

# Evaluation of Storage and Filtration Protocols for Alpine/Subalpine Lake Water Quality Samples

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**Abstract** Many government agencies and other organizations sample natural alpine and subalpine surface waters using varying protocols for sample storage and filtration. Simplification of protocols would be beneficial if it could be shown that sample quality is unaffected. In this study, samples collected from low ionic strength waters in alpine and subalpine lake inlets and outlets in the western United States were used to evaluate (1) effects of refrigerated storage time on the chemistry of unfiltered samples, and (2) differences in sample filtration protocols. No analytes exhibited significant changes when stored less than 48 h. Six analytes (pH, sodium, ammonium, potassium, chloride, sulfate) exhibited statistically significant (but small) changes when storage time exceeded 48 h. Two analytes (calcium, nitrate) were significantly higher when samples were field filtered than when filtered in the laboratory, but the differences were also small. For waters similar to those in this test, unfiltered refrigerated samples may be stored up to 48 h without compromising sample quality. The small differences between field and lab filtration do not justify the expense, training, and contamination risk of field filtration.

**Keywords** Alpine · Lakes · Protocol · Sampling · Subalpine · Water quality · Wilderness

## 1 Introduction

The chemical composition and physical characteristics of lake and stream water quality samples are subject to change during the time between collection and laboratory analysis (Hunt & Wilson, 1986; Stednick, 1991). The causes of changes may be chemical (e.g., change in valence state of ions, reaction between elements or compounds, precipitation of metals) or biological (e.g., consumption or release of compounds, particularly nitrates, via cellular metabolism or cell lysis) (Stednick, 1991). Chemical and physical properties of natural waters and their catchments are highly variable, and requirements for sampling protocols are thus also highly variable (Hunt & Wilson, 1986). No single authoritative source for sample collection, preservation, transport and storage protocols exists, and confusion may result when selecting a protocol for field sampling. For example, the US Environmental Protection Agency (USEPA) required filtration (USEPA, 1996) of samples, but also found on-site filtration of samples to be impractical (Messer et al., 1986). Both the US Geological Survey (USGS) (Wilde & Gibbs, 2004) and the USDA Forest Service (Turk, 2001) have published protocols including field filtration and refrigeration of samples for some common analytes. Past USGS guidelines (Wood,

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1976) have recommended against filtration for samples to be used for assessment of temperature, dissolved O<sub>2</sub>, Eh and pH; the US Forest Service (Fox et al., 1987) has discouraged field filtration of samples from high-altitude waters because of the risk of contamination.

Disadvantages associated with field filtration include additional cost and bulk of filtration supplies, added complexity of sampling protocols, greater training requirements for field workers, and increased likelihood of sample contamination. Some common sources of sample contamination during field collection and filtering are: (1) dust getting into the sample bottle, filter and/or syringe, (2) residue on the hands of person collecting the sample (although filtering while wearing polyethylene gloves minimizes this source of contamination), (3) exposure of the sample to the atmosphere (Metcalf, 1984) during collection and/or air space in the sample bottles; this allows transfer of CO<sub>2</sub> from air to the water and subsequent conversion to carbonic acid, and absorption or volatilization of NH<sub>4</sub> between the sample and air space, and (4) contamination from the filter medium itself (Wagemann & Graham, 1974). The very low detection levels associated with newer laboratory analytical equipment have magnified the shortcomings of field technique. Horowitz (1997) summarizes: “Unfortunately, current analytical capabilities have exceeded the current capacity to collect both uncontaminated and representative environmental samples.” It is in the researcher’s interest to eliminate field filtering from sampling protocols if it can be shown that field filtration does not contribute to greater sampling accuracy.

The effects of handling, storage, filtration, refrigeration and transport of liquid precipitation samples have been documented (e.g., Bigelow et al., 1989; Latysh & Gordon, 2004; Tang et al., 1987). However, studies examining these aspects of lake and stream water sampling are less common. Allen-Diaz, Hammerling, and Campbell (1998) compared unfiltered samples subject to seven different refrigeration/holding time treatments and found no significant differences in nitrate or pH with respect to either refrigeration or time. Ormaza-González and Villalba-Flor (1994) examined sampling protocols for coastal waters. They found significant differences between filtered and unfiltered coastal water samples for both nitrate and phosphate in these waters of high ion

concentrations and high bioactivity. Stepanian et al. (1989) examined holding times for samples of natural waters in the eastern US, but found “practically significant” changes over time for only a few analytes. Silverstein et al. (1988) made similar conclusions about the effects of both holding time and sampling protocol, but did not fully test analytes with very low concentrations. Existing work indicates that the effects of holding time and sampling protocol vary with respect to the characteristics of the waters sampled, and the significance of these effects depends on the context of the study, the magnitude of the analytes measured, the precision of laboratory techniques, and the desired accuracy of the results.

Numerous government agencies and other organizations conduct periodic sampling of remote alpine and subalpine waters. Simplification of field protocols for this type of sampling would be beneficial if it can be shown not to affect the results. Here we examine two critical aspects of lake and stream water sampling: length of storage time before filtering and analysis, and field vs. laboratory filtration. Anecdotal evidence in a long-term alpine/subalpine lake monitoring program (USDA Forest Service, unpublished data) indicated that field filtration did not significantly increase the accuracy of chemical analyses, and that short (<48 h) delays in laboratory processing of samples did not alter sample chemistry. We also observed that field-filtered samples had a greater incidence of outliers. The objective of this study is to determine if existing filtration and storage requirements for alpine/subalpine lake water quality samples are appropriate; we do not seek to address the very broad range of sample handling/preparation techniques applicable to other waters. The two hypotheses examined were (1) chemical composition of samples does not change if refrigerated (<4 °C) samples remain unfiltered up to nine days after collection; and (2) there are no differences in chemical composition between samples filtered in the field using a syringe/portable filter and samples filtered in the laboratory using a hand pump within 48 h of collection.

## 2 Study Area and Methods

The USDA Forest Service conducts annual sampling of more than 100 lakes located in alpine and

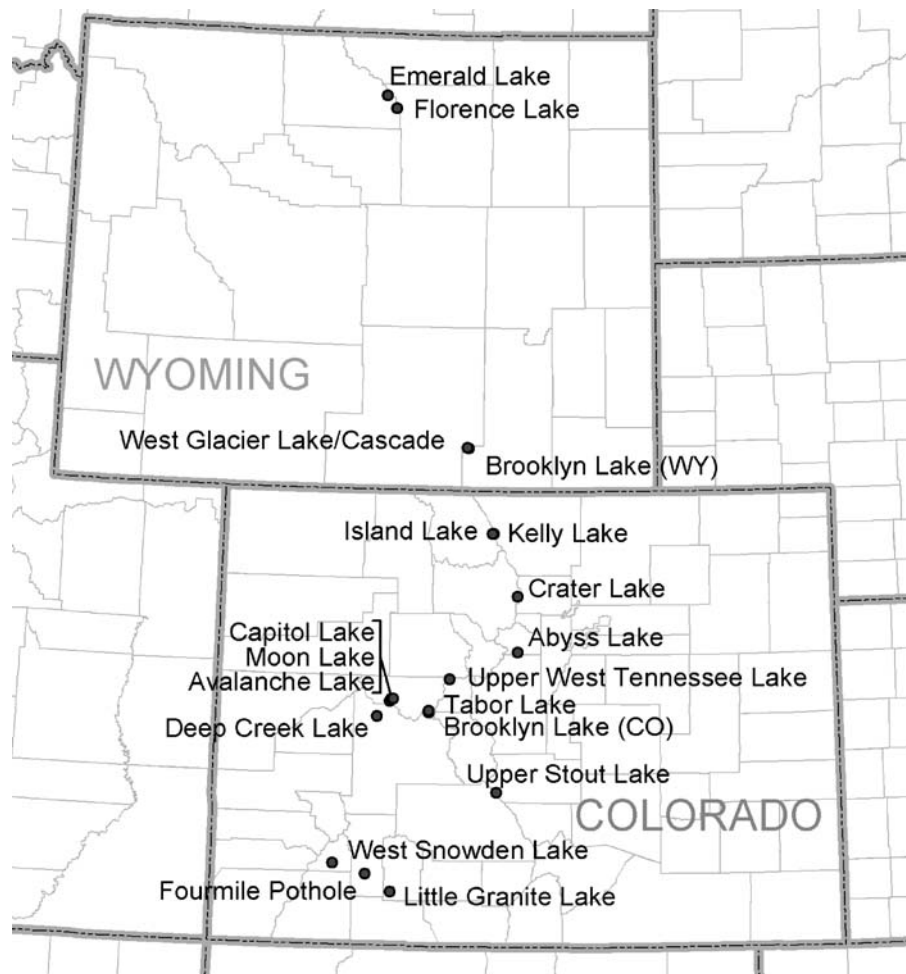
**Table 1** Sampled lakes

|                                                                                                                                                                                                                                                          | Lake sampling location<br>(Abbreviation)      | Range or wilderness<br>area | Storage time effects<br>experiment | Filtering protocol<br>experiment |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------|-----------------------------|------------------------------------|----------------------------------|
| All locations are in designated federal wilderness areas except Island and Kelly Lakes, and those in the Glacier Lakes Ecosystem Experiments Site in the Snowy Range in southeastern Wyoming. Samples were collected at the lake outlet except as noted. | Emerald                                       | Cloud Peak                  | x                                  | x                                |
|                                                                                                                                                                                                                                                          | Florence                                      | Cloud Peak                  |                                    | x                                |
|                                                                                                                                                                                                                                                          | Brooklyn, Colorado                            | Collegiate Peaks            |                                    | x                                |
|                                                                                                                                                                                                                                                          | Tabor                                         | Collegiate Peaks            |                                    | x                                |
|                                                                                                                                                                                                                                                          | Upper West Tennessee                          | Holy Cross                  | x                                  |                                  |
|                                                                                                                                                                                                                                                          | Crater                                        | Indian Peaks                |                                    | x                                |
|                                                                                                                                                                                                                                                          | Avalanche                                     | Maroon Bells                |                                    | x                                |
|                                                                                                                                                                                                                                                          | Capitol                                       | Maroon Bells                |                                    | x                                |
|                                                                                                                                                                                                                                                          | Moon                                          | Maroon Bells                |                                    | x                                |
|                                                                                                                                                                                                                                                          | Abyss                                         | Mt. Evans                   | x                                  |                                  |
|                                                                                                                                                                                                                                                          | Deep Creek                                    | Raggeds                     |                                    | x                                |
|                                                                                                                                                                                                                                                          | Island                                        | Colo. State Forest          |                                    | x                                |
|                                                                                                                                                                                                                                                          | Kelly                                         | Colo. State Forest          | x                                  |                                  |
|                                                                                                                                                                                                                                                          | Upper Stout                                   | Sangre de Cristo            | x                                  |                                  |
|                                                                                                                                                                                                                                                          | Brooklyn, Wyoming<br>Inlet East (BIE)         | Snowy Range                 |                                    | x                                |
|                                                                                                                                                                                                                                                          | Brooklyn, Wyoming<br>Inlet West (BIW)         | Snowy Range                 |                                    | x                                |
|                                                                                                                                                                                                                                                          | Brooklyn, Wyoming<br>Outlet (BO)              | Snowy Range                 | x                                  | x                                |
|                                                                                                                                                                                                                                                          | Brooklyn, Wyoming Inlet<br>Road Crossing (BR) | Snowy Range                 |                                    | x                                |
|                                                                                                                                                                                                                                                          | West Glacier Outlet, Loc.<br>#4 (WG4)         | Snowy Range                 |                                    | x                                |
|                                                                                                                                                                                                                                                          | West Glacier Outlet, Loc.<br>#5 (WG5)         | Snowy Range                 |                                    | x                                |
|                                                                                                                                                                                                                                                          | West Glacier Outlet, Loc.<br>#6 (WG6)         | Snowy Range                 |                                    | x                                |
|                                                                                                                                                                                                                                                          | West Glacier Inlet,<br>Cascade Cr (WGC)       | Snowy Range                 |                                    | x                                |
|                                                                                                                                                                                                                                                          | West Glacier Inlet<br>Snowfield (WGS)         | Snowy Range                 |                                    | x                                |
|                                                                                                                                                                                                                                                          | West Glacier Inlet<br>Waterfall (WGW)         | Snowy Range                 |                                    | x                                |
|                                                                                                                                                                                                                                                          | Fourmile Pothole                              | Weminuche                   |                                    | x                                |
|                                                                                                                                                                                                                                                          | Little Granite                                | Weminuche                   |                                    | x                                |
|                                                                                                                                                                                                                                                          | West Snowden                                  | Weminuche                   |                                    | x                                |

subalpine settings in federally designated wilderness areas and other remote sites in Colorado and Wyoming (Musselman & Slauson, 2004; Musselman et al., 1996). The lakes are all above 3,000 m elevation and range in surface area from 0.16 to 16.53 ha. Catchment areas range from 5.3 to 389.5 ha. The lakes are characterized by waters of low ionic strength and generally low biotic activity (Musselman & Slauson, 2004; Musselman et al., 1994). None of the catchments are currently glaciated, although some

have permanent snowfields. Two subsets of these lakes were used (Table 1, Figure 1) as sampling locations for work presented in this paper. Samples used in this study were collected at about 10 cm depth at the lake outlets in July or August; for two lakes, inlets were also sampled. Strict protocols were utilized to maintain sample integrity. Care was taken to avoid stirring of bottom sediment or collection of surface material. Clean polyethylene gloves were used for all sample handling. APHA Method 4110C

**Figure 1** Study area. Sites for both experiments are indicated.



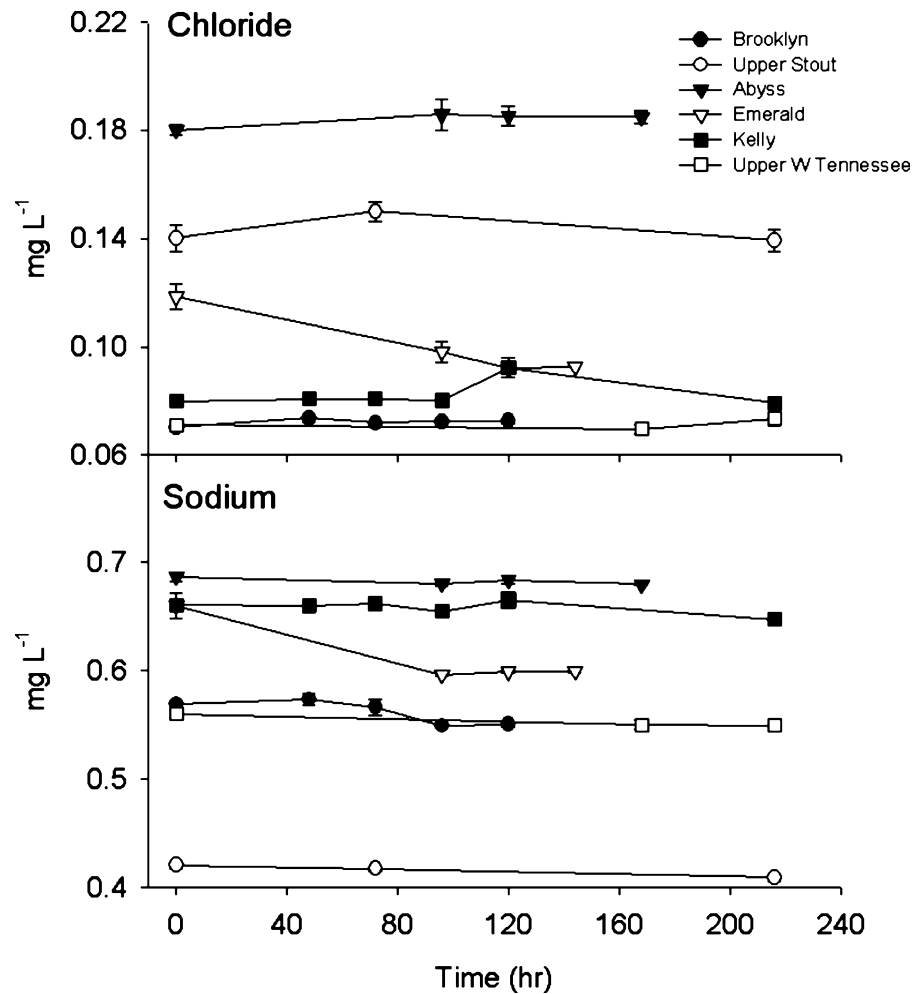
(APHA, 1998) was used for laboratory analysis of anions and cations, and Gran's (1952) method was used for pH and acid neutralizing capacity (ANC). Additional information on the laboratory, including equipment and detection limits, is available at <http://www.fs.fed.us/rm/waterlab/>.

Two separate studies were conducted. For the first, six lake outlets in northern and central Colorado and one in northern Wyoming (Table 1, Figure 1) were sampled to evaluate the effects of a delay between sampling and pre-analysis filtration. All bottles were transported to the sample site filled with deionized water and triple rinsed on site with sample water. At each location, five replicate 1-l samples were collected and immediately one aliquot was field filtered from each 1-l bottle into separate 60-ml bottles. Filtering technique for these samples follows protocols in Turk (2001), using a 30-ml syringe tipped with

a 25-mm diameter, 0.45- $\mu$ m Whatman polyethersulfone disposable filter. The 60-ml sample bottle was completely filled to avoid air space. All samples were then packed in insulated containers with snow or ice and transported back to the laboratory. The 1-l bottles were refrigerated and the separate 60-ml filtered samples were analyzed upon receipt at the laboratory. Additional 60-ml samples from the 1-l bottles were filtered and analyzed at varying intervals up to 216 h after collection.

ANC, pH, and conductivity were measured on unfiltered samples from the 1-l bottle. Concentrations of sodium, ammonium, potassium, magnesium, calcium, fluoride, chloride, nitrate, phosphate, and sulfate were measured on the filtered samples. Time effects were evaluated using a two-way, repeated-measures mixed model (Littell et al., 1996) with analyte values (usually mg/l) as the response variables. Independent

**Figure 2** Response an anion (*chloride*) and a cation (*sodium*) with significant responses to storage time. Symbols represent the mean of five replicates  $\pm$  one standard error.



variables included storage time before analysis (in hours), location, and an interaction term. An autoregressive structure was specified for the covariance matrix, and the subject (block) for repeated measures was an individual sample. A one-way ANOVA model (SAS, 2001; Sokal & Rohlf, 1995) was used to examine between-sample variability. SAS Version 8e (SAS, 2001) was used to conduct all statistical analyses.

The second study was conducted to evaluate the necessity of field filtering. Samples of 250 ml were collected at 23 locations (Table I, Figure 1) in approximately the same geographic region as for the first experiment. Sampling for this study also follows Turk (2001). At each location one sample was field filtered from the 250-ml bottle into a 60-ml bottle using a 30-ml syringe tipped with a 25-mm diameter, 0.45- $\mu$ m Whatman polyethersulfone filter. The second

250-ml sample was not field-filtered. Instead, a 60-ml sample was filtered at the laboratory using a 47-mm diameter Millipore polyvinylidene fluoride (PVDF) 0.45- $\mu$ m filter and a hand pump, following standard laboratory filtering protocols. For samples from 15 of these locations, a third 60-ml sample was filtered in the laboratory from the second 250-ml sample using the field (syringe/filter) filtering technique. Thus three comparisons are possible: syringe/filter technique in the field vs. hand pump/filter technique in the lab; syringe/filter in the field vs. syringe/filter in the lab; and syringe/filter vs. hand pump/filter, both in the lab. Polyethylene gloves were used for all sample handling. Field blanks, consisting of identical sample bottles filled with deionized water and subjected to the same filtration protocols as the samples, were taken on each sampling trip. Laboratory sample analysis included the same analytes as the first data

**Table II** Mixed repeated-measures model and one-way ANOVA results for the storage time experiment

|                                        | Analytical results |      | Detection limits | Parameter estimates |                                        | F (filter time) | Holding time |                       |
|----------------------------------------|--------------------|------|------------------|---------------------|----------------------------------------|-----------------|--------------|-----------------------|
|                                        | Test mean          | SE   |                  | Intercept           | Filter time ( $\text{h} \times 10^3$ ) |                 | EPA (h)      | $t_{\text{crit}}$ (h) |
| pH ( $\text{mol H}^+ \times 10^6$ )    | .                  | .    |                  | 0.043               | 0.127                                  | 461**           | 0            | .                     |
| ANC ( $\mu\text{Eq l}^{-1}$ )          | .                  | .    |                  | 173                 | 23.9                                   | 2.50            | 336          | .                     |
| Conductivity ( $\mu\text{S cm}^{-1}$ ) | .                  | .    |                  | 23.2                | 5.83                                   | 1.40            | 432          | .                     |
| Na                                     | 0.58               | 0.02 | 0.01             | 0.600               | −0.050                                 | 12.2**          | 432          | 88                    |
| NH <sub>4</sub>                        | 0.01               | 0.00 | 0.01             | 0.010               | 0.065                                  | 319**           | 24–72        | 76                    |
| K                                      | 0.38               | 0.02 | 0.02             | 0.378               | 0.014                                  | 5.17*           | 432          | 469                   |
| Mg                                     | 0.46               | 0.03 | 0.02             | 0.687               | −0.030                                 | 0.100           | 6 mos.       | 81                    |
| Ca                                     | 3.45               | 0.32 | 0.02             | 3.41                | −0.100                                 | 0.110           | 6 mos.       | 173                   |
| F                                      | 0.01               | 0.01 | 0.01             | 0.078               | −0.040                                 | 2.33            | 864          | 47                    |
| Cl                                     | 0.11               | 0.01 | 0.01             | 0.071               | 0.006                                  | 6.20*           | 864          | 585                   |
| NO <sub>3</sub>                        | 0.21               | 0.07 | 0.02             | 0.045               | 0.151                                  | 2.57            | 48           | 75                    |
| SO <sub>4</sub>                        | 3.36               | 0.61 | 0.05             | 2.89                | 0.121                                  | 4.92*           | 864          | 58                    |

Analytical means and standard errors (SE) are for all samples in the test ( $n=30$ ) and indicate analyte values upon arrival at the laboratory ( $t=0$ ). The quantity  $t_{\text{crit}}$  indicates estimated time for the percent change in analyte concentration to exceed one-half of the sampling precision (root MSE/intercept). EPA holding times are from USEPA (1982). Units are mg/l except as noted. ANOVA results for pH, ANC and conductivity are not available, see text.

\*=( $\text{pr} > F$ )<0.05, \*\*=( $\text{pr} > F$ )<0.01.

set. Differences between locations in the magnitude of analytes, and the lack of replication in the study design, obviated the use of ANOVA-type statistical models. Instead, differences between filtering treatments were evaluated using Wilcoxon's signed-rank test (Walpole & Myers, 1985), which is robust to differences in scale.

### 3 Results and Discussion

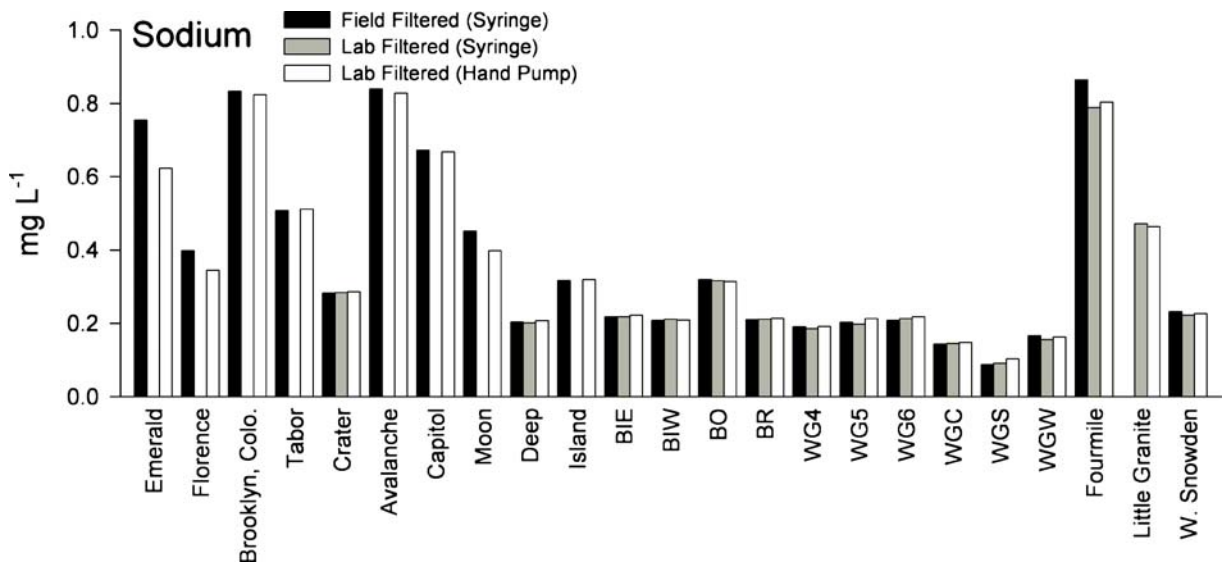
#### 3.1 Time effects of unfiltered storage

Figure 2 is an example of the response over time of two analytes (chloride and sodium) exhibiting significant responses to storage time. Variability between repetitions for all analytes was low (note the very small error bars) but variability between locations was high. For example, chloride ranged from about 0.07 mg/l at Upper West Tennessee Lake to 0.19 mg/l at Abyss Lake. This between-locations variability is typical of the other analytes in the test.

Effects of unfiltered storage time varied among analytes (Table II). Significant changes over time were evident for six analytes (pH, sodium, ammonium, potassium, chloride, and sulfate). Phosphate was below detection limits in nearly all the samples and

was not included in the analyses. Two other analytes, fluoride and ammonium, were below detection limits in many samples; thus results for these analytes should be used with caution. Changes in ammonium and pH may be partially explained by three factors. Gordon (1999) reports that these two analytes are known to be affected by prolonged contact with shipping/storage containers. CO<sub>2</sub> outgassing from the samples during the course of the test, which results in increased acidity (i.e., a significant positive coefficient for molar concentration of H<sup>+</sup> ions) over time (see Metcalf, 1984; Sommerfeld et al., 1991; Stepanian et al., 1989); this may have also occurred in the course of our test. Also, repeated opening and closing of the sample bottles may have exposed them to ambient CO<sub>2</sub> in the laboratory.

Statistically significant increases or decreases in analyte concentrations over time do not necessarily indicate changes that would invalidate an analysis. Note that, for chloride, the coefficient for filter time (i.e., increase in chloride concentration per hour of storage) is only  $6.0 \times 10^{-6}$  mg/l. The magnitude of change in an analyte that is acceptable depends on the context of the analysis and the precision of the equipment and procedures used. For example, Tang et al. (1987) noted that their criterion for statistical significance (two standard deviations of the mean)



**Figure 3** Sodium concentration by filtering method, filtering protocol experiment. Note the disparity in concentration between field-filtered and lab-filtered samples at Emerald

Lake; this sample may have been contaminated (see text). For an explanation of abbreviations, see Table I.

represented from 5% to more than 35% of the mean. Stepanian et al. (1989) compared the precision of samples with no storage time to that of samples stored for standardized intervals and used this to determine which statistical differences had “practical significance.” We were unable to use this criterion for our

study because of differences in study design, and instead used one-half of the sampling precision (root mean-squared-error/intercept) of each analyte as a threshold for the practical significance of percentage error. A ‘critical’ storage time (Table II) was thus calculated for each analyte. This is the time required

**Table III** Paired-sample mean differences, standard errors (SE), and Wilcoxon’s Signed-Rank Test results (S) for the filtering protocol experiment

|                                         | Field (syringe) vs lab (hand pump) |       |       |    |       | Field (syringe) vs lab (syringe) |       |       |    |       | Lab (hand pump) vs lab (syringe) |       |      |    |        |
|-----------------------------------------|------------------------------------|-------|-------|----|-------|----------------------------------|-------|-------|----|-------|----------------------------------|-------|------|----|--------|
|                                         | Mean                               | SE    | CV    | n  | S     | Mean                             | SE    | CV    | n  | S     | Mean                             | SE    | CV   | n  | S      |
| pH                                      | −0.003                             | 0.006 | 2.41  | 10 | −3.5  | −0.024                           | 0.024 | 0.99  | 4  | −3.0  | −0.009                           | 0.009 | 1.0  | 5  | −0.5   |
| (mol H <sup>+</sup> × 10 <sup>6</sup> ) |                                    |       |       |    |       |                                  |       |       |    |       |                                  |       |      |    |        |
| ANC (μEq/l)                             | 1.63                               | 1.98  | 1.22  | 10 | 4.5   | 2.38                             | 4.53  | 1.91  | 4  | 1.0   | 0.310                            | 0.310 | 1.0  | 5  | 0.5    |
| Conductivity (μS/cm)                    | 0.370                              | 0.175 | 0.47  | 10 | 15.0  | 0.150                            | 0.233 | 1.55  | 4  | 1.0   | 0.050                            | 0.050 | 1.0  | 5  | 0.5    |
| Na                                      | 0.005                              | 0.004 | 0.89  | 20 | 6.5   | 0.007                            | 0.005 | 0.76  | 14 | 20.5  | 0.005                            | 0.002 | 0.3  | 15 | 45.0** |
| NH <sub>4</sub>                         | −0.003                             | 0.003 | 0.91  | 20 | −9.5  | −0.001                           | 0.004 | 5.38  | 14 | 1.5   | 0.001                            | 0.001 | 1.6  | 15 | 1.0    |
| K                                       | 0.000                              | 0.003 | 12.96 | 20 | −7.5  | 0.003                            | 0.005 | 1.48  | 14 | 9.5   | 0.003                            | 0.003 | 1.1  | 15 | 18.0   |
| Mg                                      | 0.001                              | 0.002 | 2.47  | 20 | 7.0   | 0.000                            | 0.003 | 10.09 | 14 | 7.5   | −0.001                           | 0.002 | 2.7  | 15 | −9.5   |
| Ca                                      | 0.029                              | 0.011 | 0.36  | 20 | 65.0* | 0.005                            | 0.006 | 1.16  | 14 | 14.0  | −0.002                           | 0.006 | 3.6  | 15 | −0.5   |
| F                                       | 0.002                              | 0.002 | 0.92  | 20 | 3.0   | 0.000                            | 0.000 | 1.00  | 14 | 0.5   | .                                | .     | .    | .  | .      |
| Cl                                      | 0.012                              | 0.007 | 0.60  | 20 | 27.5  | 0.007                            | 0.006 | 0.87  | 14 | 15.5  | 0.000                            | 0.003 | 11.8 | 15 | 18.5   |
| NO <sub>3</sub>                         | 0.012                              | 0.006 | 0.50  | 20 | 46.0* | 0.007                            | 0.007 | 0.94  | 14 | 14.0  | −0.008                           | 0.007 | 0.9  | 15 | −13.0  |
| SO <sub>4</sub>                         | 0.043                              | 0.026 | 0.59  | 20 | 42.5  | 0.014                            | 0.007 | 0.52  | 14 | 32.5* | 0.005                            | 0.003 | 0.7  | 15 | 21.5   |

Units are mg/l except as noted.

\*=pr > |S| of < 0.05, \*\*=pr > |S| of < 0.01

**Table IV** Evaluation of variables indicating significant differences in the Wilcoxon analysis of the filtering protocol data

| Comparison, analyte                | Quality control limit<br>( $\pm$ %) | Grand mean<br>(mg/l) | Average deviation<br>$ x_i - y_i $ | Average deviation<br>(%) |
|------------------------------------|-------------------------------------|----------------------|------------------------------------|--------------------------|
| Field (syringe) vs lab (hand pump) |                                     |                      |                                    |                          |
| Ca                                 | 5.0                                 | 2.58                 | 0.029                              | 1.12                     |
| NO <sub>3</sub>                    | 10.0                                | 0.68                 | 0.011                              | 1.64                     |
| Field (syringe) vs lab (syringe)   |                                     |                      |                                    |                          |
| SO <sub>4</sub>                    | 5.0                                 | 0.77                 | 0.022                              | 2.83                     |
| Lab (hand pump) vs lab (syringe)   |                                     |                      |                                    |                          |
| Na                                 | 5.0                                 | 0.26                 | 0.006                              | 2.38                     |

Quality control limits are from USEPA (1987). Grand Mean is the mean of all values for the variable within the indicated comparison, and average deviation is the average of the absolute values of differences between paired samples.

for the change in analyte concentration to exceed the error threshold; in other words, the time required for the ‘signal’ of analyte concentration change to begin to exceed the between-sample error ‘noise.’ Critical storage times for analytes that exhibited significant change over time ranged from 58.0 h (sulfate) to 585 h (chloride). Note that, in the case of ammonium and sodium, our calculated critical storage time differs substantially from that recommended by the USEPA (1982). Precision of ANC, pH, and conductivity were not evaluated due to differences in lab analysis technique for this set of samples.

### 3.2 Filtering methods

The comparison between the field syringe/filter method and the alternative, simplified method, lab filtration with hand pump instead of field filtration, provided insight regarding the necessity of field filtration. Analysis of field blanks associated with each sample indicated that no sample contamination was introduced by the sample container or by transport. Figure 3 shows an example (sodium) of the filtering protocol experiment data as collected. Two analytes, calcium and nitrate, exhibited significantly higher (by 0.029 and 0.011 mg/l, respectively) concentrations in field-filtered samples (Table III) than in laboratory-filtered samples. As with the storage time experiment, these differences are statistically significant, but very small. Measured concentrations of calcium and nitrate ranged from 0.36–13.9 mg/l and 0.0–3.21 mg/l, respectively; the magnitude of error attributable to the difference in sampling method is small by comparison. Table IV shows average and percent

deviation values for these comparisons. Both of these results indicate variation within the quality control limits established by the USEPA (1987).

For the comparison of syringe/filter technique in the field vs. syringe/filter in the lab, only one analyte, sulfate, indicated a significant difference, with an average of 0.014 mg/l higher when filtered in the field. The syringe/filter vs. hand pump/filter comparison also had one significant difference, for sodium, with the hand pump/filter method generating samples averaging 0.005 mg/l higher. Average and percent deviations for these results are also shown in Table IV. Again, these are differences are very small relative to the magnitude of the analyte concentrations, and fall within USEPA (1987) quality control limits.

Samples at one location (Emerald Lake; Cloud Peak Wilderness, Wyoming) differed substantially (by as much as 252%) from both a duplicate sample and from values recorded at the site over the past 10 years, and were excluded from the analyses. Because the anomalies at Emerald Lake are unique in this test and in the historical record at this location, contamination from sample handling in the field is suspected as the most likely source of these differences.

### 4 Conclusions

The original hypothesis that samples stored under refrigeration for up to nine days would not exhibit significant changes in chemistry due to storage is not supported. Several analytes exhibited small but statistically significant changes during the course of the test. However, the current sampling protocol requires

analysis in less than 48 h after collection. This protocol was validated since no analytes having significant time effects exhibited changes that exceeded half of the sample variation in less than 48 h. This analysis did not evaluate field vs. lab differences.

The second hypothesis, that no differences would be detectable between samples filtered at the collection location with a syringe/Whatman filter and samples filtered < 48 h later in the laboratory using a hand pump, is partially supported. Only two analytes showed significant differences in sampling method, and in both cases, the error introduced was less than the USEPA (1987) standard for quality control. Testing the field filtering syringe method vs. the hand pump filter in the ‘clean’ environment of the laboratory of also indicated only very small differences in analyte concentrations. Errors introduced in samples using the field filtration protocol may be due to the conditions of the field environment rather than differences in the equipment used. An additional experiment designed to tightly control this aspect of sampling protocol would be beneficial.

One field-filtered sample in the test indicated possible contamination and was excluded from analysis; no samples indicated contamination during laboratory filtering or analysis. Field filtering in this experiment probably caused more problems with respect to sample quality than it prevented; field filtration for the type of samples and analysis in this test is not necessary. Fox et al. (1987) concluded similarly: “[We do] not recommend filtering (because of contamination problems and the lack of large amounts of suspended particulate in the high elevation surface waters) and sampling treatment is [thus] minimized.”

These experiments were conducted with samples from alpine and subalpine lakes with waters having low ionic strength and low biotic activity. Thus the conclusions above may be applicable only to sampling of waters with similar characteristics. Waters of greater ionic strength and more complex biotic activity could exhibit greater differences with respect to storage time and filtration protocols (e.g., Ormazá-González & Villalba-Flor, 1994). However, elimination of field filtering from sampling protocols, after careful evaluation to ensure data quality is not affected, will lower the costs and training requirements for sampling, and may help produce a greater number of valid samples.

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