than described here; microbiological indicators; and field measurements.

Acidic Deposition and Aquatic Ecosystems - Regional Case Studies, Donald F. Charles ed., contains detailed interpretations of important watershed processes in 11 regions of the United States and Canada. Experts in each region present the individual regions. Also, there are general discussions of watershed chemistry and of effects of acid deposition on aquatic ecosystems.

The eastern and western lake surveys conducted by the U.S. Environmental Protection Agency and the Forest Service are summarized in five volumes that describe the study design, sampling approach, quality assurance, and physical and chemical data for lakes thought to be sensitive to acid deposition: Eilers and others, 1987; Kanciruk and others, 1986; Landers and others, 1987; Linthurst and others, 1986; and Overton and others, 1986.

Environmental Monitoring and Assessment Program - Field Manual for Lakes, Baker and others, ed., provides detailed discussion for sampling lakes for fish, zooplankton, phytoplankton, benthic invertebrates, chlorophyll a, Secchi disk depth, and sediment diatoms.

The stream survey of the mid-Atlantic and southeastern United States (Kaufmann and others, 1988; Sale and others, 1988) describe study design, sampling approach, quality assurance, and physical and chemical data for streams thought to be sensitive to acid deposition.

The stream watersheds sampled by the U.S.G.S.'s Hydrologic BenchMark Network are described in

detail by Clark and others (2000); Mast and Turk (1999a,b); Mast and Clow (2000). These reports also provide trend analysis and quality assurance of the historic data.

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## APPENDIX 1: EXISTING PROTOCOLS

**PROJECT:** Alpine Lakes Wilderness Area

**PARAMETERS/METHODS:** variable, but include -

Ca<sup>+2</sup>, Mg<sup>+2</sup>, K<sup>+</sup>, Na<sup>+</sup>

NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, organic N, Kjeldahl N, and total P

SO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup>, F<sup>-</sup>

Si

lab alkalinity and specific conductance

Profiles of temperature and dissolved oxygen

Visibility by Secchi disk

**LABORATORY:** U.S. Geological Survey, Arvada, CO (chemistry); Dr. Fred Mangum, Provo, UT (macroinvertebrates and zooplankton)

**NUMBER OF SITES:** 60 lakes

**SAMPLING FREQUENCY:** once

**SEASONAL COVERAGE:** not specified but presumed to be summer

**SAMPLING METHOD:** Van Dorn point sampler (presumed) from raft or helicopter; 1m depth (epilimnion); 1-2m above bottom (hypolimnion); temperature and dissolved oxygen profile

**SAMPLE INTEGRITY:** not discussed

**SAMPLING LOCATION:** at deepest point

**FIELD NOTEBOOKS/FORMS:** not discussed

**TRAINING:** not discussed

**DESIGNATED SAMPLING PERSONNEL:** not discussed

**QA/QC METHODS:** not discussed

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** not discussed

**DISCUSSION:**

**REFERENCES:**

Dethier, D.P., Heller, P.L., and Safioles, S.A., 1979, Reconnaissance data on lakes in the alpine lakes wilderness area: U.S. Geological Survey Open-File Report 79-1465

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**PROJECT:** Bob Marshall Wilderness Area

**PARAMETERS/METHODS:**

DOC by persulfate oxidation, infrared CO<sub>2</sub>  
DIC by acid liberation, infrared CO<sub>2</sub>  
Ca<sup>+2</sup>, Mg<sup>+2</sup>, K<sup>+</sup>, Na<sup>+</sup> by flame atomic absorption  
Total N, NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> by persulfate digestion, cadmium reduction, phenate  
Soluble, soluble reactive, and total P by ascorbic acid  
SO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup> by ion chromatography  
ANC by Gran titration  
chlorophyll a by acetone extraction  
phytoplankton by Utermohl counts  
zooplankton by Sedgewick-Rafter counts  
water balance

**LABORATORY:** Flathead Lake Biological Station

**NUMBER OF SITES:** 2 lakes

**SAMPLING FREQUENCY:** 1-2/year

**SEASONAL COVERAGE:** July, 1991; September, 1991; April, 1992

**SAMPLING METHOD:** Van Dorn point sampler from raft; 1m depth (epilimnion); 17m (hypolimnion); also, integrated profile samples; temperature, pH, dissolved oxygen, specific conductance profiles; phytoplankton and zooplankton profiles with plankton net

**SAMPLE INTEGRITY:**

Bottles provided by laboratory, rinsed with acid and sample  
Samples filtered for some parameters  
Nitric acid preservation of cations, metals  
Some samples frozen

**SAMPLING LOCATION:** not discussed

**FIELD NOTEBOOKS/FORMS:** not discussed

**TRAINING:** not discussed

**DESIGNATED SAMPLING PERSONNEL:** not discussed

**QA/QC METHODS:** comparison of replicates; recovery of standard additions; round robin check samples

**RERUN DETERMINATION:** not discussed except as part of lab QA/QC

**QA REPORT:** not discussed

**DATA REPOSITORY:** Flathead Lake Biological Station

**DISCUSSION:**

**REFERENCES:****PROJECT:** Cabinet/Selway Phase 3**PARAMETERS/METHODS:**Ca<sup>+2</sup>, Mg<sup>+2</sup>, K<sup>+</sup>, Na<sup>+</sup>

Si, Al,

NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, PSO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup>

Chlorophyll a

Lab alkalinity (Gran titration) and specific conductance

**LABORATORY:** Rocky Mountain Forest and Range Experiment Station, Ft. Collins, CO**NUMBER OF SITES:** 2 (Upper Libby, Lower Libby)**SAMPLING FREQUENCY:** 2/year, duplicates 2/year, field (not process) blank 1/trip**SEASONAL COVERAGE:** summer only**SAMPLING METHOD:** washed gloves from raft; 0.5m depth (epilimnion); phytoplankton by integrated depth sample using pump and tubing**SAMPLE INTEGRITY:**

Bottles, 250 ml. amber plastic from Rocky Mountain Forest &amp; Range Experiment Station Lab

Samples filtered for some parameters

Phytoplankton preserved with Lugol's solution

Chlorophyll a chilled in dark

Samples shipped to laboratory by 2nd day-air on ice packs

**SAMPLING LOCATION:** at deepest part of lake**FIELD NOTEBOOKS/FORMS:**

Field notebook and bottle labels discussed in instructions to samplers

**TRAINING:** not discussed**DESIGNATED SAMPLING PERSONNEL:** not discussed**QA/QC METHODS:** not discussed**RERUN DETERMINATION:** not discussed**QA REPORT:** not discussed**DATA REPOSITORY:** R1 Excel spreadsheets and in NRIS Air database**DISCUSSION:****REFERENCES:**

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**PROJECT:** Cohutta Wilderness Area

**PARAMETERS/METHODS:**

DOC (1992-93)

Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>

Al (1994-99)

NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and PO<sub>4</sub><sup>-3</sup> (1994-99)

SO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup>, F<sup>-</sup>

Si (1994-99)

Water temperature, field conductance (1992-93), lab conductance (1994-99), lab pH, field pH (1992-93), and alkalinity (1992-93) or ANC (1994-99)

**LABORATORY:** North Georgia College, Biology Department (1992-93); Rocky Mountain Forest and Range Experiment Station (1994-98)

**NUMBER OF SITES:** Varies – 11 (1992); 9 (1993); 5 (1994); 4 (1998); 4 (1999).

**SAMPLING FREQUENCY:** not discussed

**SEASONAL COVERAGE:** 6/22 --7/09, 1992; 7/10 --7/23, 1993; 6/15 – 6/16, 1994; 5/07 – 5/09, 1998; 9/01 – 9/02, 1999 Base flow all years.

**SAMPLING METHOD:** grab samples from middle of stream

**SAMPLE INTEGRITY:**

Bottles presumably provided by laboratory

Samples filtered for some parameters (1994-99)

Nitric acid preservation and chilling of metals and P

H<sub>2</sub>SO<sub>4</sub> preservation and chilling of NH<sub>4</sub><sup>+</sup>

Samples shipped to laboratory on ice

After 1993 samples frozen

**SAMPLING LOCATION:** Perennial streams sampled mid-stream, flowing water, just below surface.

**FIELD NOTEBOOKS/FORMS:** not discussed

**TRAINING:** Provided by Professor Mac Callaham, Ph.D. (1992-93); by Dave Wergowske, M.S. (1994-99)

**DESIGNATED SAMPLING PERSONNEL:** students (1992-93); Forest Service crew (1994-99)

**QA/QC METHODS:** Review raw data for anomalous values. Lab reviews, split/blank sampling unknown (1992-93); Review raw data for anomalous values. Lab reviews acid/base balance, ion balance & theoretical/actual conductivity ratio. Lab runs blanks and split samples per its own schedule (1994-99).

**RERUN DETERMINATION:** none

**QA REPORT:** Provided with raw data (1994-99)

**DATA REPOSITORY:** Forest Air Resource Specialist

**DISCUSSION:**

**REFERENCES:**



**PROJECT:** Colorado lakes

**PARAMETERS/METHODS:**

Field pH by 2-buffer method, repetitive measurement, and check sample, Glass body Ross combination electrode

ANC by Gran titration

Specific conductance by YSI 32 meter

DOC by UV oxidation, Dohrman method

DIC by Dohrman method

Ca<sup>2+</sup>, Mg<sup>2+</sup> by inductively coupled plasma

K<sup>+</sup>, Na<sup>+</sup> by low level atomic absorption spectrophotometry

Al by DC plasma spectrometer

Si by inductively coupled plasma

NH<sub>4</sub><sup>+</sup> by Technicon AutoAnalyzer ortho and total PO<sub>4</sub><sup>-3</sup>

SO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup>, F<sup>-</sup>, NO<sub>3</sub><sup>-</sup> by ion chromatography

Color by comparator

Streamflow (inflow and outflow streams)

**LABORATORY:** U.S. Geological Survey, Arvada, CO; see discussion below

**NUMBER OF SITES:** 9 lakes, plus 4 inflows and 4 outflows

**SAMPLING FREQUENCY:** variable, 2-7/year

**SEASONAL COVERAGE:** July-September

**SAMPLING METHOD:** Van Dorn point sampler from raft; 0.5m depth (epilimnion); 1-2m above bottom (hypolimnion); temperature and dissolved oxygen profiles; duplicate and field process blank samples each trip

**SAMPLE INTEGRITY:**

Bottles provided by U.S. Geological Survey laboratory in Arvada, CO

Bottles for DOC are fired

Bottles for cations and metals are washed in nitric acid and rinsed with deionized water and sample; bottles for nutrients and anions soaked in deionized water at least 3 days and rinsed with sample

Samples filtered for most parameters

Nitric acid preservation of cations, metals

Samples delivered to laboratory at end of field trip, on ice

**SAMPLING LOCATION:** at designated buoy at deepest point (4 lakes); from shoreline in area of good circulation (5 lakes) - see discussion below

**FIELD NOTEBOOKS/FORMS:** Field notebook and bottle labels discussed in instructions to samplers

**TRAINING:** provided by project chief

**DESIGNATED SAMPLING PERSONNEL:** yes

**QA/QC METHODS:** calculated vs. measured specific conductance, anion/cation balance, round robin

samples, duplicates, field process blanks, filter blanks

**RERUN DETERMINATION:** based on deviation from quality objectives (see QA/QC methods) and historical data

**QA REPORT:** annual

**DATA REPOSITORY:** maintained by project staff and regular transfers to USEPA and USDA-FS

**DISCUSSION:** change in laboratory and sampling methods in 1990; after this time analyses performed by project scientists and all samples collected from shoreline

**REFERENCES:**

Marilyn Morrison, 1991, Data user's guide to the United States Environmental Protection Agency's long-term monitoring project: Quality assurance plan and data dictionary: EPA 600/3-91/072

**PROJECT:** Desolation Wilderness lake monitoring

**PARAMETERS/METHODS:**

Alkalinity by Gran method

Ca<sup>+2</sup>, Mg<sup>+2</sup>, K<sup>+</sup> by atomic absorption

Na<sup>+</sup> by flame emission spectroscopy

SO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> by ion chromatography (FAS-SEP column by Dionex, bicarbonate eluant)

Chlorophyll a by methanol extraction

Field pH by pH paper

Transparency by Secchi disk

Laboratory pH by pH meter and electrode

Laboratory specific conductance by conductivity meter

Laboratory alkalinity by Gran titration

Zooplankton and macroinvertebrates

Streamflow of outflow and inlets

**LABORATORY:**

Dr. Aaron Brown, Riverside, CA (major cations and anions)

Dr. Ranjit Gil, South Lake Tahoe, CA (chlorophyll a)

LTBMU (Lake Tahoe Basin Management Unit) (alkalinity)

**NUMBER OF SITES:** 1 lake, 1 outflow, 2 inflows

**SAMPLING FREQUENCY:** 3/year minimum

**SEASONAL COVERAGE:** not discussed but presumed to be summer

**SAMPLING METHOD:** Van Dorn from raft, 1.5 m below surface; some samples pumped from 1.5 m below surface; temperature profile

**SAMPLE INTEGRITY:** some samples filtered; bottles rinsed with HCl and deionized water

**SAMPLING LOCATION:** deepest part of lake; inlets and outlet not discussed

**FIELD NOTEBOOKS/FORMS:** not discussed

**TRAINING:** not discussed

**DESIGNATED SAMPLING PERSONNEL:** not discussed

**QA/QC METHODS:** not discussed

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** not discussed

**DISCUSSION:**

**REFERENCES:**

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**PROJECT:** Dolly Sods and Otter Creek Wilderness Areas amphibian study

**PARAMETERS/METHODS:**

pH, specific conductance, alkalinity and acidity, methods not discussed

DOC

Ca<sup>+2</sup>, Mg<sup>+2</sup>, K<sup>+</sup>, Na<sup>+</sup>

NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>

SO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup>

water temperature, dissolved oxygen

**LABORATORY:** Fernow Experimental Laboratory, Parsons, WVA

**NUMBER OF SITES:** 5

**SAMPLING FREQUENCY:** variable

**SEASONAL COVERAGE:** May-October

**SAMPLING METHOD:** not discussed

**SAMPLE INTEGRITY:** not discussed

**SAMPLING LOCATION:** not discussed

**FIELD NOTEBOOKS/FORMS:** not discussed

**TRAINING:** not discussed

**DESIGNATED SAMPLING PERSONNEL:** not discussed

**QA/QC METHODS:** not discussed

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** not discussed

**DISCUSSION:** Primarily an amphibian study; chemistry is ancillary.

**REFERENCES:** Unresolved: May have had analyses done by CSU soils lab one year. May presently be done by Rocky Mountain station lab.

**PROJECT:** Emigrant Wilderness

**PARAMETERS/METHODS:** Field pH by Hack Kit, Model AL36-B

**LABORATORY:** none

**NUMBER OF SITES:** 64 lakes; 26 streams; many sampled in several years

**SAMPLING FREQUENCY:** 4/year, duplicates 4/year

**SEASONAL COVERAGE:** summer

**SAMPLING METHOD:** lakes at least 1 ft. below surface, from shoreline; streams in deepest section

**SAMPLE INTEGRITY:** Bottles not discussed

**SAMPLING LOCATION:** not discussed

**FIELD NOTEBOOKS/FORMS:** not discussed

**TRAINING:** not discussed

**DESIGNATED SAMPLING PERSONNEL:** not discussed

**QA/QC METHODS:** not discussed

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** not discussed

**DISCUSSION:**

**REFERENCES:**

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**PROJECT:** George Washington National Forest rapid bioassessment

**PARAMETERS/METHODS:** not discussed

**LABORATORY:** not discussed

**NUMBER OF SITES:** not discussed

**SAMPLING FREQUENCY:** not discussed

**SEASONAL COVERAGE:** not discussed

**SAMPLING METHOD:** not discussed

**SAMPLE INTEGRITY:** not discussed

**SAMPLING LOCATION:** not discussed

**FIELD NOTEBOOKS/FORMS:** not discussed

**TRAINING:** not discussed

**DESIGNATED SAMPLING PERSONNEL:** not discussed

**QA/QC METHODS:** not discussed

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** not discussed

**DISCUSSION:** Refers to Standard Methods (below) but does not specify which of the optional methods are used

**REFERENCES:** Standard methods for the examination of water and wastewater (17th ed.), 1989, American Public Health Association, Washington, D.C.

**PROJECT:** GLEES**PARAMETERS/METHODS:**

Analytical methods and parameters not discussed

streamflow

temperature, dissolved oxygen, specific conductance, pH profiles

zooplankton

phytoplankton

chlorophyll a

**LABORATORY:** Rocky Mountain Forest and Range Experiment Station

**NUMBER OF SITES:** 4 streams, 2 lakes

**SAMPLING FREQUENCY:** weekly

**SEASONAL COVERAGE:** all year

**SAMPLING METHOD:** tubing and peristaltic pump from raft; point samples (depth not specified) and integrated samples of water column, plastic gloves used; samples collected at deepest point or buoy; temperature, dissolved oxygen, specific conductance, pH profiles; zooplankton profile with plankton net; inlet/outlet streams sampled using plastic gloves and sampling upstream from sampler

**SAMPLE INTEGRITY:** Bottles provided by laboratory, rinsed with deionized water and sample; samples filtered for some parameters; samples shipped to laboratory by overnight delivery on ice.

**SAMPLING LOCATION:** at designated buoy or deepest location (lake); inlet/outlet streams sampled upstream of lake or flume

**FIELD NOTEBOOKS/FORMS:** Field notebook and bottle labels discussed in instructions to samplers

**TRAINING:** not specifically discussed; extensive documentation of instrument calibration/servicing available onsite

**DESIGNATED SAMPLING PERSONNEL:** not discussed

**QA/QC METHODS:** not discussed

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** not specifically discussed for surface water, but presumably Rocky Mountain Forest and Range Experiment Station

**DISCUSSION:** Excellent documentation of sampling routine, availability of calibration manuals, field forms.

**REFERENCES:**

**PROJECT:** Inyo National Forest streams

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**PARAMETERS/METHODS:**

pH, method not discussed  
Specific conductance, method not discussed  
Turbidity, method not discussed  
Dissolved oxygen, method not discussed  
Streamflow, method not discussed

**LABORATORY:** not discussed

**NUMBER OF SITES:** not discussed

**SAMPLING FREQUENCY:** not discussed

**SEASONAL COVERAGE:** not discussed

**SAMPLING METHOD:** not discussed

**SAMPLE INTEGRITY:** not discussed

**SAMPLING LOCATION:** not discussed

**FIELD NOTEBOOKS/FORMS:** not discussed

**TRAINING:** not discussed

**DESIGNATED SAMPLING PERSONNEL:** not discussed

**QA/QC METHODS:** not discussed

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** not discussed

**DISCUSSION:** Refers to reference below, but does not specify which optional methods are used

**REFERENCES:**

National handbook of recommended methods for water-data acquisition, 1977, U.S. Geological Survey, Reston, VA



**PROJECT:** Lye Brook Wilderness Area

**PARAMETERS/METHODS:**

Field pH by 2-buffer method  
Alkalinity by Gran titration  
Specific conductance by YSI Model 32 meter  
DOC by persulfate oxidation, infrared dispersion  
Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup> by Perkin Elmer 3030B  
Inorganic and organic monomeric Al by pyrocatechol violet  
NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup> by ion chromatography  
Color, filtered, by spectrophotometry  
Visibility by Secchi disk  
Water temperature by Cole Parmer thermistor (lakes) or mercury thermometer (streams)  
Macroinvertebrates, sediment chemistry, fish tissue chemistry

**LABORATORY:** Vermont DEC Reginald A. LaRosa Laboratory

**NUMBER OF SITES:** 3 lakes and 6 stream sites

**SAMPLING FREQUENCY:** variable, 1-8/year

**SEASONAL COVERAGE:** May-October

**SAMPLING METHOD:** Kemmererpoint sampler from canoe; 1m depth (epilimnion); 1-2m above bottom (hypolimnion); temperature profiles

**SAMPLE INTEGRITY:**

Bottles provided by laboratory, rinsed with deionized water and sample  
Samples filtered for some parameters  
Presumably, N Nitric acid preservation of cations, metals  
Samples shipped to laboratory on ice

**SAMPLING LOCATION:** not discussed

**FIELD NOTEBOOKS/FORMS:** Field notebook discussed

**TRAINING:** not discussed

**DESIGNATED SAMPLING PERSONNEL:** not discussed

**QA/QC METHODS:** not specifically discussed

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** not discussed

**DISCUSSION:**

**REFERENCES:**

Vermont Department of Environmental Conservation. 1989. Field methods manual. VT DEC, Waterbury, VT  
Vermont Department of Environmental Conservation. 1992. Laboratory quality assurance plan. VT DEC, Waterbury, VT.

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**PROJECT:** Mission Mountains

**PARAMETERS/METHODS:**

Field pH by pH paper  
Field alkalinity by titrator, fixed endpoint  
Periphyton  
lab pH, alkalinity (Gran titration), and specific conductance

**LABORATORY:** Rocky Mountain Forest and Range Experiment Station, Ft. Collins, CO

**NUMBER OF SITES:** 20 lakes

**SAMPLING FREQUENCY:** once only, in 1995

**SEASONAL COVERAGE:** summer

**SAMPLING METHOD:** washed hands from shoreline; 0.5m depth (epilimnion)

**SAMPLE INTEGRITY:**

Bottles, 250 ml., amber plastic from Rocky Mountain Forest & Range Experiment Station Lab  
Samples shipped to laboratory by 2nd day-air on ice packs

**SAMPLING LOCATION:** at downwind part of lake

**FIELD NOTEBOOKS/FORMS:** Field notebook and bottle labels discussed in instructions to samplers

**TRAINING:** not discussed

**DESIGNATED SAMPLING PERSONNEL:** not discussed

**QA/QC METHODS:** not discussed

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** R1 Excel spreadsheets and NRIS Air database

**DISCUSSION:**

**REFERENCES:**

**PROJECT:** "Mount Baker-Snoqualmie N.F. Lake Inventory" – Method used on MBSNF since 1996 to collect lake water samples to support the needs of Region 6 Air program relating to monitoring for acidic deposition. The variables included, and methods followed, fairly closely follow those used in Phase I of the Western Lakes Survey (EPA 1985), which was a component of the nationwide survey of surface waters conducted by the EPA in the mid-1980s.

**PARAMETERS/METHODS:**

Major ions - Lab analysis of:  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{K}^{+}$ ,  $\text{Na}^{+}$ ,  $\text{Cl}^{-}$ ,  $\text{SO}_4^{-2}$  (mg/l). Collect 500 ml sample at 1.5 m depth with Van Dorn.

Nitrate-nitrite and total dissolved P - Lab analysis only. Western Lake Survey standards and QA/QC followed. Collect sample by Van Dorn at 1.5 meter depth.

pH - Lab analysis only because of low confidence in Hydro-lab results in initial years (likely due to the very dilute nature of the oligotrophic and ultra-oligotrophic waters being sampled). Collect sample by Van Dorn at 1.5 meter depth.

Conductivity: In situ – measure at 1.5 m, 3.0 m, 5.0 m, and varied additional intervals for deeper lakes with a Hydro-lab or other equipment with equivalent precision and accuracy (microsiemens/cm). Lab - (microsiemens/cm).

Acid Neutralizing Capacity: Lab only – difference between the sum of the basic cations and the acidic anions (not equivalent to method of computing alkalinity).

Secchi depth : In situ average of depth lowering and raising (meters).

Temperature : In situ only – measure at 1.5 m, 3.0 m, 5.0 m, and varied additional intervals for deeper lakes with a Hydro-lab or other equipment with equivalent precision and accuracy. In some cases where electronic equipment was not available, a profile was estimated by measuring temperatures of Van Dorn samples collected at each depth with a field mercury thermometer.

Dissolved Oxygen: In situ measurement abandoned due to problems with Hydro-lab and other field equipment. No measurements planned for near term.

Phytoplankton – A 250 ml bottle with Lugals solution is used to hand collect sample at surface (per laboratory recommendation). Lab analyzes species composition and volume.

Zooplankton – Samples collected with a 1.0 feet diameter opening tow net. When possible, samples are collected by pulling the plankton net from just above the lake bottom to the surface. In very deep lakes, samples are collected to whatever depths are practical (before death occurs from drowning in bloody small raft in white caps). Lab analyzes to species compositional and volume, accompanied by in depth narrative discussion

Chlorophyll a – A 250 ml amber bottle is used to receive a sample collected at 1.5 meter depth from a Van Dorn.

Fish – No samples have yet been collected during this program. Samples may be collected by either gill netting or hook and line in the future in selected lakes if such sampling would markedly increase the knowledge of fish conditions above the current database maintained by inland fish biologists of the Washington State Department of Fish and Wildlife. Such a scenario has not yet arisen in the lakes since 1996

**LABORATORY:** All variables except for Total Phosphorous, Chlorophyll a, phytoplankton, and zooplankton are analyzed by the U.S. Forest Service Laboratory in Fort Collins, Colorado (Louise O'Deen coordinator). Laboratory QA/QC is available upon demand. A duplicate sample is submitted every 5-10 samples. The Ft. Collins lab runs splits every 5-10 samples, and sends out a replicate to a second lab every \_\_\_ samples. In 1996-1998 some replicate samples were also sent to a private lab in Gainesville, Florida (suspended due to cost). Chlorophyll a, TP, and phytoplankton are analyzed by Aquatic Analysts in Portland, Oregon (Jim Sweet coordinator). Laboratory QA/QC is available upon demand. Zooplankton samples are analyzed by Mike Swayne in Portland, Oregon. Laboratory QA/QC is available upon demand.

All sample bottles are acid washed, leak proof, and clearly marked for use in the field, with any appropriate preserving agents. All samples are kept cold with ice packs in coolers in the field, and shipped overnight delivery to labs for analysis. Plan to send a duplicate sample from one lake, to the lab. Check for accuracy. In addition, send a replicate sample to another contracted lab. Compare results, change labs if necessary."

**NUMBER OF SITES:** Approximately 10-15 lakes sampled each year. Almost all lakes sampled in Class I Wilderness Areas.

**SAMPLING FREQUENCY:** Most sites sampled only once in the Fall. Few have been sampled in more than one year to date since 1996 when the program started.

**SEASONAL COVERAGE:** Every lake to be sampled in any one year is at least sampled in the Fall, preferably after Fall turnover (the goal). In some years, some of these Fall lakes are also sampled in the Spring during melt out. The goal is to collect samples during pH spikes due to melting snow pack. The rough indicator used to approximate this time is when about 10-20% of the lake surface is ice free.

**SAMPLING METHOD:** Most Fall water quality samples are collected in a Van Dorn at 1.5 meter depth (per Western Lakes Survey methods) from a raft near what is known (or thought) to be the deepest point of the lake. In very shallow lakes/ponds grab samples were taken by wading. In the spring, grab samples are taken at the outlet by hand.

**SAMPLE INTEGRITY:**

- Zooplankton preserved with an unknown solution
- Phytoplankton preserved with Lugols solution
- Samples shipped by overnight delivery to laboratory on ice packs

**SAMPLING LOCATION:** Fall samples – From raft at approximately at deepest point if known, otherwise near estimated deepest point. Spring samples – Grab sample at outlet.

**FIELD NOTEBOOKS/FORMS:** All observations and notes recorded in field in Rite-in-Rain notebook. No forms presently in use.

**TRAINING:** Training of Tyler Patterson by Barry Gall. Intermittent consultation regarding sampling methods and data interpretation with Joe Eilers (a lead in EPA's Western Lakes Survey, and currently an environmental consultant ).

**DESIGNATED SAMPLING PERSONNEL:** Barry Gall (hydrology and fisheries MBSNF) and Tyler Patterson (fisheries MBSNF) are only samplers to date.

**QA/QC METHODS:** Not documented to date. Lab QA/QC is available from contracted labs.

**RERUN DETERMINATION:** Available from lab upon request.

**QA REPORT:** Available from lab upon request.

**DATA REPOSITORY:** Available from lab upon request.

**DISCUSSION:**

**REFERENCES:**

**PROJECT:** Okanogan-Wenatchee National Forests Lake Inventory – Method used on Wenatchee National Forest since 1995 and the Okanogan NF beginning in 2001, to collect lake water samples to support the needs of Region 6 Air program relating to monitoring for acidic deposition. The variables included, and methods followed, fairly closely follow those used in Phase I of the Western Lakes Survey (EPA 1985).

High lakes have been sampled on the Wenatchee National Forest since 1989 using R6 protocol. Collection of visual observations of terrestrial habitat and amphibians is also conducted.

**PARAMETERS/METHODS:**

Major ions - Lab analysis of:  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{-2}$  (mg/l). Collect 500 ml sample at 1.5 m depth with Van Dorn.

Nitrate-nitrite and total dissolved P - Lab analysis only. Western Lake Survey standards and QA/QC followed. Collect sample by Van Dorn at 1.5 meter depth.

pH - Lab analysis only because of low confidence in Hydro-lab results in initial years (likely due to the very dilute nature of the oligotrophic and ultra-oligotrophic waters being sampled). Collect sample by Van Dorn at 1.5 meter depth.

Conductivity: In situ – measure at 1.5m, 3.0m, 5.0m, and varied additional intervals for deeper lakes with a Hydro-lab or other equipment with equivalent precision and accuracy (microsiemens/cm).  
Lab - (microsiemens/cm).

Acid Neutralizing Capacity: Lab only – difference between the sum of the basic cations and the acidic anions (not equivalent to method of computing alkalinity).

Fecal Coliform: A 250 ml sample is collected near the outflow of the lake. Analysis is conducted by local health department laboratories. This is not done at every lake due to a 24 hour turn-around time, but extra effort is made at high use lakes and areas used by pack stock.

Secchi depth : In situ average of depth lowering and raising (meters).

Temperature : In situ only – measure at surface, 1.5 m, and at 1-2 m intervals to the bottom for all lakes with a Hydro-lab or other equipment (YSI meter) with equivalent precision and accuracy. In some cases where electronic equipment was not available, a profile was estimated by measuring temperatures of Van Dorn samples collected at each depth with a field mercury thermometer.

Dissolved Oxygen: In situ measurement at surface, 1.5m, and at 1-2m intervals to the bottom (taken in conjunction with temperature).

Phytoplankton – A 250 ml bottle with Lugals solution is used to hand collect sample at surface (per laboratory recommendation). Lab analyzes species composition and volume.

Zooplankton – Samples collected with a 1.0 foot diameter opening tow net. When possible, samples are collected by pulling the plankton net from just above the lake bottom to the surface. In very deep lakes, samples are collected to whatever depths are practical (before death occurs from drowning in bloody small raft in white caps). Lab analyzes to species composition and volume, accompanied by in depth narrative discussion.

Chlorophyll a – A 250 ml amber bottle is used to receive a sample collected at 1.5 meter depth from a Van Dorn.

Fish – Samples are collect using hook and line. Number of personnel and hours spent fishing are recorded to determine catch-per-unit-effort (CPUE). If possible, 20 samples are collected. After collection, the length of each fish is recorded, visual observations of condition (lesions), and we have previously taken otolith samples to determine year class (otoliths were examined by local WDFW biologist until 1998). Starting in 2001 we intend to begin taking non-lethal scale samples which will be examined by USFWS at the Leavenworth Fish Hatchery.

**LABORATORY:** All variables except for Total Phosphorous, Chlorophyll a, phytoplankton, and zooplankton are analyzed by the U.S. Forest Service Laboratory in Fort Collins, Colorado (Louise O'Deen coordinator). Laboratory QA/QC is available upon request. A duplicate sample is submitted every 5-10 samples. The Ft. Collins lab runs splits every 5-10 samples, and sends out a replicate to a second lab periodically (frequency unknown). In 1996-1998 some replicate samples were also sent to a private lab in Gainesville, Florida (suspended due to cost and low confidence in lab). Chlorophyll a, TP, and phytoplankton are analyzed by Aquatic Analysts in Portland, Oregon (Jim Sweet coordinator). Laboratory QA/QC is available upon request. Zooplankton samples are analyzed by Allan Vogel, (contracted through Jim Sweet) in Keizer, Oregon. Laboratory QA/QC is available upon request.

All sample bottles are acid washed, leak proof, and clearly marked for use in the field, with any appropriate preserving agents. All samples are kept cold with ice packs in coolers in the field, and shipped overnight delivery to labs for analysis.

**NUMBER OF SITES:** Approximately 5 lakes sampled each year. Most lakes sampled are in Class I Wildernesses, some in Class II wildernesses.

**SAMPLING FREQUENCY:** Most sites sampled only once in the Fall. Few have been sampled in more than one year to date since 1996 when the program started.

**SEASONAL COVERAGE:** Every lake to be sampled in any one year is at least sampled in the Fall, preferably after Fall turnover (the goal). In some years, some of the selected lakes are first sampled in the Spring during melt out to attempt to capture any acid flush event. The rough indicator used to approximate melt out is when about 10-20% of the lake surface is ice free. (The Okanogan-Wenatchee National Forests have not conducted any spring sampling as of 2001.)

**SAMPLING METHOD:** Most Fall water quality samples are collected in a Van Dorn at 1.5 meter depth (per Western Lakes Survey methods) from a raft near what is believed to be the deepest point of the lake. In very shallow lakes/ponds grab samples were taken by wading. In the spring, grab samples are taken at the outlet by hand.

**SAMPLE INTEGRITY:**

Phytoplankton preserved with Lugols solution  
Samples shipped by overnight delivery to laboratory on ice packs

**SAMPLING LOCATION:** Fall samples – From raft at approximately at deepest point if known, otherwise near estimated deepest point. Spring samples – Grab sample at outlet.

**FIELD NOTEBOOKS/FORMS:** All observations and notes recorded in field in Rite-in-Rain notebook and on forest lake monitoring forms, prepared from the R6 High Lakes protocol.

**TRAINING:** Training of personnel in the use of sampling equipment is done by Diane Driscoll. Review and practice in using equipment is conducted a few days prior to the field trip with any personnel that may assist in the collection of water chemistry, zooplankton or phytoplankton samples.

**DESIGNATED SAMPLING PERSONNEL:** Diane Driscoll (Fisheries biologist) or a district fish biologist trained in the use of collection protocols is responsible for water chemistry, zooplankton and phytoplankton samples

**QA/QC METHODS:** Not documented to date. Lab QA/QC is available from contracted labs.

**RERUN DETERMINATION:** Unknown.

**QA REPORT:** None at this time.

**DATA REPOSITORY:** Available from MBS air quality specialist.

**DISCUSSION:**

**REFERENCES:** R6 High Lakes Protocol.



**PROJECT:** Ouachita National Forest

**PARAMETERS/METHODS:** not discussed

**LABORATORY:** not discussed

**NUMBER OF SITES:** not discussed

**SAMPLING FREQUENCY:** not discussed

**SEASONAL COVERAGE:** not discussed

**SAMPLING METHOD:** not discussed

**SAMPLE INTEGRITY:**

Bottles rinsed with sample

Samples filtered for some parameters

Acid preservation of some samples

Samples on ice

**SAMPLING LOCATION:** not discussed

**FIELD NOTEBOOKS/FORMS:** Field form shown in instructions to samplers

**TRAINING:** not discussed

**DESIGNATED SAMPLING PERSONNEL:** not discussed

**QA/QC METHODS:** not discussed

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** not discussed

**DISCUSSION:** Instructions say to put broken acid ampoule in sample bottle for acidified samples.

**REFERENCES:**

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**PROJECT:** Pacific Southwest lake protocol

**PARAMETERS/METHODS:**

Water temperature

Ca<sup>+2</sup>, Mg<sup>+2</sup>, Na<sup>+</sup>

NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, ortho and total PO<sub>4</sub><sup>-3</sup>

SO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup>, Br<sup>-</sup>

Lab pH, alkalinity, and specific conductance

**LABORATORY:** Rocky Mountain Forest & Range Experiment Station Lab.

**NUMBER OF SITES:** not discussed

**SAMPLING FREQUENCY:** not discussed

**SEASONAL COVERAGE:** not discussed

**SAMPLING METHOD:** Grab samples with bottle capped until under water surface and before removing from lake. Rinsed with sample 3 times. Collected at depth 0-.5m as needed to avoid disturbing sediment. Long gloves worn by sampler and only used once. Bottles labeled before sampling.

**SAMPLE INTEGRITY:**

Bottles are 250 ml, brown plastic from Rocky Mountain Forest & Range Experiment Station Lab, filled with deionized water.

Samples chilled immediately after collection and shipped to lab within 3 days of collection.

Duplicate and blank samples (10% each).

Chain of custody followed.

QAC checklist used.

**SAMPLING LOCATION:** At or near outlet of lake; well mixed area.

**FIELD NOTEBOOKS/FORMS:** Field notebook and bottle labels discussed in instructions to samplers. Lake photographs taken.

**TRAINING:** not discussed

**DESIGNATED SAMPLING PERSONNEL:** not discussed

**QA/QC METHODS:** not discussed. A QA/QC checklist is used; it is unclear what it contains.

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** not discussed

**DISCUSSION:** Lake photographs (3) taken at each site.

**REFERENCES:**

**PROJECT:** Rainbow Lake Wilderness Area

**PARAMETERS/METHODS:**

pH, alkalinity, specific conductance; methods not discussed

Ca<sup>+2</sup>, Mg<sup>+2</sup>, K<sup>+</sup>, Na<sup>+</sup>

Al

NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Kjeldahl N

SO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup>

Color

Methods not discussed but said to be appropriate for low detection limits

**LABORATORY:** not discussed

**NUMBER OF SITES:** 8 lakes

**SAMPLING FREQUENCY:** 3/year

**SEASONAL COVERAGE:** spring, summer, fall

**SAMPLING METHOD:** not discussed but presumably from boat by grab or point sampler; temperature profile, dissolved oxygen profile

**SAMPLE INTEGRITY:** not discussed

**SAMPLING LOCATION:** at deepest point

**FIELD NOTEBOOKS/FORMS:** not discussed

**TRAINING:** not discussed

**DESIGNATED SAMPLING PERSONNEL:** not discussed

**QA/QC METHODS:** not discussed

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** not discussed

**DISCUSSION:**

**REFERENCES:**

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**PROJECT:** Region 1 Phases 2-3

**PARAMETERS/METHODS:**

Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup> by ion chromatography

Si, Al by Lachat flow injection system

SO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>-3</sup> by ion chromatography

F<sup>-</sup> by ion specific electrode lab pH (Acid Rain Analysis System), alkalinity (Gran titration) and specific conductance

**LABORATORY:** Rocky Mountain Forest and Range Experiment Station, Ft. Collins, CO

**NUMBER OF SITES:** not discussed; duplicates and field (not process) blanks collected

**SAMPLING FREQUENCY:** not discussed

**SEASONAL COVERAGE:** not specified but presumed to be summer

**SAMPLING METHOD:** washed gloves from raft (phase 3); 0.5m depth

**SAMPLE INTEGRITY:**

Bottles not discussed

Samples shipped to laboratory by 2nd day-air on ice packs

**SAMPLING LOCATION:** from windward shoreline (or outlet) at 0.5 m below surface (phase 2)

**FIELD NOTEBOOKS/FORMS:** Field notebook and bottle labels discussed in instructions to samplers

**TRAINING:** not discussed

**DESIGNATED SAMPLING PERSONNEL:** yes

**QA/QC METHODS:** see refs.

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** not discussed

**DISCUSSION:**

**REFERENCES:**

Handbook of Methods for Acid Deposition Studies (EPA 600/4-87/026)

Standard Methods (APHA)

**PROJECT:** Region 2

**PARAMETERS/METHODS:**

At all lakes-

pH

alkalinity

specific conductance

DOC

Ca<sup>+2</sup>, Mg<sup>+2</sup>, Na<sup>+</sup>

NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, ortho and total PO<sub>4</sub><sup>-3</sup>

SO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup>, Br<sup>-</sup>

At long-term monitoring lakes in addition to parameters above-

Si

F<sup>-</sup>

Al

K<sup>+</sup>

**LABORATORY:** Rocky Mountain Forest and Range Experiment Station

**NUMBER OF SITES:** not discussed

**SAMPLING FREQUENCY:** 3/year for long-term monitoring lakes, presumably once for initial inventory lakes

**SEASONAL COVERAGE:** June-August for long-term monitoring lakes, presumably similar for initial inventory lakes

**SAMPLING METHOD:** grab sample using rubber gloves; depth of 0.5m or less (if necessary to avoid disturbing sediments)

**SAMPLE INTEGRITY:**

Bottles provided by laboratory, rinsed with deionized water and sample

Samples shipped to laboratory within 7 days of collection, on ice packs

Some samples filtered (for long-term monitoring lakes only)

10% of samples collected in duplicate (20% for long-term monitoring lakes)

5% of samples are field (not process) blanks (20% for long-term monitoring lakes)

**SAMPLING LOCATION:** near flowing outlet of lake or point with good circulation, away from vegetation and easily disturbed sediments

**FIELD NOTEBOOKS/FORMS:** Field notebook and bottle labels shown and discussed in instructions to samplers

**TRAINING:** by water chemistry scientists (long-term lakes sampling only)

**DESIGNATED SAMPLING PERSONNEL:** not discussed

**QA/QC METHODS:** not discussed

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** Regional office

**DISCUSSION:**

**REFERENCES:**

**PROJECT:** "Region 6 Lake Inventory" – Method adopted by Aquatics departments on R6 Forests (1993 Handbook - Levels I and II, version 1.2 – has not been updated since). This methodology was planned to be edited and updated by a regional team, but that has not yet occurred and is not scheduled.

**PARAMETERS/METHODS:**

major ions - Lab analysis of:  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{-2}$  (mg/l). Collect 500 ml sample "at mid-depth or at the thermocline using the Van Dorn water sampler". No laboratory equipment/method cited.

Nitrate-nitrite and total dissolved P - (detection limit of 1.0 microgram/l), no equipment/method cited

pH -Measure 3 feet below surface (nearest tenth pH unit). No equipment/method cited.

Conductivity: In situ – measure 3 feet below the surface (microsiemens/cm). No equipment/method cited.

Lab - (microsiemens/cm). No equipment/method cited.

Alkalinity – Lab (microsiemens/cm). No equipment/method cited.

Secchi depth – Average of depth lowering and raising (meters).

Temperature and Dissolved Oxygen – "Row out to the deepest part of the lake. Lower profiling device to the bottom and stabilize. Record temperature and dissolve oxygen. Raise the probe until a one degree (f) change in temperature, or a 0.5 mg/l change in D.O., is observe. Record this depth to the nearest foot, temperature to the nearest tenth of a degree, and D.O. in mg/l to the nearest tenth of a mg/l. Continue raising probe and marking the depth with each one degree change in temperature of 0.5 mg/l change in dissolved oxygen until you reach the top." No equipment type cited.

Phytoplankton – " A 500 ml bottle with 1.25 ml of Lugals solution is used to collect sample at mid-depth or at the thermocline using the Van Dorn water sampler. Ask the contracted water lab to analyze for species composition and volume". No laboratory method cited.

Zooplankton – "A 250 ml bottle with 10 ml 1% formalin and two to three pellets of BHT is used to store samples. The sample will be collected by pulling the plankton net from three feet above the bottom to the surface. Record haul length. If the lake in less than 300 feet, repeat the vertical tow until a length of 30 feet is obtained." Identification method/level not cited.

Chlorophyll a – "A 250 ml amber bottle with 1 ml manganese carbonate is used to collect a sample a mid-depth or at the thermocline using the Van Dorn sampler. Ask the contracted lab to analyze for chlorophyll a. Send lab unfiltered sample." No laboratory equipment/method cited.

Fish – "Sampling techniques include either gill netting or hook and line". Sampling is destructive, with a series of observations and measurements of each fish being made, including contents of stomach, etc.

**LABORATORY:** Not specified, contract labs apparently used. "Contracts for lab analysis must be secured before field season and sample bottles obtained from lab. All bottles should be acid washed, leak proof, clearly marked by the lab for the field, with appropriate preservation added. Sample bottles should be picked up the week prior to sampling. All water samples are collected at the thermocline or mid-depth. All bottles will be double bagged to keep out dust, kept cold during storage and processed within 96 hours. Generally, samples will be overnight expressed from the field. Record results on Form - Lab Water Chemistry.

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When selecting a contract lab ask the lab what their standard is for quality assurance and quality control. Make sure it matches that of the U.S. EPA. Ask them to specify sample storage, analytical techniques, accuracy and precision checks, and detection limits. If the lab can not meet the detection limits listed in this handbook use another lab.

Plan to send a duplicate sample from one lake, to the lab. Check for accuracy. In addition, send a replicate sample to another contracted lab. Compare results, change labs if necessary."

**NUMBER OF SITES:** not discussed

**SAMPLING FREQUENCY:** not discussed

**SEASONAL COVERAGE:** not discussed

**SAMPLING METHOD:** Van Dorn point sampler from raft or boat at mid-depth or thermocline; temperature profile; zooplankton profile with plankton net; phytoplankton point sample at mid-depth or thermocline. "All water quality samples are collected at the deepest point from a raft or boat with the appropriate equipment. Be sure all equipment is properly secured and appropriate clothing is worn (i.e. warem jacket, pants, hat). If you are using a small raft, be sure the other surveyor on the shore is able to see you at all times. If renting a boat, be sure the anchor line reaches the bottom of the lake. Record field results on the Form – Field Water Chemistry."

**SAMPLE INTEGRITY:**

- Zooplankton preserved with formalin and BHT
- Phytoplankton preserved with Lugols solution
- Samples shipped by overnight delivery to laboratory on ice packs
- Analyses to be completed within 96 hours

**SAMPLING LOCATION:** at deepest point

**FIELD NOTEBOOKS/FORMS:** Field form shown and discussed in instructions to samplers.

**TRAINING:** not discussed

**DESIGNATED SAMPLING PERSONNEL:** not discussed

**QA/QC METHODS:** not discussed

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** not discussed

**DISCUSSION:**

**REFERENCES:**



**PROJECT:** Shoshone Wilderness lake protocol

**PARAMETERS/METHODS:**

Field pH and specific conductance using NADP protocols

Ca<sup>+2</sup>, Mg<sup>+2</sup>, K<sup>+</sup>, Na<sup>+</sup>

NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup>, F<sup>-</sup>

lab alkalinity (Gran titration) and specific conductance

**LABORATORY:** U.S. Geological Survey, Arvada, CO until 1995, then Rocky Mountain Forest & Range Experiment Station Lab (chemistry); Dr. Fred Mangum, Provo, UT until 1997, then BLM Bug Lab, Logan, UT (macroinvertebrates and zooplankton)

**NUMBER OF SITES:** 2 lakes

**SAMPLING FREQUENCY:** inlet and outlet 3/year; hypolimnion, epilimnion, zooplankton and macroinvertebrates 1/year in summer

**SEASONAL COVERAGE:** spring, summer, and fall

**SAMPLING METHOD:** Van Dorn point sampler from raft; 0.5m depth (epilimnion); middle of hypolimnion; temperature profile; zooplankton profile with plankton net; inlet/outlet sampled mid-stream/mid-depth using rubber gloves and sampling upstream from sampler; macroinvertebrates by Surber sampler

**SAMPLE INTEGRITY:**

Bottles provided by laboratory, rinsed with deionized water and sample

Samples filtered for some parameters

Nitric acid preservation of cations, metals

Zooplankton and macroinvertebrates preserved with 70% ethanol

Samples shipped to laboratory within 3 days of collection, on ice packs

Maintain chain of custody for all samples.

**SAMPLING LOCATION:** Inlet, outlet, and deepest part of lake.

**FIELD NOTEBOOKS/FORMS:**

Field notebook and bottle labels discussed in instructions to samplers

**TRAINING:** Samplers are trained by other samplers that collect samples on a regular basis.

**DESIGNATED SAMPLING PERSONNEL:** Changes with time, typically a Hydrologist, Hydrologic Technician, Air Quality Specialist or volunteers who have been trained.

**QA/QC METHODS:** Duplicates and blanks.

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** Bridger-Teton NF. Will be input to NRIS-Air. Backup copies of data available from RMRS Lab.

**DISCUSSION:** Chemistry methods probably those used by USGS low-ionic strength unit. Description of non-compliance for samples prior to 1985 provided by letter (George Langstaff 11/22/85).

**REFERENCES:**

- AQRV Action/Monitoring Plan for the Bridger/Fitzpatrick Wildernesses, USFS 1984.
- Quality Assurance Project Plan for Monitoring Air Quality Related Values for the Bridger and Fitzpatrick Wildernesses.
- Wind River Mountains Air Quality Program Methods Manual, USFS 1995(?).

**PROJECT:** Sierra Nevada lakes

**PARAMETERS/METHODS:**

Field pH by 1-buffer method, Markson Model 95 meter and Graphic Controls PHE 52539 electrode

Field alkalinity by Gran titration

DOC

Ca<sup>+2</sup>, Mg<sup>+2</sup>, K<sup>+</sup>, Na<sup>+</sup> by atomic absorption spectrophotometry (Varian Techtron Model AA6)

Fe, Mn, Si, Al, Pb

NO<sub>3</sub><sup>-1</sup> as NO<sub>2</sub><sup>-</sup> by hydrazine reduction

NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>-3</sup> by indophenol blue and molybdenum blue

SO<sub>4</sub><sup>-2</sup> by barium chloranilate

Cl<sup>-</sup> by mercury thiocyanate

**LABORATORY:** Not specifically discussed, presumably, analyses done by the project research staff

**NUMBER OF SITES:** 73 lakes

**SAMPLING FREQUENCY:** once

**SEASONAL COVERAGE:** not specified but presumed to be summer

**SAMPLING METHOD:** from raft; unknown depth, presumably a grab sample; zooplankton vertical profile with plankton net

**SAMPLE INTEGRITY:**

Bottles washed with HCl, rinsed with deionized water and sample

Samples filtered for some parameters

Samples shipped to laboratory chilled

**SAMPLING LOCATION:** near center of lake

**FIELD NOTEBOOKS/FORMS:** not discussed

**TRAINING:** not discussed

**DESIGNATED SAMPLING PERSONNEL:** not discussed

**QA/QC METHODS:** not discussed

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** not discussed

**DISCUSSION:**

**REFERENCES:**

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**PROJECT:** Sipsey Wilderness Area

**PARAMETERS/METHODS:**

DOC (1992-93)

Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>

Al (1994-99)

NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> (1991-93), NH<sub>4</sub><sup>+</sup>, and PO<sub>4</sub><sup>-3</sup> (1994-99)

SO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup>, F<sup>-</sup>

(1994-99)

Water temperature, field conductance (1992-93), lab conductance (1994-99), lab pH, field pH (1992-93), and alkalinity (1992-93) or ANC (1994-99)

**LABORATORY:** University of Alabama, Biology Department (1992-93); Rocky Mountain Forest and Range Experiment Station (1994-98)

**NUMBER OF SITES:** Varies -17 (1992); 4 (1993); 4 (1994); 3 (1998).

**SAMPLING FREQUENCY:** not discussed

**SEASONAL COVERAGE:** 6/07 – 6/11 (1991); 6/11 - 6/25, 1992; 7/02 - 7/09, 1993; 7/06, 1994; 2/12 - 3/16, 1998. Base flow all years.

**SAMPLING METHOD:** grab samples from middle of stream

**SAMPLE INTEGRITY:**

Bottles presumably provided by laboratory

Samples filtered for most parameters (1991-98)

Nitric acid preservation and chilling of cations

Samples shipped to laboratory on ice

After 1993 samples frozen

**SAMPLING LOCATION:** Perennial streams sampled mid-stream, flowing water, just below surface.

**FIELD NOTEBOOKS/FORMS:** not discussed

**TRAINING:** Provided by Professor Milton Ward, Ph.D. (1991-93); by Dave Wergowske, M.S. (1994-99)

**DESIGNATED SAMPLING PERSONNEL:** students (1992-93); Forest Service crew (1994-99)

**QA/QC METHODS:** Review raw data for anomalous values. Lab reviews, split/blank sampling unknown (1992-93); Review raw data for anomalous values. Lab reviews acid/base balance, ion balance & theoretical/actual conductivity ratio. Lab runs blanks and split samples per its own schedule (1994-98).

**RERUN DETERMINATION:** none

**QA REPORT:** Provided with raw data (1994-98)

**DATA REPOSITORY:** Forest Air Resource Specialist

**DISCUSSION:**

**REFERENCES:**

**PROJECT:** Summit Lake, WA

**PARAMETERS/METHODS:**

DOC (8/95 split and 6/96 only)  
Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup> (analysis method AAS)  
Total P (analysis method Ascorbic Acid Chl)  
SO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> (analysis method IC)  
SiO<sub>2</sub> (analysis method unknown)  
Lab pH, ANC, conductivity (analysis method ARAS)  
Phytoplankton and zooplankton on some samples  
Secchi disk transparency with a 20cm limnological disk

**LABORATORY:**

Acid-base chemistry: USDA-Forest Service water lab, Fort Collins, CO. (QA samples sent to Illinois State Water Survey and QST Environmental in Gainesville, FL.)

TP, Chlorophyll a: Aquatic Analysts, Portland OR

**NUMBER OF SITES:** 1 lake (11 samples total), 1 adjacent pond (once only)

**SAMPLING FREQUENCY:** 1-3/year

**SEASONAL COVERAGE:** Nov 1993; Apr, Jul 1994; Jul, Aug, Oct 1995; Mar, Jun 1996; Apr, Aug, Sept 1997.

**SAMPLING METHOD:** Water samples taken from an inflatable boat except under high wind conditions when samples were taken from shore (Nov 1993, Sept 1997). Surface samples only except for July 1995 and Aug 1995 when depth profiles (0.5-1m, 5m, 15m, 25m) were done. Trace-metal grade Van Dorn samplers were used for sample collection. Samples for major ion chemistry were stored in new Nalgene 1 L bottles pre-rinsed in de-ionized water and rinsed three times with the lake water.

Samples for total phosphorus were placed in Nalgene bottles and preserved with sulfuric acid.

**SAMPLE INTEGRITY:**

Bottles discussed, rinsed with deionized water  
Samples shipped to laboratory overnight, on ice packs

**SAMPLING LOCATION:** near deepest part, and twice from shore due to high winds.

**FIELD NOTEBOOKS/FORMS:** not discussed

**TRAINING:** not discussed

**DESIGNATED SAMPLING PERSONNEL:** yes

**QA/QC METHODS:**

ion balance (without RCOO<sup>-</sup>); calculated pH (assuming P<sub>CO2</sub> = 10<sup>-3.2</sup> atm, ANC (CB-CA), and specific conductance.

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Duplicates (3x), blanks (3x), and splits (4x) used.  
Measured pH within 0.25 units of calculated pH (based on ANC).  
Measured ANC within 5\_eq/l of calculated ANC  
Anion and cation difference more than 5\_eq/l

**RERUN DETERMINATION:** not discussed

**QA REPORT:** In final report mentioned below.

**DATA REPOSITORY:** not discussed (Excel file available from Janice Peterson).

**DISCUSSION:** Chemistry methods those used by Rocky Mountain Forest and Range Experiment Station

Also sampled/described as part of this study: bathymetry, phytoplankton, zooplankton, chlorophyll a, snow chemistry, sulfur isotope (lake and snow), sediments (H<sub>2</sub>O, LOI, Cu, Zn, TP, 14C, 210Pb, diatoms)

**REFERENCES:** Eilers, J.M.; Gubula, C.P.; Sweets, P.R.; and Vaché, K.B. 1998. Limnology of Summit Lake, Washington. Its acid-base chemistry and paleolimnology. A final report to the Forest Service – Mt. Baker-Snoqualmie National Forest. 60p.

**PROJECT:** Native brook trout streams in the mountains of Virginia

**PARAMETERS/METHODS:**

pH and ANC, methods not discussed

Ca<sup>+2</sup>, Mg<sup>+2</sup>, K<sup>+</sup>, Na<sup>+</sup>

Si

NO<sub>3</sub><sup>-</sup>

SO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup>

**LABORATORY:** not discussed

**NUMBER OF SITES:** 65-78 streams

**SAMPLING FREQUENCY:** 4/year

**SEASONAL COVERAGE:** quarterly

**SAMPLING METHOD:** not discussed

**SAMPLE INTEGRITY:** not discussed

**SAMPLING LOCATION:** not discussed

**FIELD NOTEBOOKS/FORMS:** not discussed

**TRAINING:** not discussed

**DESIGNATED SAMPLING PERSONNEL:** not discussed

**QA/QC METHODS:** not discussed

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** not discussed

**DISCUSSION:**

**REFERENCES:**

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**PROJECT:** Wind River Mountains

**PARAMETERS/METHODS:**

Field pH and specific conductance  
Major cations, major anions, and ANC  
Streamflow  
Zooplankton  
Macroinvertebrates

**LABORATORY:** Rocky Mountain Forest and Range Experiment Station (chemistry); Dr. Fred Mangum, Provo, UT until 1998 then BLM Bug Lab, Logan UT (zooplankton, macroinvertebrates)

**NUMBER OF SITES:** 3 lakes (inlet, outlet, hypolimnion, epilimnion)

**SAMPLING FREQUENCY:** Inlet and outlet 3/year; mid-lake samples of hypolimnion, epilimnion, zooplankton and macroinvertebrates 1/year in summer

**SEASONAL COVERAGE:** spring, summer, fall

**SAMPLING METHOD:** Van Dorn point sampler from raft about 10 ft. below thermocline (hypolimnion); grab sample without gloves (epilimnion); temperature profile; zooplankton profile with plankton net; inlet/outlet sampled in area of maximum flow without gloves and sampling upstream from sampler; macroinvertebrates by Surber sampler; field (non-process) blanks, replicates

**SAMPLE INTEGRITY:**

Maintain chain of custody for all samples.  
Bottles provided by laboratory, rinsed with deionized water and sample  
Samples filtered for some parameters  
Samples shipped to laboratory on ice packs

**SAMPLING LOCATION:** Inlet, outlet, and at deepest point

**FIELD NOTEBOOKS/FORMS:** Field notebook and bottle labels shown and discussed in instructions to samplers

**TRAINING:** Samplers are trained by other samplers that collect samples on a regular basis.

**DESIGNATED SAMPLING PERSONNEL:** Changes with time, typically a Hydrologist, Hydrologic Technician, Air Quality Specialist, or volunteers who have been trained.

**QA/QC METHODS:** Duplicates, blanks, and inter-lab analysis using the Central Analytical Lab.

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** Bridger-Teton NF. Will be input to NRIS-Air. Backup copies of data available from RMBS lab.

**DISCUSSION:** careful attention to instructions for sampling personnel



**REFERENCES:**

- AQRV Action/Monitoring Plan for the Bridger/Fitzpatrick Wildernesses, USFS 1984.  
Quality Assurance Project Plan for Monitoring Air Quality Related Values for the Bridger and  
Fitzpatrick Wildernesses. USFS 1987.  
Wind River Mountains Air Quality Program Method Manual, USFS 1995 (?)

**PROJECT:** Yolla Bolly - Middle Eel wilderness

**PARAMETERS/METHODS:** Field pH, methods not discussed

**LABORATORY:** field data only

**NUMBER OF SITES:** 5 lakes

**SAMPLING FREQUENCY:** 3/year

**SEASONAL COVERAGE:** summer

**SAMPLING METHOD:** not discussed

**SAMPLE INTEGRITY:** not discussed

**SAMPLING LOCATION:** not discussed

**FIELD NOTEBOOKS/FORMS:** Field form shown

**TRAINING:** not discussed

**DESIGNATED SAMPLING PERSONNEL:** not discussed

**QA/QC METHODS:** not discussed

**RERUN DETERMINATION:** not discussed

**QA REPORT:** not discussed

**DATA REPOSITORY:** not discussed

**DISCUSSION:**

**REFERENCES:**

## APPENDIX 2: DISSOLVED OXYGEN

There are several methods for determining the concentration of dissolved oxygen. The instrument described below is typical of many other related instruments. Differences among instruments may require different procedures, as indicated in manufacturers instructions for use.

The YSI dissolved oxygen probes have to be fully filled with KCL filling solution to function properly. This problem can be difficult to detect, especially with probes that are completely empty of solution. If bubbles are observed under the clear plastic membrane, or if the probe is dry, the solution and membrane should be replaced as described below. If in doubt whether the probe is out of solution, replace the solution and membrane.

### *Principle of operation:*

The probe is a simple electrical circuit with two electrodes, a gold ring around the perimeter and a central silver-chloride triangle. A filling solution of potassium chloride makes the electrical contact between the two. If there is no KCL, there will be no electrical contact, yielding bogus numbers. There also is a thermistor that measures temperature and provides temperature adjustments to the DO measurement circuit.

The probe and membrane measure DO concentrations by measuring the electrical current needed to consume a steady-state flow of oxygen into the probe. Electrical reactions at the electrode reduce oxygen in the probe reservoir to near zero and the oxygen concentration in the lake or stream is nearly constant, thus setting up a steady-state diffusion of oxygen through the membrane that is directly proportional to the oxygen concentration in the water. The calibration of the zero and redline functions assures that the proper voltage is applied across the electrodes to allow the electrode reaction to take place.

Replace the old membrane and filling solution by:

1. Unscrewing the protective shroud from the end of the probe.
2. Pulling off the O-ring holding the old membrane on and discarding the old membrane.
3. Purging the old KCL by holding the probe upside down, and gently pumping the black rubber diaphragm on the side of the probe with a pencil (blunt end).
4. Return the probe to a vertically upright position and begin adding KCL solution to the reservoir, alternating this filling with gentle pumping on the diaphragm.
5. When no more bubbles are released through the hole connecting the diaphragm to the main electrode reservoir with repeating pumping, remove any bubbles from the surface of the KCL solution. It helps greatly to mound the solution above the gold electrode surface and brush bubbles off with the end of the KCL solution bottle. Finish by carefully adding as much solution as will stay on top of the probe without getting new bubbles on it.
6. Remove a new membrane from the kit and hold by upper end between your thumb and index finger.
7. Using thumb of opposite hand hold bottom edge of membrane against the threaded portion of the probe and, gently stretching the membrane, in one smooth motion pull it over and down onto the electrode area and hold to probe with index finger of the hand holding the bottom edge of the membrane.
8. Carefully roll the O-ring around the membrane and into the groove that holds the O-ring. There should be no bubbles or wrinkles. Minor wrinkles may be removed by gentle stretching of the membrane.
9. Trim excess membrane off.

10. Replace protective shroud.

Calibration of the meter is done by:

1. Turn meter on and adjust the redline and zero settings. The meter needs to run several minutes to reach a steady state of oxygen diffusion through the membrane.
2. Put probe in water, preferably in a shaded area. Even the shade of a rock in the lake or stream is fine. Allow the probe to come to the temperature of the water, which will take several minutes.
3. Record the water temperature.
4. Shake off any water from the membrane and put the probe in the air chamber, avoiding any buildup of pressure by leaving the cap loose until the probe is fully in the chamber, then tighten the cap. If the chamber is pressurized the calibration will be in error.
5. Place the probe in the water, close to the surface as possible and shaded if possible. If the air chamber is submerged very much it will pressurize and the calibration will be in error.
6. After the temperature re-stabilizes use the temperature and calibration table to calculate the saturation oxygen concentration at sea level. Adjust this number by the measured atmospheric pressure from an altimeter to the atmospheric pressure at the site, in atmospheres.
7. Set the calibration mode to the calculated oxygen concentration for the temperature and atmospheric pressure.
8. Remove the probe from the air chamber, place in the lake or stream, and move through water so that a water velocity of about 1 foot/second is maintained across the membrane. This keeps the oxygen concentration from being depleted at the external membrane surface.
9. Record the oxygen concentration after it stabilizes.

*Example calibration notes:*

YSI Model 54A, #320295 (Identify instrument)

Correction factor 0.65 (Atmospheric pressure from altimeter)

Calibration temperature = 13.8°C (temperature measured with air chamber on probe)

$0.65 \times 10.02 \text{ ppm @ } 13.8^\circ\text{C} = 6.5 \text{ ppm}$  (calculated saturation concentration at 0.65 atmospheres pressure and air chamber temperature)

Initial reading 6.4 ppm (what instrument read before calibration to calculated value)

Water temperature = 13.0°C (measured water temperature without chamber)

DO = 6.4 ppm (measured dissolved oxygen concentration in water without chamber)

## APPENDIX 3: FIELD FORMS

NRIS-Air could develop field data templates to ensure that all required data are collected with proper precision and in proper metric. A field recorder for quick download to a template for easy migration to NRIS would also add quality control. Two field forms could be developed, one for synoptic (inventory) sampling (would need additional categories where lakes are only visited once such as elevation, latitude and long, forest name, district name, wilderness name, lake size, site descriptors, photo reminder) and one for long-term monitoring (add wilderness or admin unit name). This is an example list of items to be included on both synoptic and long-term monitoring field forms.

Location: Ned Wilson Lake Site: Buoy Date: 7/04/2000 Time: 12:00

Personnel: Don Campbell, Norm Spahr

Observations: 15-20 trout (brook?) observed, 10-12 in.; many mosquitoes

Weather: Fair, no recent rain, snowmelt complete Wind speed/direction: from SW, ~10 mph%  
Cloud Cover: ~35% Atmospheric Pressure: 0.70 atm. Air Temp: 15.7 °C.

Field Measurements- Water Temp: 12.2 °C Spec. Cond: lab only D.O.=7.6ppm pH=6.93  
Secchi Disk Depth: 4.2 m

Sampling Depth: 1.0 m Sampling Method: Van Dorn Blank/Replicates?: 1 blank, 1 rep.

Profile? (If yes, attach): Yes

Calibration notes-

pH: 4.00 + 7.00 buffers, Orion Ross 8102 Combination electrode, meter #W310289, Orion Model SA250

4.70 dilute acid standard read 4.74, aliquots 1 pH = 6.74, 2 pH = 6.78, 3 pH = 6.72

D.O.:

YSI Model 54A, #320295

D.O. Correction factor 0.70 (Atmospheric pressure from altimeter)

Calibration temperature = 12.5°C, sea level saturation 10.6 ppm

$0.70 \times 10.6 \text{ ppm} @ 12.5^\circ\text{C} = 7.4 \text{ ppm}$  (calculated saturation concentration at 0.70 atmosphere pressure and air chamber temperature)

Initial reading 6.4 ppm, adjusted to read 7.4 ppm

Thermistor (on D.O. instrument) calibrated at office, see data in calibrations log.



## APPENDIX 4: QUALITY ASSURANCE TOOLS

**Table 1.** Conductance factors (F) of ions.

Ion	F	Ion	F
Ca <sup>+2</sup>	59.47	NO <sub>3</sub> <sup>-</sup>	71.42
Mg <sup>+2</sup>	53.0	Cl <sup>-</sup>	76.31
Na <sup>+</sup>	50.08	SO <sub>4</sub> <sup>-2</sup>	80.0
K <sup>+</sup>	73.48	HCO <sub>3</sub> <sup>-</sup>	44.5
H <sup>+</sup> (from pH)	349.65	OH <sup>-</sup>	198
NH <sub>4</sub> <sup>+</sup>	73.50		

Calculated Conductance = Sum(F x Concentration in µeq/L)/1000

Data from Morrison (1991)

**Table 2.** Guidelines for reanalysis of samples based on agreement between cations vs. anions and calculated vs. measured specific conductance. In column "% Ion Difference" and "% Conductance Difference), the larger values to the left are from Morrison (1991) and should be considered mandatory levels. The smaller values to the right are achievable and should be used to produce higher-quality data.

A. Cation-Anion Balance		
Total Ion Strength (µeq/L)	% Ion Difference	
<50	>60	>25%
50<100	>30	>15%
100 or greater	>15	>10%

  

B. Calculated vs. Measured Specific Conductance		
Measured Specific Conductance (µS/cm)	% Conductance Difference	
<5	>50	>20
5<30	>30	>15
30 or greater	>20	>10

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## APPENDIX 5: FIELD CHECKLIST

### *Before departing from trailhead-*

1. Do you know how to get where you're going? Do you have the necessary maps, compass, GPS, etc. to get to a site you are not familiar with?
2. Do you have the necessary safety, communications, survival, and food supplies for the trip if an emergency occurs?
3. Do you have the necessary bottles, field instruments, field forms and notebooks, processing equipment and preservatives (if needed), camera (if needed)?

### *On-Site-*

1. Where are you and how do you know? Indicate on field sheet.
2. Is the routine measurement site useable, or did you have to select an alternate site (if so, describe)?
3. Assemble all bottles, instruments, forms and notebooks. Fill in necessary info on location, date, time, personnel, instrument models and serial numbers, conditions.
4. Indicate whether this is a grab, point, or auto sample. Record precautions taken to avoid contamination, e.g., use of gloves, rinsing of point sampler, etc.
5. Take pictures of site and surrounding area, if needed.
6. Label bottles.
7. Calibrate instruments, indicate what calibration approach was used.
8. Collect field data and sample, indicate whether duplicate and blank samples are being collected.
9. Chill all samples immediately. Filter and preserve samples (if protocol requires).

### *On Return to Trailhead-*

1. Make sure samples are grouped by site and all information was properly recorded on bottles, field sheets, and notebooks.
2. Pack samples in cooler with plenty of ice.
3. Ship samples as soon as possible to lab (but avoid shipping late in the week when samples can get stuck on delivery trucks).





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June 2001