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# **Chemistry of Precipitation, Streamwater, and Lakewater from the Hubbard Brook Ecosystem Study: A Record of Sampling Protocols and Analytical Procedures**

Donald C. Buso  
Gene E. Likens  
John S. Eaton

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## Abstract

The Hubbard Brook Ecosystem Study (HBES), begun in 1963, is an on-going, long-term effort to understand the structure and function of forest watersheds and associated aquatic ecosystems at the Hubbard Brook Experimental Forest in New Hampshire. Chemical analyses of streamwater and precipitation collections began in 1963, and analyses of lakewater collections began in 1967. This publication documents these collection methods, sites, and analytical techniques, providing a complete record to ensure the integrity of HBES data. The evolution of the HBES chemical data management system and the development of quality assurance procedures are described, as is the general algorithm by which ecosystem chemical inputs and outputs are calculated. These data represent a unique and important contribution to ecosystem science and provide an internationally recognized benchmark for assessing ecological changes.

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# HUBBARD BROOK EXPERIMENTAL FOREST

West Thornton, New Hampshire

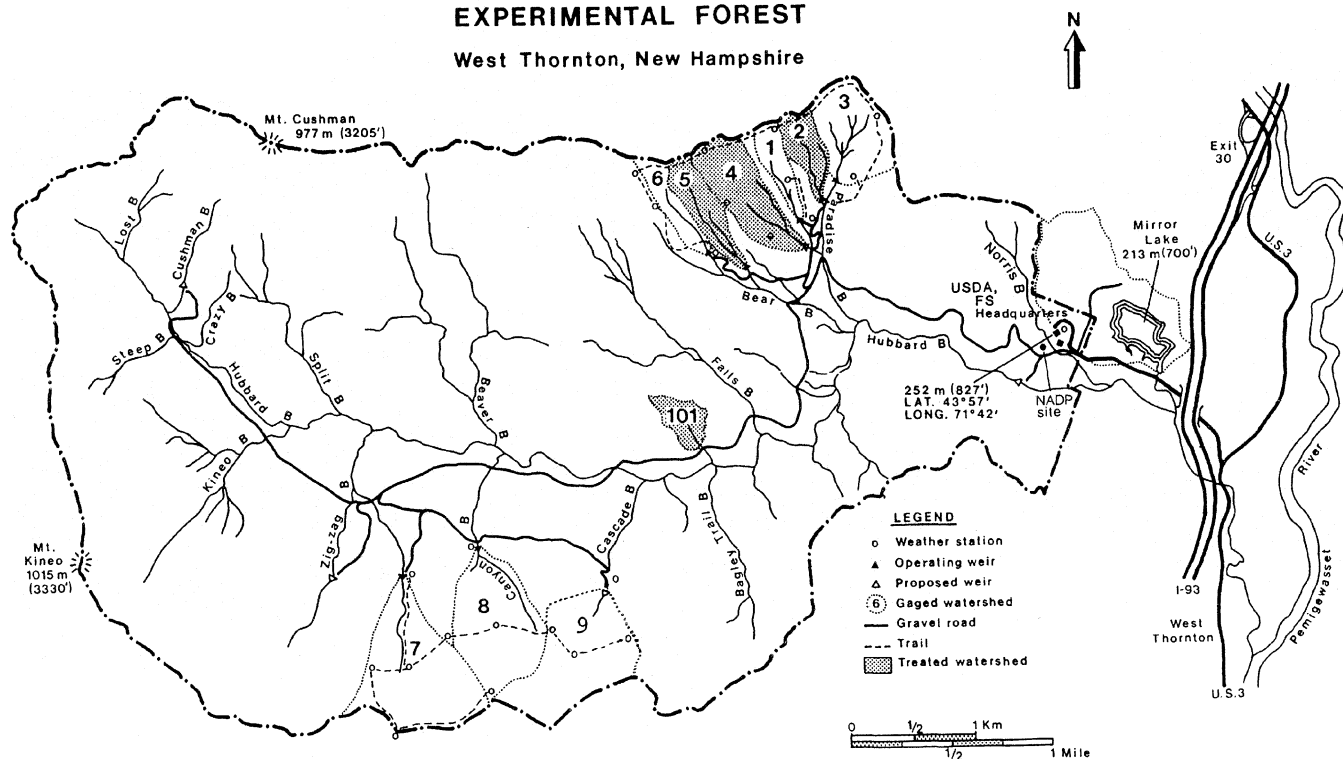


Figure 1.—The Hubbard Brook Experimental Forest in New Hampshire.

## Introduction

Long-term data are fundamental to understanding ecosystem structure, function, and change, and provide a basis for formulating meaningful and testable questions (Likens 1992). The long-term record of precipitation, streamwater, and lakewater chemistry is the foundation for many of the studies done as part of the Hubbard Brook Ecosystem Study (HBES) at the Hubbard Brook Experimental Forest (HBEF) (Fig. 1). These records provide critical data for the ecological assessment of important environmental problems at the local, regional, and national level.

The HBES was begun in 1963 by plant ecologist F.H. Bormann and limnologist G.E. Likens at Dartmouth College in collaboration with geologist N.M. Johnson at Dartmouth and R.S. Pierce, soil scientist with the USDA Forest Service's Northeastern Forest Experiment Station. Their goal was to establish chemical input/output relationships for small, forest watersheds and associated aquatic ecosystems at the HBEF with respect to natural processes and whole-watershed manipulations (see Likens et al. 1977; Likens and Bormann 1995).

This report documents the methods and protocols, including necessary changes in procedures and analytical techniques,

for field sampling, sample handling, and chemical analyses for the long-term data collected at the HBEF. The impetus for completing this report was the death of John Eaton, who began his career with the HBES in 1964 as a technician employed to collect and analyze samples. Later, he was responsible for data management and laboratory facilities. Great effort was required to reconstruct Eaton's work because of his extensive involvement in the HBES. His death also underscored the need to record all procedures, no matter how routine.

These long-term chemical data, in combination with continuous hydrometeorological measurements (Federer et al. 1990), are used to quantify the temporal variability of ecosystem inputs and outputs, calculate net nutrient retention or depletion from the watershed-ecosystems, estimate nutrient-biota interactions, and provide data for evaluating watershed ecosystem experiments. The resulting database is unique to ecosystem science because the HBEF was one of the first sites at which this integrated approach to watershed-ecosystem research was attempted, and great care was taken to ensure consistency during data collection, measurement, and analysis. In addition, this continuous database is the longest and most detailed of its kind in the world.

## Standard Protocols

### Collection Frequency

**Routine Samples.** There has been little change in our methods for collecting samples of precipitation and streamwater that were established at the beginning of the study. The first streamwater sample was collected from the biogeochemical reference watershed W-6 (Fig. 1) on 26 March 1963, by G.E. Likens and R.S. Pierce, as a specimen for analytical trials. Since the formal inception of the HBES on 1 June 1963, samples of precipitation and streamwater have been collected from W-6 and other sites on a weekly basis (Tables 1-2 and Appendix A). There have been two exceptions: from 4 December 1967 through 2 April 1968, and from 26 August 1968 through 6 May 1969, sampling from W-6 was reduced to biweekly collections due to budgetary constraints. Uninterrupted collections of inlet and lake water from nearby Mirror Lake began in June 1967 (Table 3).

On the basis of hourly, daily, and weekly sampling during the first 2 years of the study, and because concentrations were weakly correlated with discharge for most solutes, Likens et al. (1967) and Johnson et al. (1969) concluded that weekly samples were appropriate for characterizing average annual streamwater chemistry. At that time, only concentrations of sodium, aluminum, hydrogen ion (pH), nitrate, and dissolved silica were significantly correlated (slope significantly different from zero, at  $p < 0.01$ ) with discharge in W-6. Except for nitrate, which ranged from below analytical detection limit ( $< 0.01$  mg/L) to about 2 mg/L seasonally, concentrations of solutes varied less than threefold, though stream discharge varied by more than five orders of magnitude ( $10^{-2}$  to  $10^3$  L/s) (Likens et al. 1977; Likens and Bormann 1995).

The lack of strong relationships between concentration and discharge affected research at the HBEF in another important way. It allowed scientists to sample routinely at several sites because they did not have to expend limited financial and analytical resources monitoring a single site. Thus, adjacent, small forest watersheds could be compared on a long-term basis, a unique approach that has become the hallmark of the HBES.

More than 3 decades later, concentration-discharge relationships in W-6 have changed significantly for some solutes, e.g., calcium and sulfate (Fig. 2), and have been the subject of detailed study (Likens et al. 1998). However, most solute-discharge correlations have remained the same, e.g., ammonium and dissolved silica (Fig. 2), and total solute concentration in streamwater has remained nearly constant even though flow can vary dramatically (Fig. 3). Thus, the original rationale for maintaining a standard weekly sampling protocol remains valid for determining average concentrations or outputs on a seasonal or annual basis.

Even with weak concentration-discharge relationships, frequency of stream sampling can affect the calculation of nutrient outputs for a discrete period (see Data Calculations: Streamwater Outputs). The rapid hydrologic response of the HBEF watersheds further complicates this situation. For

**Table 1.—Data availability for precipitation chemistry from bulk collectors at RG-1, RG-11, RG-19, and RG-22, and a wet-only collector at RG-22, 1963-99<sup>a</sup>**

Site	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99											
RG-1 bulk																																																
RG-11 bulk																																																
RG-19 bulk																																																
RG-22 bulk																																																
RG-22 wet only																																																
Averaged bulk																																																

<sup>a</sup>A = complete analyses available for calcium, magnesium, potassium, and sodium; B = set A and pH, ammonium, sulfate, nitrate, and chloride; C = set B and phosphate and dissolved silica.

**Table 2.—Data availability for streamwater chemistry from HBEF, 1963-99<sup>a,b</sup>**

Site	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99			
W-1	A	A	A	A	A	A	A	A	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
W-2	A	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
W-3	A	A	A	A	A	A	A	A	A	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
W-4	A	A	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
W-5	A	A	A	A	A	A	A	A	A	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
W-6	A	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
W-7	A	A												B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	
W-8														B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	
W-9														B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	
W-101								B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
Hubbard Bk																																								

<sup>a</sup>A = complete analyses available for calcium, magnesium, potassium, and sodium; B= set A and pH, ammonium, sulfate, nitrate, chloride, phosphate, and dissolved silica; C= set B and acid neutralizing capacity, dissolved inorganic carbon, and dissolved organic carbon.

<sup>b</sup>All sites are sampled on a weekly basis except W-101 and Hubbard Brook, which are sampled monthly.

**Table 3.—Data availability for Mirror Lake outlet, inlets, outseepage site, and profile samples, 1963-99<sup>a,b</sup>**

Site	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99		
Lake outlet					A	A	A	A	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
NE inlet					A	A	A	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
NW inlet					A	A	A	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
W inlet					A	A	A	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
Outseepage																																							
Lake profile					A	A	A	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B

<sup>a</sup>A = complete analyses available for calcium, magnesium, potassium, and sodium; B= set A and pH, ammonium, sulfate, nitrate, chloride, phosphate, and dissolved silica; C = set B and acid neutralizing capacity, dissolved inorganic carbon, and dissolved organic carbon.

<sup>b</sup>Outlet and inlet samples are collected on a weekly basis. Seep is sampled monthly. Profiles are collected seasonally.

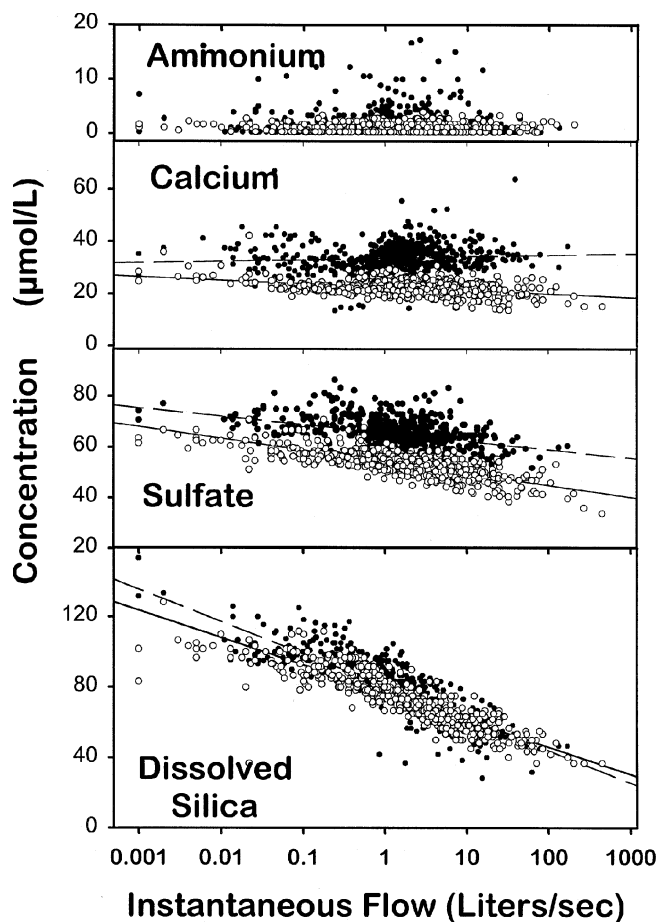


Figure 2.—Concentration discharge relationships in W-6 for 1963 to 1976 (•) and 1983 to 1996 (◦).

example, the flow rate in W-6 can change from < 0.5 to > 50 L/s in less than 12 hours in response to heavy rain or rapid snowmelt (Hornbeck 1973).

Therefore, rather than modeling changes in concentration, as has been done in the nearby but hydrologically different Mirror Lake watershed (Bukaveckas et al. 1998; Winter et al. 1989), we attempted to capture the effects of extreme hydrologic events (e.g., hurricanes) with more frequent samples to augment the routine samples obtained during those episodes. Significantly, the results of such “event sampling” in W-6 indicate that streamwater chemistry returns rapidly to near seasonal average values after peak discharge (Fig. 4). See Streamwater Collections for a description of the protocol for additional streamwater samples.

**Sample Filtration.** Precipitation and streamwater samples are not filtered routinely because particulate concentrations at HBEF usually are extremely low, ranging from 0.01 to 4.2 mg/L of oven-dry matter (Eaton et al. 1969; Bormann et al. 1974). In fact, W-6 is among the least turbid of streams measured in New England, seldom exceeding 1 Jackson

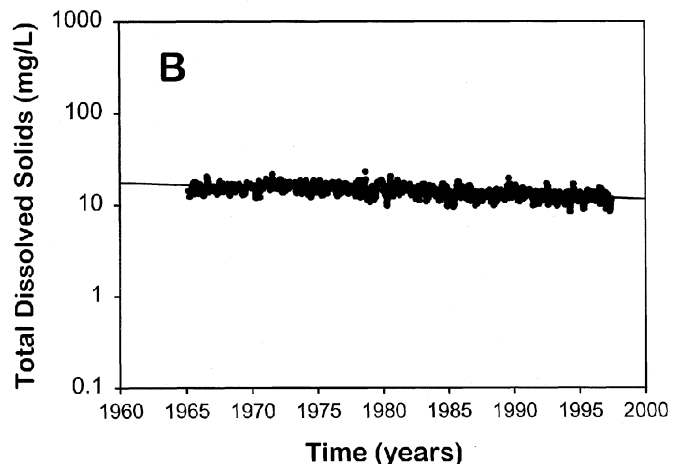
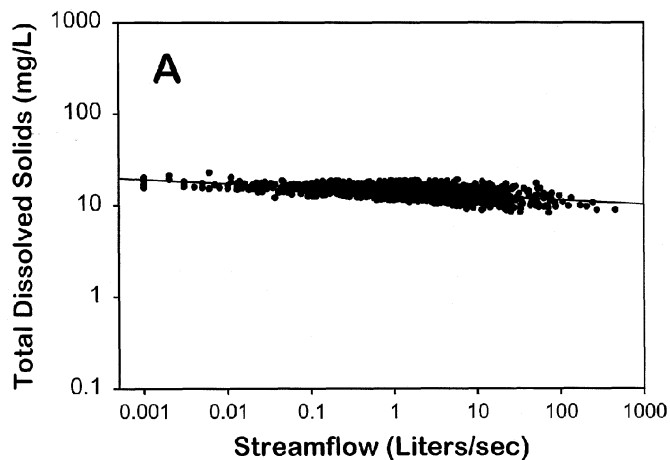


Figure 3.—Relation of total dissolved solids in streamwater with (A) discharge and (B) time.

Turbidity Unit over four orders of magnitude change in discharge (Martin and Hornbeck 1994). This clarity is due not only to the stability of the HBEF forest but also to the well-drained, coarse-textured soils which minimize overland flow (Bormann and Likens 1979), and the absence of true clays in this relatively young, glaciated terrain. Eaton et al. (1969) found that filters may undergo a net loss of weight after use, suggesting that filter mass contributes to contamination of the sample. Rather than being filtered, the rare samples with apparent turbidity are allowed to settle several hours or overnight and then are decanted into clean bottles.

**Sample Preservation.** Between June 1963 and January 1965, reagent-grade chloroform (1 mL/L) was added to all precipitation and streamwater samples immediately following collection in the field. Chloride data for weekly samples taken during this period were not used to determine annual chloride budgets but were retained in the database. Since 1965, none of the water samples collected from the HBEF has been treated with preservative prior to analysis. If shipment from HBEF to analytical facilities could not be accomplished within several days of collection, the samples



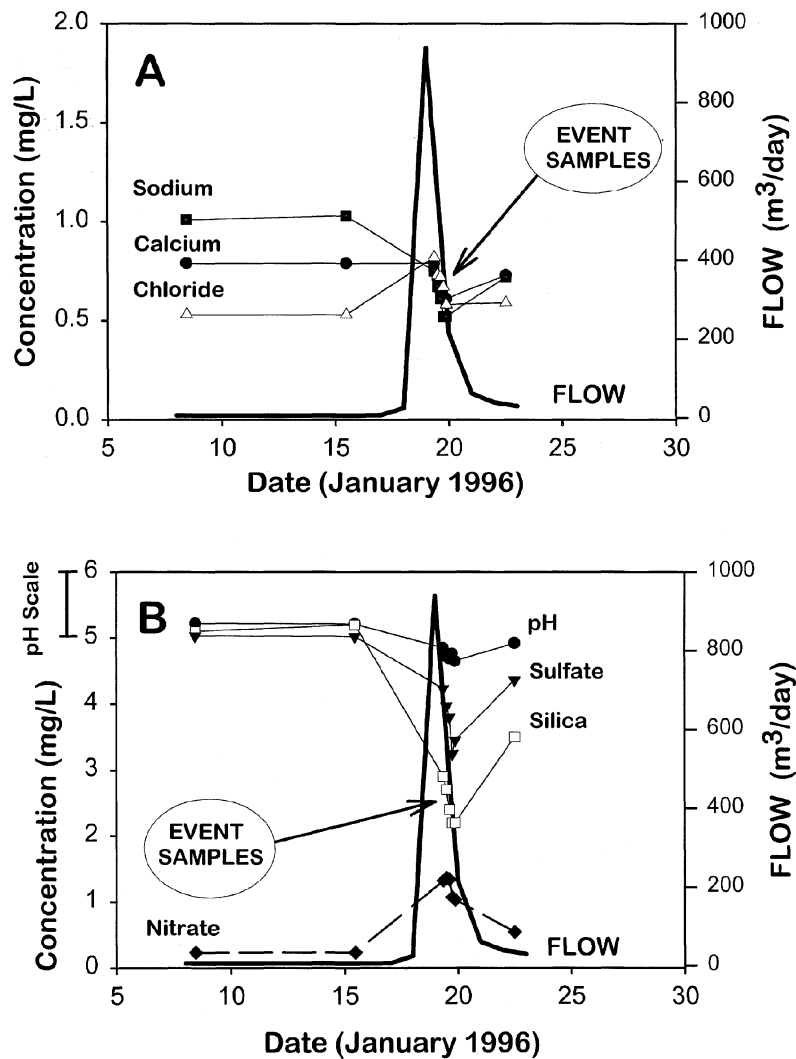


Figure 4.—Streamwater event for W-6 on 19-20 January 1996 for (A) calcium, sodium, chloride, and discharge, and (B) pH, sulfate, nitrate, dissolved silica, and discharge.

were refrigerated. Upon arrival at the analytical facility, samples usually remained in the original shipping container at room temperature until all analyses could be completed.

Nitrate in unpreserved samples from the HBEF is relatively stable over several months. In a test in 1998, 47 streamwater samples analyzed within 24 hours of collection and then after 3 to 4 months of storage without preservative or refrigeration had similar nitrate concentrations (linear regression slope = 0.95, y-intercept = 0.02,  $R^2 = 0.97$ ). This constancy is remarkable given that this test involved different laboratories, equipment, and operators, and a time delay of several months. Results were similar for anions in samples reanalyzed from 1970 to 1972. From 1963 to 1965, reanalyses of hundreds of samples from 2 months to several years after collection indicated that concentrations of cations did not change beyond the error of the original analysis (Appendix B). This chemical stability probably is due to the low ionic strength of the solutions (streamwater ranges from

15 to 20 S/cm specific conductance; dissolved solids are < 20 mg/L), well-aerated conditions (dissolved oxygen and carbon dioxide are near equilibrium with ambient air), low pH (< 6.0), and low biological activity. Since 1965, samples that are placed in archival storage are treated with 1.0 mL of chloroform per remaining liter of volume following completion of analyses.

Unfortunately, most of the water samples stored at Dartmouth College until about 1968 were discarded during the 1970's following the relocation of the HBES analytical facilities from Dartmouth to Cornell University in September 1969. Further reductions of stored samples were required in July 1983 following a second relocation of the analytical facilities to the Institute of Ecosystem Studies (IES) in Millbrook, New York. The current cataloged sample inventory includes all weekly samples of precipitation and streamwater from W-6 collected since January 1968 (Veen et al. 1994). Streamwater samples from W-5 dating to about 1970 are

**Table 4.—Linear regression statistics comparing solute concentrations in W-5 streamwater samples from 1975 with reanalyzed values in 1995<sup>a</sup>**

Solute	slope	y-intercept	R <sup>2</sup>	p value
Calcium	0.67	21.5	0.66	< 0.001
Magnesium	0.84	4.9	0.85	< 0.001
Potassium	0.97	0.3	0.95	< 0.001
Sodium	1.03	0.4	0.92	< 0.001
Hydrogen ion	0.64	8.6	0.06	.290
Sulfate	0.67	43.7	0.52	< 0.001
Nitrate	0.40	-4.7	0.54	< 0.001
Chloride	0.99	3.4	0.62	< 0.001

<sup>a</sup>Calculated from concentrations in µeq/L; p values < 0.10 indicate correlation between analytical results is significant.

represented by one or two weekly samples selected for each month of collection through 1982. Since 1983, all streamwater and precipitation samples have been stored at the USDA Forest Service's Archive Building at the HBEF.

Changes can occur in samples stored for decades, even with the addition of chloroform. Tests conducted in 1994 on preserved HBEF streamwater samples collected during the 1970's indicated that nitrate decreased by up to 100 percent (complete loss) in some samples, and that pH decreased by several tenths of a unit in others (Table 4, Fig. 5). Conversely, base cations (calcium, magnesium, potassium, and sodium) were relatively stable (within analytical error). Old and new chloride values were offset by a constant (linear regression slope = 0.99, y-intercept = 0.12 mg/L), possibly reflecting chloride derived from the preservative. These results suggest that the preservative effects of chloroform decrease with time and that the most profound changes may occur in solutes that are biologically active (e.g., nitrate) or pH sensitive (e.g., aluminum). This complex issue remains under investigation (see Quality Assurance Procedures).

**Sample Equipment Preparation and Cleaning.** Throughout the study, bottles used to collect and store streamwater samples have been acid-washed, low- or high-density polyethylene (LDPE or HDPE). Re-washed LDPE bottles were used for storage until 1974; since that time, only virgin bottles (fresh from manufacturer) have been used. Polycarbonate or polypropylene bottles have not been used because they shatter at low temperatures in the field. Glass bottles were used only to collect samples for specific projects (e.g., analyses for dissolved organic carbon). From 1963 to 1973, all bottles and field collection gear were cleaned at the HBES analytical facilities at Dartmouth College (1963-69), or Cornell University (1969-73). Since 1973, cleaning has been conducted at HBEF in the USDA Forest Service's facility, now the R.S. Pierce Ecosystem Laboratory (Pierce Lab).

The acid-washing procedure is similar for all bottles for precipitation, streamwater, and lakewater samples and for devices used to collect precipitation. Plasticware is rinsed

with or soaked in 50 percent (~ 6N) reagent-grade HCl, purged with laboratory tap water to remove the acid, and flushed with deionized water (DIW) at least three times. The final DIW rinse is allowed to stand in a tightly capped container at least overnight, and the solution is checked for specific conductance before use. A conductance of < 2 µS/cm is considered acceptable; otherwise, the bottles or containers are re-rinsed, soaked, and tested again. Stored collectors that exceed 2 µS/cm following a second rinse are set aside for re-washing with acid. For analysis of trace metals, the plasticware is soaked in reagent-grade 6N nitric acid, and DIW only is used for rinsing.

**Deionized Water Quality.** Laboratory tests of the final DIW rinse of collection equipment indicate that no measurable contaminants are present when standard washing protocols are followed strictly. The DIW used for washing at HBEF has a pH of 5.6 ±0.1, and a conductance of about 0.6 S/cm when fresh (after 1 day standing in a 50-L polyethylene carboy, DIW reaches about 1.5 S/cm as it equilibrates with the atmosphere and any carboy leachates). Fresh DIW has no solute concentrations at levels higher than are detectable with the analytical methods currently in use, except hydrogen ion and dissolved carbon dioxide (both < 10 µmol/L). The DIW is provided by a pump-driven demineralizer system (Millipore Q model) that includes an activated carbon column, two mixed-bed resin ion-exchange columns, and an organic exchange column, in that order. The columns are changed whenever fresh DIW conductance exceeds 1 µS/cm, which occurs three to four times a year. Tap water at the Pierce Lab is not chlorinated (UV light-sterilized and filtered) and is relatively dilute (total dissolved solids < 30 mg/L).

## Field Procedures

### Precipitation Collections

**Collection Procedures and Equipment.** Precipitation is collected weekly with bulk collectors (Likens et al. 1967), that is, collectors that are continuously open to the atmosphere. During the warmer months, approximately 1 May to 1 November, rainfall is collected using HDPE funnels connected to LDPE bottles with laboratory-grade polyvinyl (Tygon)<sup>1</sup> tubing and various polypropylene, polyethylene, or nylon fittings (see Figure 2 in Likens et al. 1967). Individual plastic pieces of the collection system are replaced at least every 3 years. Funnels and bottles are held on laboratory clamp stands that are attached to wooden posts so that the funnel lip is about 2 m above the ground. The posts are centered in rain gauge clearings in the forest. These areas are cleared periodically to keep vegetation low. All trees have been removed so that no portion of the surrounding canopy intersects a 45-degree angle from the lip of the funnel upward. During routine mowing or maintenance of the

<sup>1</sup>The use of trade, firm, or corporation names in this report is for the information and convenience of the reader. Such use does not constitute an official endorsement or approval of the U.S. Department of Agriculture or the Forest Service of any product or service to the exclusion of others that may be suitable.

clearings, the funnels are covered with clean, new polyethylene bags.

While washing sampling apparatus, laboratory personnel wear laboratory-grade polyethylene or vinyl gloves to avoid contaminating clean parts. Clean collectors are stored (capped or covered) in polyethylene bags with 500 to 1,000 mL of deionized water left in each bottle or bucket. Equipment is transported to and from the field in polyethylene bags. Bottle caps are screwed tight and bucket lids are seated firmly. The collection equipment is set up in the field carefully so that clean surfaces do not come in contact with bare hands or with clamping devices.

The theoretical weekly capacity of the collector bottle is exceeded an average of three times each season. It is assumed that precipitation entering the reservoir bottle mixes completely, and that any lost overflow volume has the same chemical composition as the remaining solution. During each warm season, the funnels are dry (no precipitation) an average of three times. However, the entire apparatus is replaced and washed each week. About once each year, the funnel/bottle apparatus collects unmelted snow. At such times, the funnels are wrapped in clean polyethylene bags on site and returned without disassembly to the Pierce Lab, where the snow and ice are melted fully.

During the cold months (approximately November to April), open barrels or large-mouth buckets are used to collect precipitation. These are mounted on the same posts described earlier. All collections are thawed if necessary, weighed, and then poured off into clean, 500-mL polyethylene bottles at the Pierce Lab. Prior to February 1982, large (120-L), plastic barrels (Rubbermaid "Brute" containers) were used to collect snow. While containers seldom were overtopped with snow, it was difficult to clean and transport them from the collection site to the lab. Since 1982, 21-L, HDPE buckets have been used; they are replaced with new containers about every 3 years. The buckets have a snow-depth capacity of 340 mm (before settling). This capacity is exceeded an average of two times each winter. In such instances, mounded snow is tamped carefully below the bucket lip with the clean underside of the new bucket lid.

**Contamination.** Our goal has been to collect the cleanest possible precipitation samples to quantify ecosystem deposition. Because bulk-precipitation collectors are open continuously to atmospheric inputs, sample contamination is a potentially significant problem. From the beginning, we have attempted to define the degree of contamination that is unacceptable, and to document instances of lesser contamination in field notes (Appendix C). The

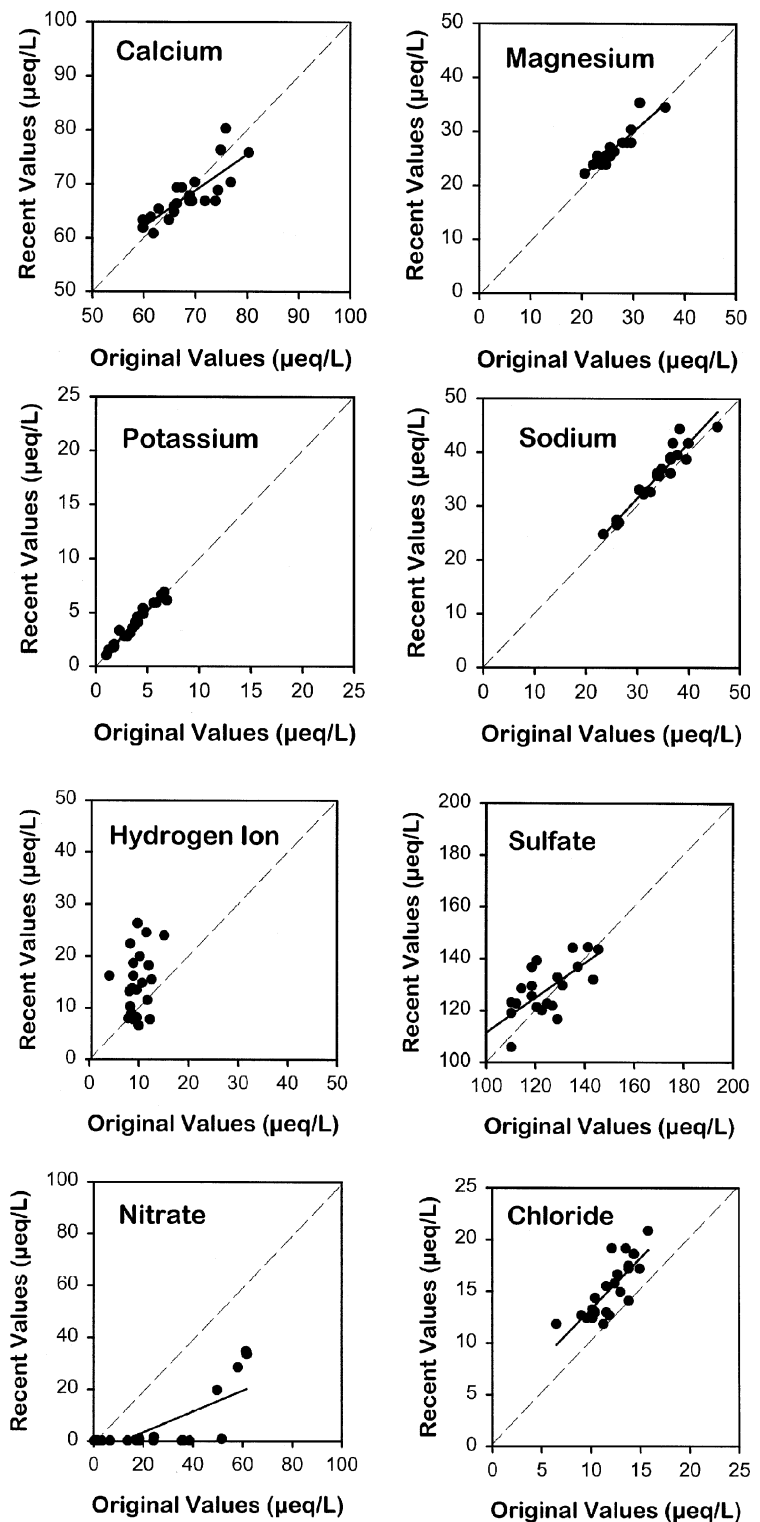


Figure 5.—Reanalysis of 20-year old streamwater samples (see Table 4). Dashed line describes 1:1 relationship.

protocol for rejection of precipitation samples has been based on a three-level approach: 1) if the sample is obviously discolored, turbid, or odiferous due to gross contamination, the sample is rejected without further analysis; 2) if an uncontaminated sample from a replicate bulk collector shows large differences in the initial pH and specific conductance, the sample is rejected; and 3) if there is any uncertainty at level 1 or 2, the sample is analyzed as usual and compared against predetermined benchmarks for ion balance and long-term average concentrations (see Quality Assurance Procedures). Should the sample fail quality control standards at level 3, the sample data are coded for rejection but retained in the database (Fig. 6).

The primary sources of natural contamination at the HBEF are unidentifiable fine particulate material (FPM), pollen, insect bodies, and bird droppings (in order of frequency), with the most numerous incidents occurring during the summer. Although several very fine particles (< 0.5 mm) are visible in about 95 percent of all samples, there are seldom enough of them to warrant sample rejection prior to analysis. Collection bottles or buckets are allowed to stand without agitation before the sample aliquot is decanted. Comparisons of bulk-precipitation samples free of FPM and those samples that have been decanted to remove FPM showed no difference in chemistry.

Gross contamination, most often the result of visible bird feces, is rare at W-6; an average of one sample per year (< 2 percent of total) is rejected without analysis. Since 1963, only 103 W-6 bulk-precipitation samples (about 6 percent) have been analyzed and then rejected. Rain gauge 11 (RG-11) has been the primary site for precipitation collections at the HBEF watersheds since 1969. To prevent the loss of bulk collections at the experimental watersheds due to field contamination or collector damage (e.g., windstorm, hail, vandalism) at RG-11, a second collector was established at rain gauge 1 (RG-1) in 1972 (see Figure 1 in Federer et al. 1990; Appendix A). Rain gauge 22 (252 m elevation; 2.5 km east of WS-6; Fig. 1) has both bulk and wet-only collectors (Appendix A). These collectors have been used for measurement of deposition near the Pierce Lab and Mirror Lake watershed.

Since 1972 there have been no instances of gross contamination or damage simultaneously at RG-1 and RG-11. As a result, there is a continuous record of collections from the experimental watersheds. By comparing these duplicate collections with and without modest contamination, we have been able to examine the effect of FPM on precipitation chemistry at the HBEF. The chemistry in these bulk collectors is nearly identical. There are no significant differences ( $p < 0.05$ ; Mann-Whitney rank sum test of paired data from 1987 to 1996) between median values of raw weekly concentrations for any solute in samples without gross contamination (Table 5). Comparing each ion on a sample-by-sample basis (linear regression analysis; Table 6) demonstrates that most ions are well matched (Fig. 7). Correlations were poorest for potassium, ammonium, phosphate, and dissolved silica paired tests (Fig. 7).

**Table 5.—Nonparametric p-values (Mann-Whitney rank sum test) for comparison of median weekly bulk-precipitation chemistry collected simultaneously at RG-1 and RG-11, 1987-96<sup>a</sup>**

Solute	p value
Calcium	0.368
Magnesium	0.660
Potassium	0.608
Sodium	0.878
Ammonium	0.913
pH	0.876
Sulfate	0.889
Nitrate	0.785
Chloride	0.413
Phosphate	0.831
Dissolved Silica	0.295

<sup>a</sup>P values > 0.10 indicate no significant difference in medians between sites.

**Table 6.—Linear regression statistics comparing weekly bulk precipitation chemistry, collected simultaneously at RG-1 and RG-11, 1987-96<sup>a</sup>**

Solute	Slope	Y-intercept	R <sup>2</sup>	p value
Calcium	0.99	0.00	0.91	< 0.001
Magnesium	0.82	0.01	0.70	< 0.001
Potassium	0.57	0.03	0.46	< 0.001
Sodium	0.90	0.01	0.90	< 0.001
Ammonium	0.74	0.07	0.64	< 0.001
pH	1.00	0.01	0.94	< 0.001
Sulfate	0.97	0.10	0.97	< 0.001
Nitrate	0.98	0.07	0.92	< 0.001
Chloride	0.92	0.01	0.85	< 0.001
Phosphate	0.31	0.03	0.07	< 0.001
Dissolved silica	0.82	0.00	0.40	< 0.001

<sup>a</sup>Calculated from concentrations in  $\mu\text{eq/L}$ ; p values < 0.10 indicate correlation between analytical results is significant.

At the collection sites next to the Pierce Lab (RG-22), contamination by bird feces is more frequent. These incidents and occasional contamination from the nearby buildings and parking lot have resulted in 139 sample rejections (10 percent of total) in the bulk collections since 1969.

Contamination of precipitation samples by washing acid or salts in the laboratory is rare because precautions are taken to test the final deionized-water rinse of each container, clean collectors are handled carefully, and storage bottles are rinsed with sample water three times (see Resolving Analytical Problems: Precipitation Samples). Because the

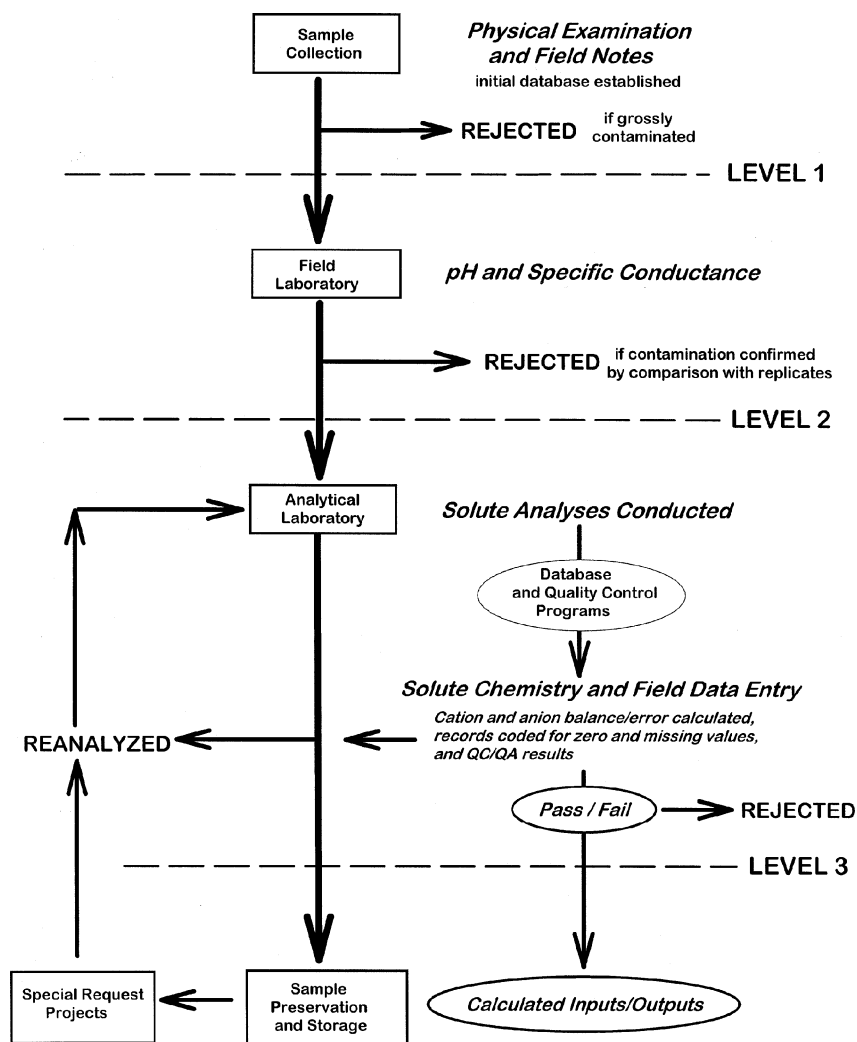


Figure 6.—Flow chart of field protocols, quality assurance procedures, and analytical sequences applied to sample processing. Levels 1, 2, and 3 refer to rejection criteria (see text).

frequency distribution of concentrations in samples that are considered uncontaminated can be similar to that for samples rejected for visible contamination (Fig. 8), following strict chemical criteria alone might remove “good” samples with high concentrations from the database. We have tried to avoid distorting the long-term data by elimination of uncontaminated samples or inclusion of grossly contaminated ones (see Quality Assurance Procedures).

**Collector Efficiencies.** Precipitation volume at the HBEF is determined independently by a network of standard rain gauges at HBEF (Federer et al. 1990). In an ongoing study of collection efficiency since 1987, it has been determined (by weight) that the funnel and bottle apparatus collects an average of about 90 percent of the catch recorded in an adjacent standard rain gauge, and that efficiency did not relate to precipitation volume. Bulk snow buckets had an average seasonal collection efficiency of about 85 percent; efficiency declined with lower precipitation volume. Collection efficiencies may be below 100 percent due to a lack of wind shielding around bulk-collector openings (Leonard and

Reinhart 1963). The funnel and bottle apparatus is designed to prevent evaporation (Likens et al. 1967). However, during transition periods between rain and snow seasons, and at catch volumes < 100 mL, evaporation from the open snow buckets can occur; this may artificially increase ion concentrations. When evaporation is suspected, based on low volume and low total catch, the database record is flagged (see Quality Assurance Procedures, Appendix C). Calculating deposition fluxes with or without these data has little effect on an annual basis because volumes < 100 mL represent < 0.1 percent of the total annual catch. The primary importance of these efficiency measurements is to detect gross physical problems with the chemical collectors, e.g., spillage, leaks, vandalism.

**Collection Site Changes.** During 1963-69, chemistry from several combinations of precipitation collection sites was used to calculate deposition (Appendix A). This approach was taken in response to two conflicting problems that were difficult to solve during that period of modest funding: 1) the need to obtain as many uncontaminated precipitation

samples as possible; and 2) the need to reduce expenses resulting from redundant chemical analyses. When two or more clean collections were analyzed, an average chemistry of the individual sites was recorded in the database (21 percent of records prior to 1990) and coded as such (see Precipitation Inputs). Occasionally, samples were physically composited when the quantity of precipitation was insufficient to analyze for most of the constituents (< 25 mL in any sample). Composited samples were not used in calculations of deposition, and all such records are coded in the chemical database (see Quality Assurance Procedures).

Until 1969, we did not maintain a separate chemical database for each precipitation collection site, though a printed copy of analytical results is on file for each sample. Since July 1969, chemical data from collections at the Pierce Lab and from the experimental watersheds have been compiled independently. Locations of precipitation collectors and sources of chemical data since 1963 are listed in Appendices A and B.

**Variability in Precipitation Chemistry.** Initially, there was concern that precipitation chemistry might vary significantly from the lower to the upper elevations in the experimental watersheds. Two-way analysis of variance conducted by Likens et al. (1967) on samples from 1964-65 showed no significant differences ( $p > 0.01$ ) in concentrations of base cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ) for samples from three rain gauges near W-6 (RG-11: 550 m; RG-10: 690 m; and RG-9: 770 m (see Figure 1 in Federer et al. 1990). On the basis of data from 1971-72, Likens et al. (1977) reported significantly higher concentrations of nitrate ( $p < 0.05$ ) and sulfate ( $p < 0.01$ ) in the bulk collector at RG-22 compared with the collector at RG-11, and suggested that this might be due to the effects of human activity in the lower Hubbard Brook Valley and around the Pierce Lab.

More recently, analysis of weekly precipitation chemistry collected from 1979 to 1990 from RG-22 and RG-11 revealed no significant differences ( $p > 0.05$ ) in solutes from bulk collectors on a spatial basis within the HBEF (Table 7: Mann-Whitney rank sum test of medians). Initial data from a bulk collector established in 1995 at rain gauge 19 (RG-19) in W-8 seem to corroborate those findings.

There are differences in solute concentrations between wet-only collectors and bulk collectors (Table 7). Base-cation concentrations were significantly higher ( $p < 0.05$ ) in weekly bulk-precipitation chemistry compared to weekly wet-only chemistry collected concurrently at RG-22 from 1979 to 1990 (Martin et al. 2000). For ammonium, pH, sulfate, nitrate, and chloride concentrations, there were no significant differences ( $p > 0.05$ ) between wet-only and bulk

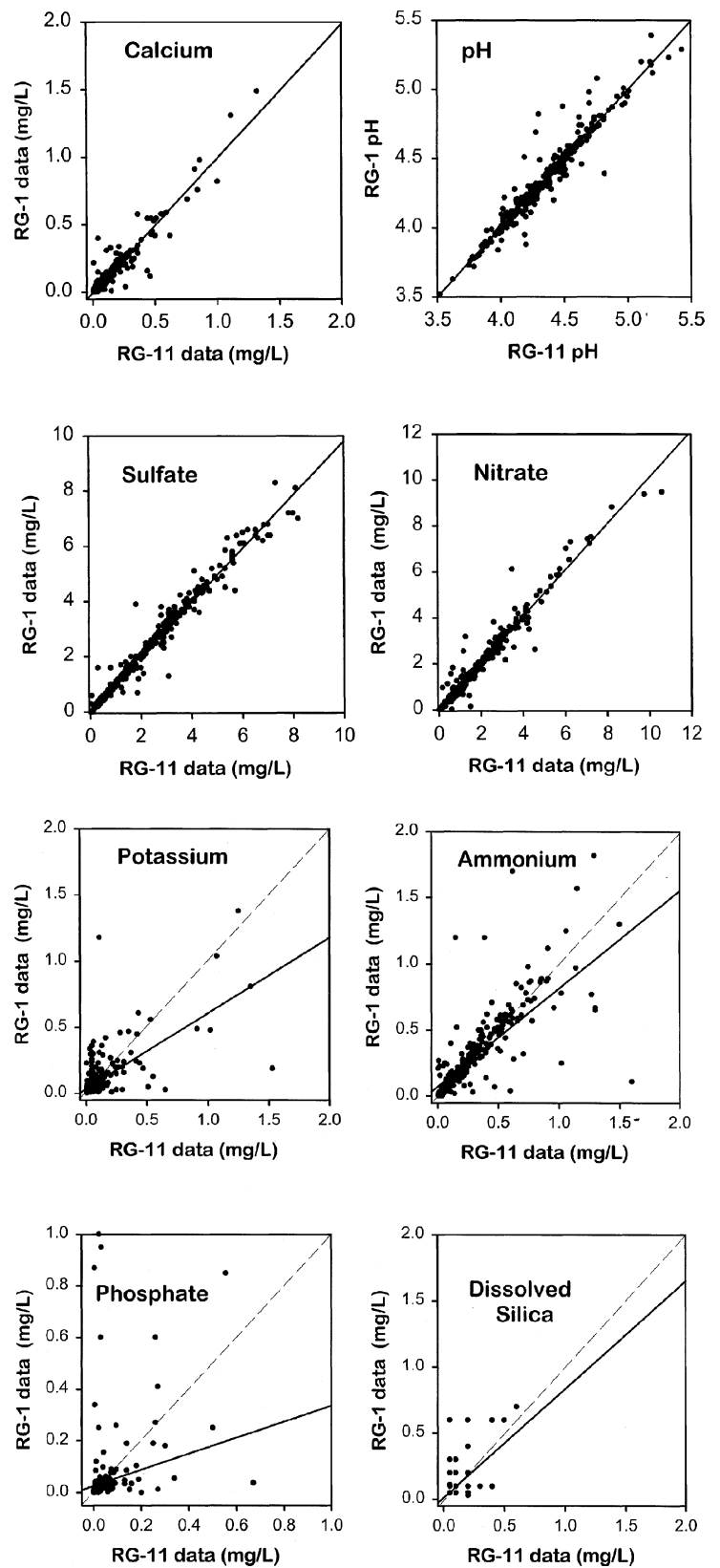


Figure 7.—Comparison of bulk-precipitation chemistry from RG-1 and RG-11 (see Table 5). Dashed line describes 1:1 relationship.

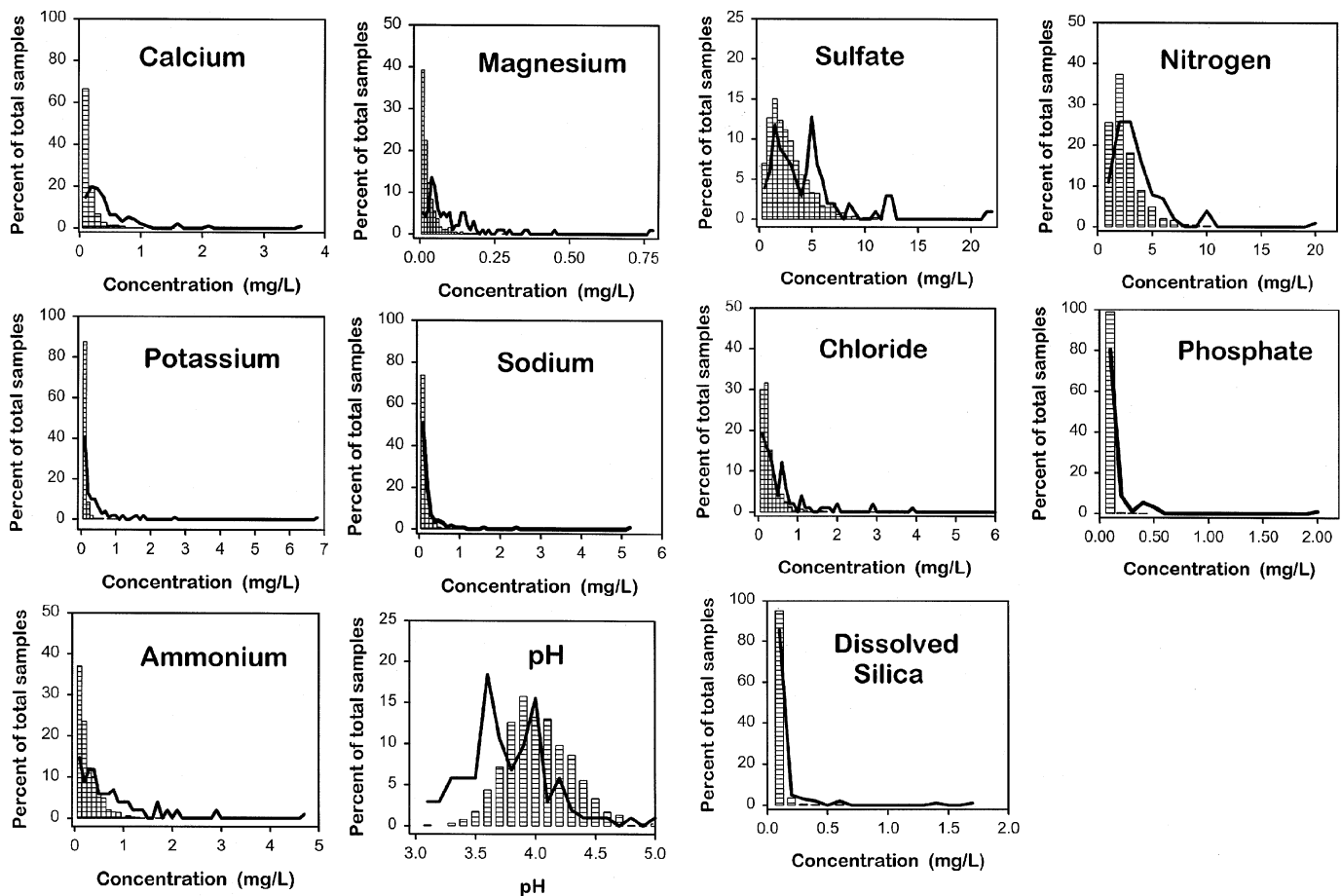


Figure 8.—Frequency histograms of concentrations of solutes in clean (bars) and contaminated (solid line) bulk-precipitation samples.

chemistry. However, variability in precipitation chemistry from week to week typically was much higher than that between different collector types (Fig. 9).

The different effects of spatial, temporal, and collector variability on precipitation chemistry at the HBEF have become understood only after years of collection and careful analysis. From 1966 to 1969 when bulk precipitation was collected only at one site and clean bulk samples were not available each week, some substitution of wet-only samples was required (see Appendix A) to provide data for ecosystem inputs. Given the low spatial variability and high temporal variability of precipitation, there was less bias from occasional substitution than from using fewer samples. Thus, the use of uncontaminated samples from a variety of collector sites and types within the HBEF during this period seems to have been a reasonable approach to calculating input concentrations for watershed-ecosystems, and does not represent a significant bias to calculated deposition from 1966 to 1969.

**Table 7.—Nonparametric p-values (Mann-Whitney rank sum test) for comparison of median weekly bulk-precipitation chemistry collected simultaneously from bulk-collector sites at RG-11 and RG-22 (pair A), and wet-only collector and bulk collector at RG-22 (pair B)<sup>a</sup>**

Solute	p value	
	Pair A	Pair B
Calcium	0.584	0.002
Magnesium	0.702	0.004
Potassium	0.227	< 0.001
Sodium	0.227	0.005
Ammonium	0.303	0.752
pH	0.929	0.130
Sulfate	0.997	0.280
Nitrate	0.328	0.085
Chloride	0.413	0.003
Phosphate	0.591	< 0.001
Dissolved silica	0.367	0.041

<sup>a</sup>P values < 0.10 indicate significant difference in medians between sites or collector types.

Perhaps more importantly, it was recognized from the beginning of the HBES that deposition must be calculated for each specific watershed within the HBEF based on Thiessen-weighted average precipitation volume for that area (Likens et al. 1967; Federer et al. 1990). This approach is necessary because there is a significant increase ( $p < 0.001$ ; Mann-Whitney rank sum test of median annual data) in precipitation volume (about 17 percent more) from Mirror Lake to W-6 (Fig. 1).

### Streamwater Collections

**Collection Procedures and Equipment.** Stream samples are collected weekly from sites located 5 to 10 m above each of the permanent watershed gauging stations to avoid disturbance due to routine maintenance. There have been variations of several meters in the exact point of sampling since 1963, but analysis of stream chemistry over long (hundreds of meters) elevational gradients indicates that significant changes are highly unlikely over such short distances (Johnson et al. 1981; Lawrence and Driscoll, 1990). No samples are taken from the weir basin itself or from below the v-notch or flume because of potential contamination from stream-gauge construction materials such as iron and concrete, or ponded debris. Time of collection (Eastern Standard Time) and water temperature ( $^{\circ}\text{C}$ ) are recorded for each sample.

Usually, streamwater is collected by placing a bottle under a small waterfall. Care is taken so that the person collecting the sample does not contaminate the clean bottles and caps. If contamination occurs or is suspected, an alternate bottle is used. At times of extremely low flows, a clean syphon or syringe is used to withdraw water from an undisturbed natural pool. Such situations are recorded in field notes and coded in the database. The collection bottle always is rinsed at least three times with streamwater before filling. For most of the record, 500-mL low-density, new polyethylene bottles were used to collect and store samples. Since 1992, clean, 1-L LDPE bottles have been used for field collection. Samples are poured off in the laboratory into clean, acid-washed, sample-rinsed 500-mL bottles for shipment and permanent storage.

**Event Sample Protocol.** When practical, single samples are taken during periods of relatively high flow throughout the year. About three or four times a year, a sequence of samples is taken by field personnel during the rising and falling limbs of the hydrograph of an event (12- to 24-hour period). This procedure can generate six to eight samples, each of which is treated using standard protocols. These samples are used to evaluate changes in concentration-discharge relationships for various solutes (Johnson et al. 1969).

Battery-powered, automatic samplers (e.g., NCON sequential samplers or ISCO programmable auto-samplers) have been used but are problematic for routine samples.

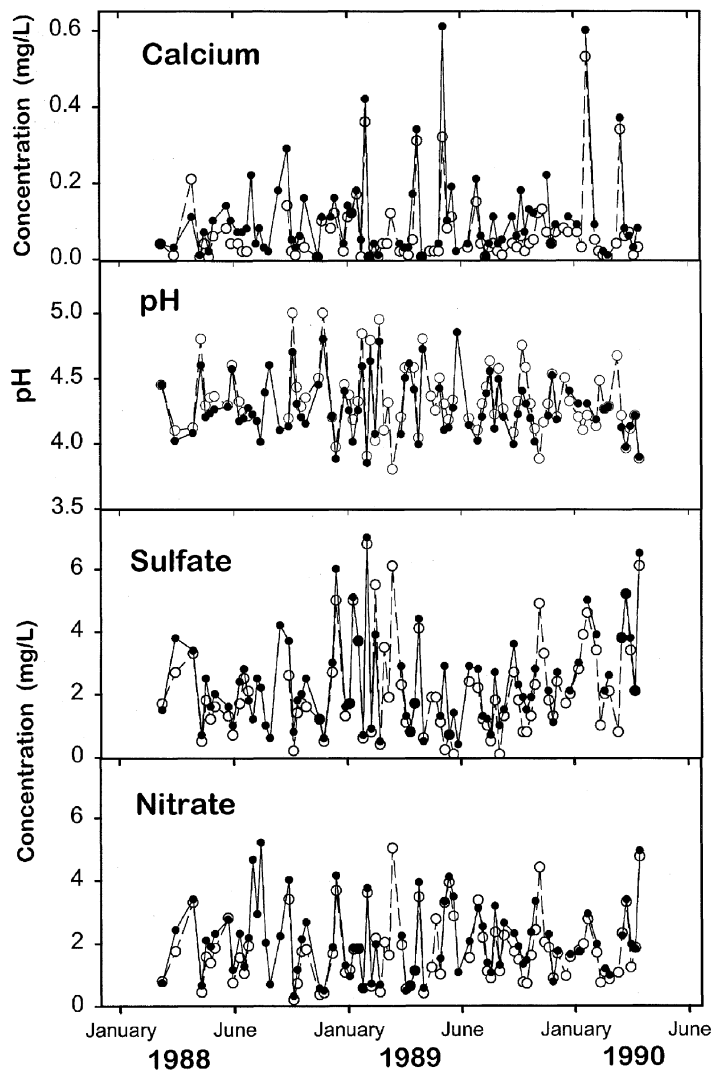


Figure 9.—Comparison of concentration data from simultaneously collected, weekly samples of co-located bulk (●) and wet-only (◊) collectors at RG-22, 1988 to 1990.

Difficult field conditions (e.g., freeze-thaw cycles and remote locations) promote sampler breakdowns; if the timing is inaccurate, neither volume-weighted nor event samples are valid. During the 1960's and early 1970's, such samplers were not commonly procureable, nor if they had been, were research funds available to purchase them.

### Mirror Lake Collections

**Streamwater Collection Procedures and Equipment.** Weekly collections of water samples from the Mirror Lake outlet and the northeast (NE), northwest (NW), and west (W) inlets (see Figure III.B.3-9 in Likens 1985) began in June and July of 1967, respectively. From June 1976 to May 1979, all



inlet and outlet sampling was discontinued due to a hiatus in funding (Table 3). Sample protocols for these sites are identical to those established for the HBEF experimental watersheds except that Mirror Lake samples are taken at the first available perennial waterfall above or below the lake, regardless of the location of the gauging station. At the outlet, the sample site is located on a concrete dam and the sample is taken from lakewater falling over or leaking through the (untreated, natural wood) spillway boards. Since 1979, the lake inlets have had gauging stations (small, galvanized-steel Parshall flumes) installed by the Water Resources Division of USDI Geological Survey (USGS) (Winter 1985). A similar, larger flume was installed by the USGS on the Mirror Lake outlet, below the concrete dam, in October 1989. Samples of a stream starting in an area of subsurface seepage down-gradient of the lake (Winter 1985) have been collected on a monthly basis since 1989 when a flume was installed there.

#### **Lakewater Collection Procedures and Equipment.**

Samples from Mirror Lake have been taken at a central location that is at the deepest part (11 m) of the lake (see Figure IV.B-2 in Likens 1985). In general, chemical profiles of the lake have been collected at discrete depth intervals of 1 to 2 m on a seasonal basis (four to six times a year), though with greater intensity during periods when scientists were actively pursuing specific projects on the lake (Table 3).

The following protocol was established in 1990: six samples are taken by peristaltic pump at 2-m intervals from the surface (0.5 m) to a depth of 10 m; clean, 250-mL polyethylene bottles and clean, 300-mL glass BOD bottles are used. One sample at each depth is passed through a 45-mm diameter, in-line, glass-fiber filter (Whatman GF/F, 0.45- $\mu$ m pore) and analyzed for all major cations and anions (Table 3). The unfiltered sample is analyzed for total phosphorus. Samples in the glass bottles are analyzed for pH, dissolved inorganic carbon (DIC), and acid neutralizing capacity (ANC) immediately upon return to the laboratory. In addition, epilimnetic water is filtered (from 250 to 500 mL, with six repetitions) through 25-mm diameter, in-line, GF/F filters to obtain chlorophyll samples. These filters are sealed in a plastic petrie dish and frozen as soon as possible for later analysis.

Concurrent with the collection of the chemical samples, profiles of temperature and specific conductance are recorded. Field instruments have included Whitney thermistor Underwater Thermometers (1967-90), various Yellow Springs Instrument Co. (YSI) meters (1990-98) and Cole-Parmer Instrument Co. probes (1998 to present). The meters are calibrated with NBS-traceable, glass-mercury thermometers (precision  $\pm 0.1^\circ\text{C}$ ). Samples for dissolved oxygen are collected at each depth and analyzed by Winkler titration at the Pierce Lab. Secchi disk (20-cm diameter) transparency is determined during the ice-free season. All of the procedures described follow methods in Wetzel and Likens (1991). Prior to 1990, water-sample collection devices were various types of open-ended, mechanical-closure bottles (e.g., Kemmerer or VanDorn bottles made of stainless

steel, glass, PVC, or acetate plastic) lowered to the appropriate depth and closed by trigger messenger released from the surface. Filtration for chlorophyll samples was conducted on large sample volumes upon return to the Pierce Lab. Few samples for solute analysis were filtered prior to 1990.

## **Analytical Methods**

### **General Protocols**

We have maintained rigorous quality controls throughout the study for detecting and measuring variation due to sample contamination and analytical error. When it has been necessary to change procedures, we have overlapped the methods for several months to more than a year to avoid artifacts in the database. In fact, the analytical methods used for the long-term data set of precipitation, streamwater, and lakewater chemistry have changed relatively little (Fig. 10). In 1963, samples were taken immediately to analytical facilities at Dartmouth College and analyzed within several days. With the arrival of D.W. Fisher as a cooperater in 1964, aliquots of each sample were separated: one bottle was retained for analyses and long-term storage at Dartmouth; the other was sent to Fisher for additional analyses at the USGS laboratory in Washington, DC. Acquisition and installation of a Technicon AutoAnalyzer (model I) at the authors' laboratory at Cornell University in May 1970 greatly improved our analytical capability, and allowed us to overlap methods prior to Fisher's departure from the HBES in June 1972. A similar significant increase in analytical capacity occurred in 1976 with the installation of an ion-chromatograph used for anion analyses. Improvements in precision and efficiency of sample processing were further realized with the introduction of data reduction software. This replaced hand-drawn standard curves and tedious desktop calculator regression analyses. These changes took place as instruments were upgraded and personal computers became available in the 1980's. Currently, the IES Analytical Lab is applying a laboratory information management system (LIMS) to solute analyses, data processing, and quality control.

Relocation of the HBES analytical facilities to Cornell in 1969 and to IES in 1983 required that samples be shipped, usually by parcel post (4 or 5 days delivery). Exhaustive tests at Cornell of samples collected and analyzed within several days and samples stored at room temperature for weeks revealed no detectable changes in solute concentration due to delays in analyses (unpublished data). Currently, the full suite of solutes is completed within 3 months of collection.

### **IES Laboratory Quality Assurance**

The IES Analytical Laboratory, under the supervision of J.S. Eaton (until 1988) and K.C. Weathers (since 1989), has participated in numerous interlaboratory analytical audits. These comparisons have been conducted with cooperating institutions of the HBES (e.g., Forest Service and Syracuse University), with national programs for laboratory evaluations (e.g., biannual USDI Geological Survey roundrobin), and

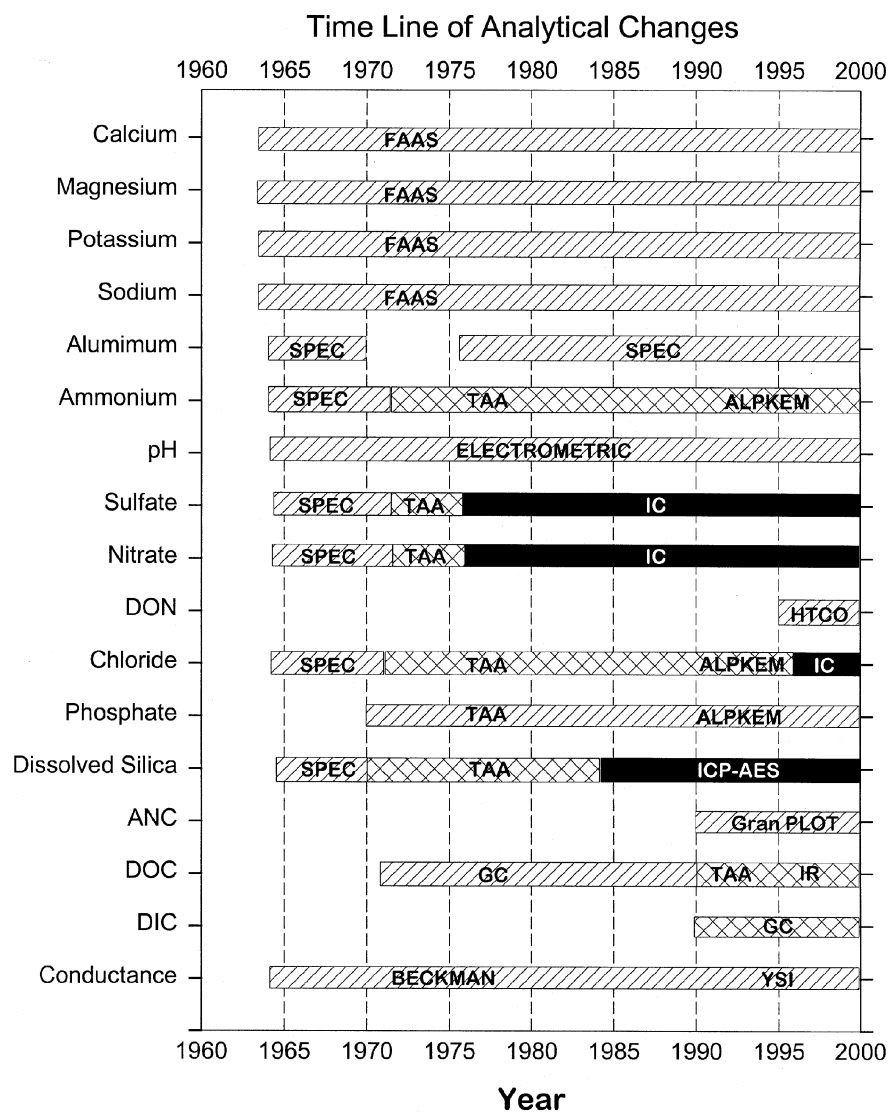


Figure 10.—Analytical methods used for the long-term data set of precipitation, streamwater and lakewater chemistry. Abbreviations are defined in Appendix B.

with other laboratories involved in long-term studies (e.g., Illinois State Water Survey).<sup>2</sup> The IES laboratory also measures on a regular basis a suite of solutes in standard samples obtained from both commercial and institutional (e.g., National Institute of Standards and Technology) providers. Approximately 15 percent of the samples analyzed in the IES laboratory are for quality assurance purposes, including user provided blind samples and matrix spikes. Method detection limits are determined for each solute about six times annually and quadruplet

measurements are made for every 40 samples analyzed to provide precision estimates for each technique. The audit programs and standard samples have assured us that IES analyses are as accurate and reproducible as current technical methods allow. For example, in 1984, the IES laboratory was one of 54 that analyzed 10 constituents in a sample of snowmelt water as a part of an intercalibration sponsored by the USGS. The IES laboratory was the only facility that received the highest rating for all 10 analyses. Specifications for quality control and instrument accuracy not documented in Appendix B will be included in the IES lab procedures handbook.<sup>3</sup>

<sup>2</sup>Eaton, J.S.; Weathers, K.C.; Likens, G.E. 1986. Inter-laboratory comparison report between the Institute of Ecosystem Studies and the Illinois State Water Survey. U.S. Environmental Protection Agency Mountain Cloudwater Chemistry Program. Unpublished report on file at the Institute of Ecosystem Studies, Millbrook, NY. 24 p.

<sup>3</sup>Weathers, K.C.; Schmidt, D.A. Standard Procedures and quality control manual for the Institute of Ecosystem Studies analytical laboratory. Institute of Ecosystems Studies occasional publication. In preparation.

## Analyses

The analytical methods used for HBES samples, systematic problems with these techniques, and alternative methods tested are discussed in the following section (see also Appendix B and Quality Assurance Procedures). The order of discussion of each solute matches the format used in our chemical database files.

**Calcium, Magnesium, Potassium, and Sodium.** These base cations have been measured by flame atomic absorption spectrophotometry (FAAS) by or under the supervision of the authors over the entire period of record. Since the inception of the HBES, the development of more sophisticated instruments (e.g., Beaty 1978) and data reduction software have greatly improved precision and lowered detection limits, though this advantage has been offset somewhat by a significant decrease in concentrations with time, particularly for samples of precipitation.

From June 1963 to December 1965, no water samples were analyzed with a lanthanum-oxide-HCl solution, an additive that dampens interferences from aluminum, dissolved silica, and phosphorus in FAAS analyses of calcium and magnesium (Perkin-Elmer 1968). These data were reported in Likens et al. (1967), though these authors noted the potential for underestimation of these base cations and already had begun rectifying the apparent discrepancy. The results of base-cation analyses with and without lanthanum were reported in Johnson et al. (1968) and Likens et al. (1967), as:

- a) No change in concentrations of calcium or magnesium in precipitation, probably because interfering solutes were low.
- b) No significant change in the observed concentration of magnesium in streamwater.
- c) A 60-percent increase in the observed concentration of calcium in streamwater.

Subsequently, calcium data for weekly streamwater samples from June 1963 to December 1965 were adjusted upward 1.6-fold in the data files (printed copies of the original analytical summary sheets are on file). Lanthanum has been used in FAAS analyses for calcium and magnesium since January 1966.

**Aluminum.** Aluminum analyses were performed by D.W. Fisher from June 1964 to June 1970, primarily on samples from W-2, W-4, and W-6. Ninety-one percent of the streamwater samples for this period were analyzed but only about 24 percent of the precipitation samples were evaluated. Precipitation samples for 1964 to 1970 were problematic because the analytical method could not discriminate below 0.1 mg/L (Fisher et al. 1968), and because clean precipitation at the HBEF contains only trace amounts of aluminum (< 0.01 mg/L on average). Bulk-precipitation samples from collectors fitted with screens to prevent particulate contamination (from 1964 to 1966) may

have been contaminated with aluminum. As a result, aluminum deposition for this early period was estimated (Likens et al. 1977; Likens and Bormann 1995). For these early data, resolution was much better when aluminum concentrations were relatively high, as they can be in HBEF streamwater at pH 5 or less. The use of more modern spectrophotometers has improved reproducibility and lowered detection limits of the ferron method. Thus, since the resumption of analyses in June 1976, aluminum has been measured with greater accuracy in precipitation samples. Aluminum is not determined routinely for inlet, outlet, or profile samples from Mirror Lake because these waters have pH's near or above 6, i.e., aluminum is found only in negligible quantities (< 0.05 mg/L).

Recognizing that the original ferron method (Rainwater and Thatcher 1960) cannot discriminate between various aqueous aluminum species (Driscoll 1984), we have investigated alternative techniques, including extraction with a buffered organic solvent (MIBK) and analyses by FAAS (Barnes 1975), or ion-exchange column fractionation and pyrochatecol-violet (PCV) chelation followed by automated colorimetric analysis (McAvoy et al. 1992). The MIBK/FAAS method was rejected when problems were encountered using a volatile, toxic, organic solvent in the small field laboratory at the HBEF.

To compare the ferron method with the PCV chelation method (prior to a planned conversion to the latter), a test was conducted on 63 weeks of precipitation and streamwater samples collected in 1991 and 1992. For precipitation samples, the difference between analyses usually was less than the expected error of the analysis ( $\pm 0.01$  mg/L). For streamwater samples, PCV chelation detected less aluminum than the ferron method (regression analysis: slope = 0.88, intercept = 0.17 mg/L). This result suggests that the ferron technique is a measure of total aluminum. The substantial scatter ( $R^2 = 0.49$ ) in the regression results suggested that the difference between total (ferron) and monomeric (PCV) aluminum might be difficult to predict. The pH of the streamwater samples (pH 5) typically is near a critical asymptote for aluminum solubility (Driscoll and Postek 1996). As a result, it is possible that nonlinear polymerization may have occurred due to changes in pH, oxidation/reduction potential, and temperature during storage. This change would have contributed to the weak relationship between the PCV and ferron methods that was observed (Berdén et al. 1994).

The ferron-derived, weekly aluminum concentrations had a much better fit ( $R^2 = 0.69$ ) with streamwater pH than the PCV-derived aluminum ( $R^2 = 0.23$ ). However, interlaboratory comparisons conducted with Syracuse University revealed no significant differences ( $p > 0.10$ ; Mann-Whitney nonparametric rank sum test of median values) for aluminum determined at each facility by the PCV method. Reanalysis of 50 W-6 streamwater samples collected from 1967 to 1969 resulted in a surprisingly good relationship (regression slope = 0.97, intercept = 0.005 mg/L,  $R^2 = 0.87$ ) between total aluminum concentrations determined more than 25 years apart by the ferron method (Fig. 11 A).

Thus, the original ferron technique was retained because:

- a) The new PCV chelation method did not compare well enough with the results from the ferron method to assure continuity with the long-term record.
- b) The degree to which the monomeric aluminum might polymerize during short-term storage was unpredictable, and the PCV method seemed sensitive to this effect.
- c) Long-term storage did not seem to affect the results as determined by the ferron method.

Because ferron analysis apparently provides a value for total aluminum, it is less useful in ecosystem process studies than the differentiation between organic- and inorganic-bound aluminum fractions (Driscoll and Postek 1996; Hooper and Shoemaker 1985). Also, an accurate determination of the ion balance for W-6 is difficult because the ionic equivalence for total aluminum and dissolved organic carbon (DOC) can only be estimated (see Ion Balance and Ion Error). However, using a negative charge of about 6  $\mu\text{eq}/\text{mg C}$  per liter for DOC at pH 5.0 (Oliver et al. 1983) leaves an average aluminum proton reference level (PRL) of about +2.0 to reach ionic balance in most weekly streamwater samples (Table 8). This is not an unreasonable average valence state for total aluminum given the possibility that some of the measured aluminum may be in polymeric or non-ionic forms. At an average pH of 5.0 for W-6, the model described by Sullivan et al. (1989) for aluminum PRL predicts a valence between +2.0 and +2.5.

Stream samples collected from W-5 and W-6 on a monthly basis since 1982 by C.T. Driscoll at Syracuse University (see Lawrence et al. 1986) were used with the chemical equilibrium model ALCHEMI (Schecher and Driscoll 1995) to estimate the equivalence charge associated with various aluminum species (unpublished data). The PRL for total aluminum in W-6 streamwater at pH 5 ranged from +0.5 to +3.0, while inorganic, monomeric aluminum had a charge of about +2.0 at the same pH (Fig. 11 B).

Agreement between the empirical data and theoretical considerations lends confidence to the ferron-derived total aluminum values in the HBES database. Further, total aluminum values in streamwater have declined significantly (linear regression slope =  $-0.005 \text{ mg/L-yr}$ ;  $p < 0.01$ ) since 1976 (Fig. 12), so it is important to support ferron analyses for the foreseeable future to track this trend.

**Ammonium.** The spectrophotometric method used to determine ammonium in the HBEF streamwater and precipitation samples from 1964 to 1972 was accurate to  $\pm 0.10 \text{ mg/L}$  (Fisher et al. 1968) compared to  $\pm 0.01 \text{ mg/L}$  reported by Rainwater and Thatcher (1960), and  $\pm 0.06 \text{ mg/L}$  reported by Gambell and Fisher (1966) for this method. Difficulties in measuring ammonium consistently in streamwater samples in the early years may have had an

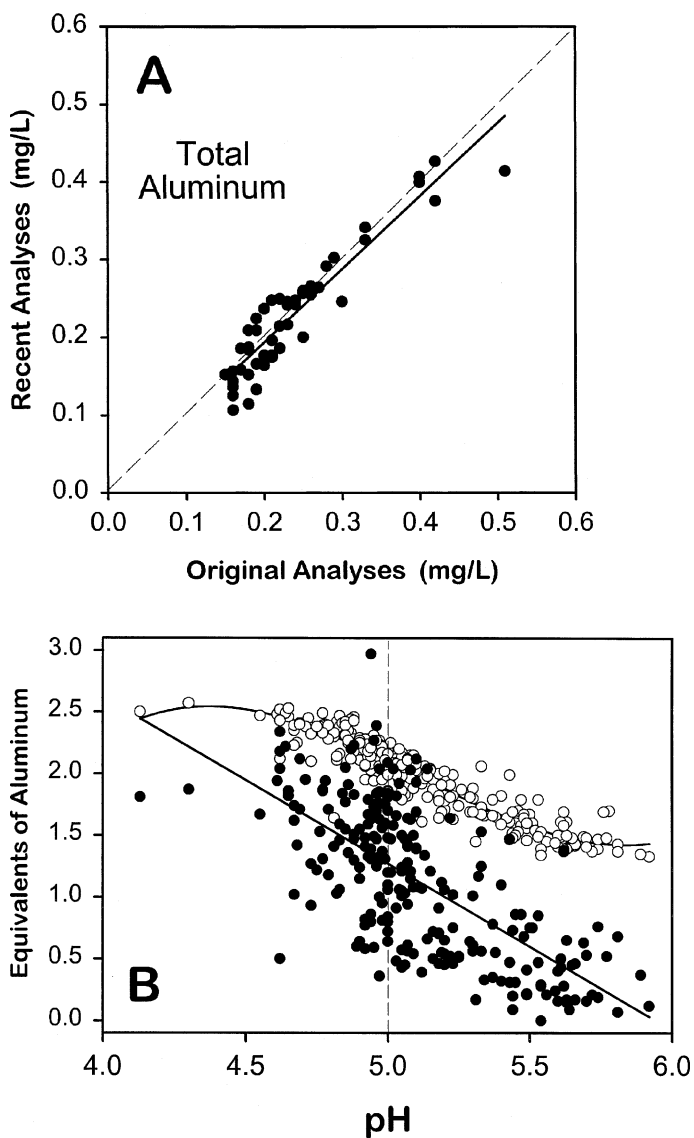


Figure 11.—(A) Reanalysis of stored streamwater samples: comparing total aluminum data from 1967 to 1969 with analyses done in 1996. Dashed line describes 1:1 relationship; (B) Charge equivalency of total aluminum (●) and inorganic, monomeric aluminum (○) at varying pH's in streamwater from HBEF (unpublished data, C.T. Driscoll).

impact on the long-term chemical database. Measured ammonium in W-6 (and W-4) streamwater was systematically higher and more variable from 1964 to 1971 than at any time since (Fig. 13). The 1965-66 W-6 annual (water-year; see Data Calculations) volume-weighted average was driven by exceptionally high weekly ammonium concentrations ( $\sim 0.9 \text{ mg/L}$ ) in samples taken in November 1965 and February 1966. Ammonium values in this high range are indicative of waters polluted with organic sewage effluent (e.g., Wetzel 1975), an improbable occurrence for W-6 or W-4. Ammonium in W-2, which had been clearfelled and then treated with an herbicide in 1966, remained near the detection limit.

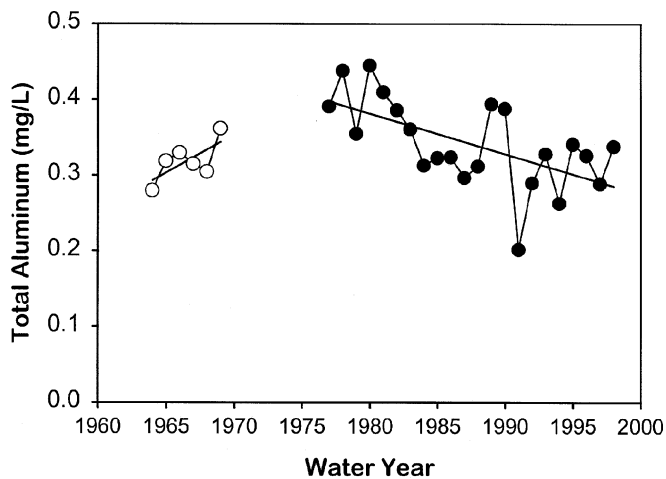


Figure 12.—Trends in annual, volume-weighted average total aluminum in W-6 streamwater, 1964-1970 (○) and 1976 to present (●).

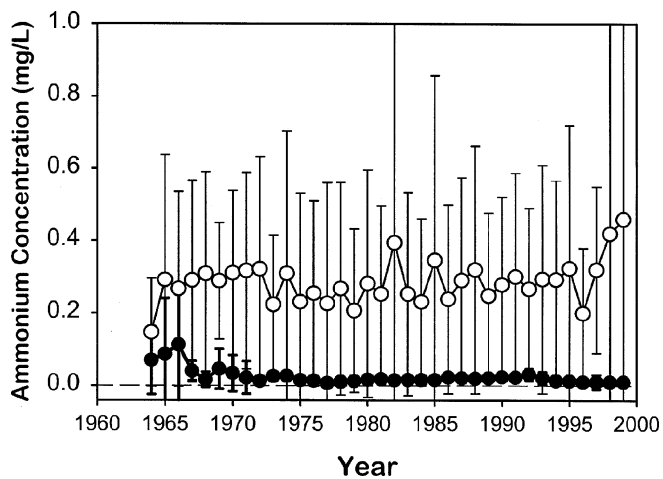


Figure 13.—Arithmetic mean annual ammonium concentration plus or minus one standard deviation for bulk precipitation (○) and streamwater (●) in W-6.

The ion balances for individual samples with high ammonium indicate a substantial cation excess, suggesting analytical error or unmeasured anions. A variety of naturally-occurring solutes (e.g. non-ionic, organic compounds containing nitrogen) and volatile ammonia-based floor and window cleaners can interfere with the Nessler reagent method used by Fisher (Rainwater and Thatcher 1960; American Public Health Association 1998; Skougstad et al. 1978). However, the average ion balance derived from the 1965-66 water-year data (excluding the charge from aluminum because that is uncertain) does not indicate a cation excess attributable to a systematic analytical error or contaminant for the entire year (Fig. 14). Because we cannot verify that any specific ammonium value was incorrect, none of the individual values has been removed, and the annual data have not been rejected.

By mid-1966, the resolution for streamwater ammonium had improved to 0.01 mg/L, according to analytical summary sheets. Variability in streamwater then decreased substantially (Fig. 13). Since 1966 there has been no significant trend ( $p > 0.10$ , linear regression) in annual, volume-weighted average ammonium concentration in streamwater from the untreated HBEF watersheds. Ammonium in precipitation at HBEF has not changed significantly ( $p > 0.10$ , linear regression) in concentration or annual variability (mean concentration and standard deviation:  $0.28 \pm 0.33$  mg/L) since first measured in 1964.

Since December 1970 for W-1, late 1969 for W-101, and June 1967 from the Mirror Lake inlet, outlet, and profile sites, samples have been analyzed for ammonium by an automated spectrophotometric technique (Appendix B). These samples had been preserved with chloroform and stored at Cornell University after base-cation analyses were complete. Beginning in June 1971, HBEF precipitation, streamwater, and lakewater samples were analyzed routinely for ammonium with this method. Samples from W-3 and W-5,

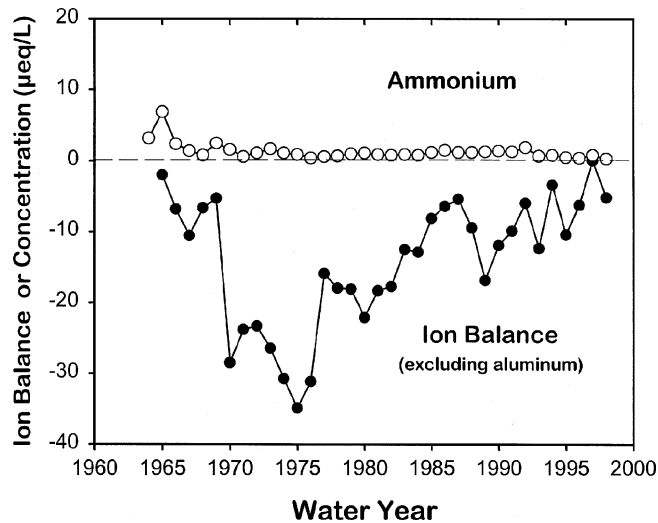


Figure 14.—Annual, volume-weighted average ion balance (●) and annual, volume-weighted average ammonium concentrations (○) in W-6 streamwater. Aluminum equivalence not applied; complete ion balances prior to 1965 not available.

for which there was no previous anion record, were included (Tables 1-3). The ammonium analysis was switched to the automated method for HBEF precipitation and for samples from W-1, W-2, and W-6 in June 1972. Values derived by D.W. Fisher's technique until June 1972 have been retained in the database. Since that time, the only substantial changes in the ammonium analyses have been related to newer instruments (e.g., Alpkem Flow Solutions III Analyzer replaced the Technicon AutoAnalyzer in 1993), improvements in lower detection limits, and hardware upgrades for the automated systems.

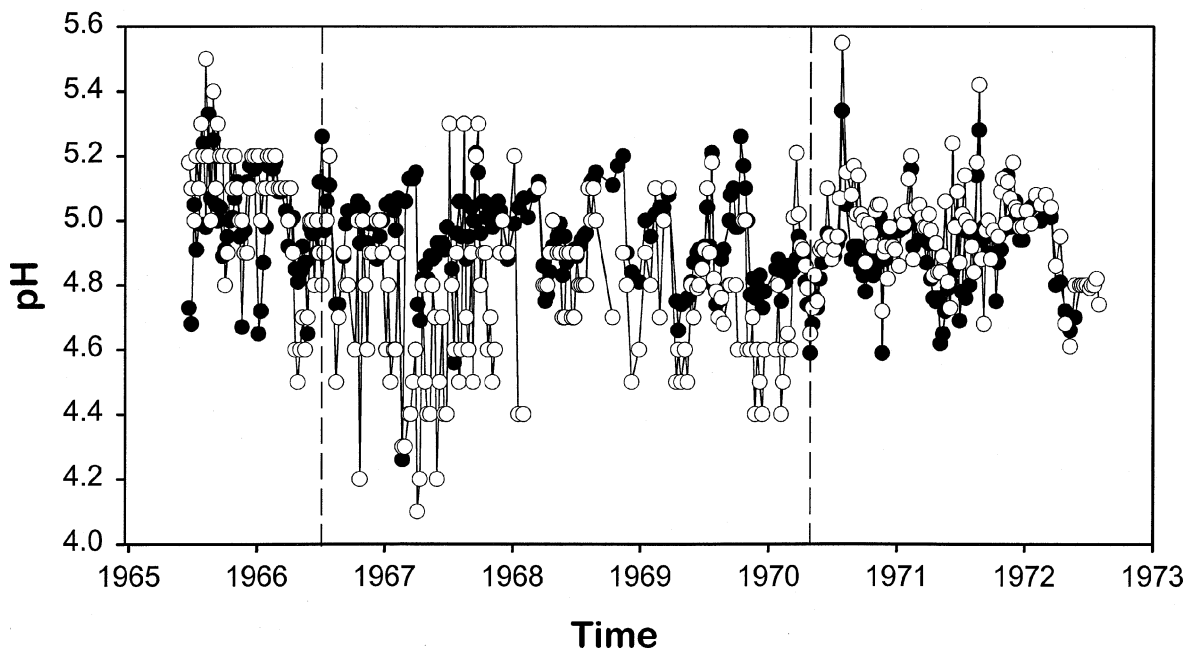


Figure 15.—Comparison of weekly W-6 streamwater pH values measured by D.W. Fisher (●) and the authors (○) from 1963 to 1972. Values for the period between the dashed lines are significantly different (see text).

**pH.** The pH of streamwater samples was measured occasionally by the authors as early as 1963, and systematically beginning in 1965, but not all of these values were incorporated into the long-term chemical database. From June 1964 to June 1972, pH was measured by D.W. Fisher on every aliquot submitted for analyses of ammonium, nitrate, sulfate, and chloride. These USGS pH's were used in the long-term database for W-2, W-4, and W-6 (Table 2) and for all precipitation chemistry files because Fisher was able to use the complete ion balances to confirm the USGS pH values (Fisher et al. 1968). Early precipitation samples that may have been contaminated with HCl washing acid (from particulate screens or poorly rinsed bottle caps) were flagged in the database (see Quality Control Procedures). Chemistry data files for W-3, W-5, and W-101 (Table 2) contain pH values only from the authors because these samples were not sent to Fisher for anion analyses (see Ion Balance and Ion Error). The pH for W-1 was determined by the authors from June 1965 to June 1970, by Fisher from June 1970 to June 1972 while anions were determined in his laboratory, and by the authors thereafter. For lakewater collected since sampling began in 1967, pH has been determined by the authors, first at Dartmouth College, then at Cornell University (after August 1969), and at the HBEF after 1973.

The streamwater pH datasets derived from duplicate W-6 samples and recorded by the authors and by Fisher from 1965 to 1972 (Fig. 15) are statistically different ( $p < 0.01$ ; Mann-Whitney rank sum test of group medians) primarily because the author's pH's tend to be lower from 1966 to 1970 (Fig. 15). By mid-1970, the datasets were better matched (slope of the regression line = 0.99), with an offset

of  $< 0.1$  pH unit. Fisher measured the pH of samples that were up to several weeks old, while the authors determined pH within 2 days of collection. This unavoidable delay along with possible instrument dissimilarities may account for the significant differences observed in the first 5 years of this comparison. At the least, the improved correlation in the last 2 years indicates that there was consistency between the measurement techniques before the end of Fisher's participation in the HBES. After June 1972, the pH of HBEF precipitation, streamwater, and lakewater samples has been measured at the Pierce Lab with equipment used exclusively for that purpose.

Fisher did not document the type of meter nor the calibration technique used on HBES samples (Fisher et al. 1968), but it seems reasonable that previously established USGS standards and instruments were used (Gambell and Fisher 1966: Beckman Zeromatic model with paired-glass pH and reference electrodes; see Barnes 1964 and Appendix B). Until 1972, the authors used an analog Beckman (model N) pH meter (Appendix B).

From June 1972 to June 1996, an analog meter was used (Orion model 401 or 407A) with separate glass pH and KCl reference electrodes (Appendix B). In June 1997, the analog meter was replaced with a digital meter (Orion 710A) with paired electrodes of the same type used on the previous meters. All other protocols have remained the same. The 407A and 710A meters operated concurrently for 6 months to test for pH bias. Results indicated no significant differences in pH ( $p > 0.10$ : Mann-Whitney rank sum test of medians). Linear regression analysis showed that the values from each

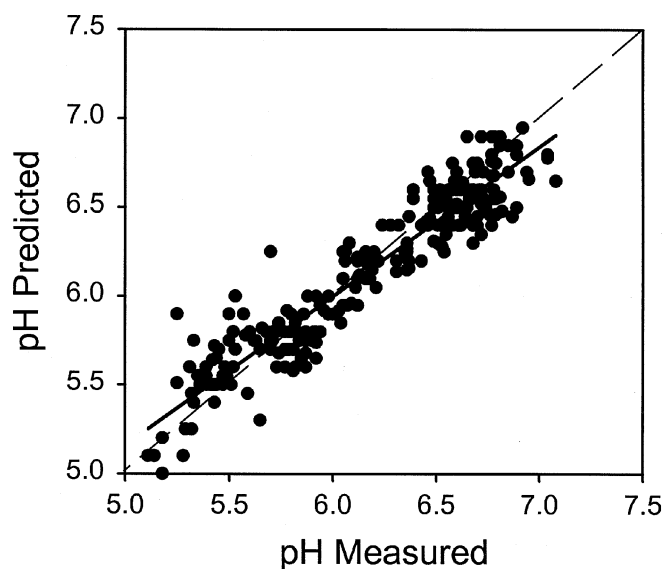


Figure 16.—Predicted pH (from measured ANC and DIC) compared to measured pH for samples of W-6 streamwater and Mirror Lake water. Dashed line describes 1:1 relationship.

meter were nearly identical (slope = 0.99, y-intercept = -0.02,  $R^2 = 0.99$ ). We also tested the pH meter component in the titrator used to measure alkalinity (Orion 940) with identical electrodes against the 407A benchtop meter for 3 years. Linear regression analysis revealed a modest distortion to pH (slope = 0.96) above or below a range from pH 5 to 6, but the datasets were not significantly different ( $p > 0.10$ ; Mann-Whitney rank sum test of group means). Results were similar for a 6-month comparison of the 710A and 940 meters. pH values generated by the 940 titrator system are recorded on field notes (Appendix C) but not entered into the long-term database.

Measuring pH in dilute, low-ANC samples can be difficult due to slower electrode reaction times and drift (wavering readings), possibly caused by carbon-dioxide gas exchange (Galloway et al. 1976; Stauffer 1990), even though all of our systems include high-flow reference electrodes to reduce this effect (Orion Research 1997). Tests were conducted on 251 streamwater and lakewater samples to calculate a theoretical pH based on measurements of ANC and DIC for samples with a pH above 5 and a positive ANC (Herczeg and Hesslien 1984; Munson and Gherini 1993). The theoretical pH's matched the measured pH's approximately but with some bias (Fig. 16, linear regression slope = 0.84), and the scatter ( $R^2 = 0.88$ ) suggests that reproducibility between the model and meter pH's is no better than 0.2 unit. This approach continues to be investigated as a tool for confirming pH measurements, though more sophisticated measurements may be needed to understand fully the partitioning of the DIC components and/or the influence of organic solutes on ANC.

pH measurements of acidic precipitation (average pH 4.2, range: 3 to 5 since 1964: Table 8) usually are much more stable than for streamwater or lakewater. Electrode response is rapid and drift is essentially nonexistent unless the electrode is failing. Ion balances for precipitation samples suggest no substantial error in the measurement of pH (see Ion Balance and Ion Error).

Finally, in more than 30 blind tests of quality control solutions (dilute solutions of nitric and sulfuric acid usually pH 4 to 5) provided by the USGS since 1981 in support of the National Atmospheric Deposition Program (NADP 1990), pH measured at the HBEF has rarely differed by more than  $\pm 0.05$  unit (average  $\pm 0.03$ ) from the pH of the known solution.

On the basis of independent test results, parallel pH analyses conducted with separate instruments, consistent data on ion balance, and general stoichiometric models, we are confident that the pH data in the long-term record are as accurate as available technology allows.

**Sulfate.** From June 1964 to June 1972, sulfate was analyzed by D.W. Fisher (Appendix B) for all precipitation samples and streamwater samples from W-2, W-4, and W-6. During this time, at Dartmouth College, the authors also attempted to measure sulfate by gravimetric and turbidometric techniques (Rainwater and Thatcher 1960; Rossum and Villarruz 1961). These methods were too insensitive at low sulfate concentrations ( $< 5$  mg/L) and too cumbersome to perform on a routine basis. As a result, these data were not included in the chemical database.

Beginning in September 1970, samples of streamwater (W-1 and W-101) and Mirror Lake water collected and stored at Cornell University since 1967 were analyzed for sulfate with the newly established TAA technique (Appendix B). The TAA sulfate method is sensitive to natural color (McSwain et al. 1974). However, streamwater at HBEF usually is colorless due to low organic carbon content (average DOC concentration of W-6 is 2 mg/L). In June 1972, the original TAA technique was modified to increase sensitivity in the low range ( $< 1$  mg/L) of the analysis.

Sulfate was determined by the TAA method in several streamwater samples from W-5 beginning in October 1970; routine analyses for W-3 and W-5 samples began in June 1971. After June 1972, all sulfate values in the long-term precipitation or streamwater database are from analyses done or supervised by the authors. Since December 1976, sulfate has been measured by ion exchange chromatography (IC) first at Cornell and at IES after July 1983 (Appendix B).

**Nitrate.** From June 1964 to June 1972, nitrate was measured by D.W. Fisher, using a spectrophotometric method (Appendix B). After obtaining a TAA in May 1970, the authors began measuring nitrate in July at Cornell University. Samples of precipitation, streamwater, and lakewater stored since January 1970 at Cornell were analyzed for nitrate. Only

**Table 8.—Volume-weighted average ion concentrations and ion balances of annual bulk-precipitation and streamwater samples in W-6 calculated for 1967-71 and 1991-95<sup>a</sup>**

Solute	Precipitation		Streamwater	
	1967-71	1991-95	1967-71	1991-95
Calcium	7.2	3.8	72.1	39.2
Magnesium	3.3	2.0	29.5	18.3
Potassium	1.5	1.1	6.3	4.3
Sodium	5.2	5.2	35.1	30.8
Aluminum	0.4	0.4	23.0	21.5
Ammonium	13.9	11.9	1.4	1.0
Hydrogen ion	76.6	50.4	15.3	11.3
Sulfate	57.4	39.1	124.0	96.6
Nitrate	25.3	26.3	33.2	3.9
Chloride	10.9	6.6	14.9	13.3
Phosphate	0.1	0.1	0.1	0.1
Bicarbonate	0.0	0.0	0.0	0.0
Dissolved organic carbon	n/a	n/a	166	166
Dissolved silica	1	1	62	61
Sum of cations	108.1	74.8	182.7	126.4
Sum of anions	93.7	72.1	172.2	113.9
Difference	+14.4	+2.7	+10.5	+12.5
pH	4.12	4.30	4.82	4.95
Calculated ANC	n/a	n/a	-20.0	-14.0
Measured ANC	n/a	n/a	n/a	-8.3

<sup>a</sup>The equivalent charge on aluminum is assumed to be +3 for precipitation and +2 for streamwater. Ion values are in µeq/L; DOC and dissolved silica concentrations are in µmol/L.

nitrate values for W-1 and W-101, and Mirror Lake water were entered into those specific databases. Streamwater samples from W-5 were measured for nitrate occasionally beginning in October 1970, but nitrate analyses were not done routinely for this site and W-3 until June 1971. Precipitation values and W-2, W-4, and W-6 streamwater values were compared with Fisher's data, but not retained in official records until June 1972. Following a period of concurrent analyses, the TAA method was replaced by the IC technique at Cornell in January 1977. The IC method continued to be used following the relocation to IES in July 1983 (Appendix B).

**Dissolved Organic Nitrogen.** In the late 1970's, attempts were made to analyze for dissolved organic nitrogen (DON) using UV-light and chemical oxidation techniques on a variety of water samples from HBEF, but these analyses were not done on a routine basis. During 1993 and 1994, DON was measured at Cornell in weekly collections of streamwater from W-6 using high-temperature persulfate digestion with subsequent cadmium-reduction and colorimetric analysis for nitrite (Hedin et al. 1995). Since 1995, monthly samples of W-6 streamwater were analyzed for DON at Syracuse. The Cornell and Syracuse data sets are not a part of the long-term chemical record. Since 1995,

DON has been measured in routine weekly samples from W-6, W-7, W-8, W-9 and RG-11 by scientists at the Northeastern Research Station's Forestry Sciences Laboratory at Durham, New Hampshire (Campbell et al. 2000). This high-temperature catalytic oxidation technique (HTCO; Merriam et al. 1996) results in a determination of total dissolved nitrogen (TDN). DON is calculated by subtracting ammonia-nitrogen and nitrate-nitrogen (determined on separate sample aliquots by the authors) from TDN (Appendix B).

**Chloride.** Chloride was determined spectrophotometrically for the HBES in streamwater and precipitation samples from June 1964 to June 1970, by D.W. Fisher and independently in precipitation samples from September 1965 to August 1966, by F.H.T. Juang and N.M. Johnson at Dartmouth College. Agreement was better than 3 percent between samples, standards, and blanks tested by Fisher and Juang (Juang and Johnson 1967). The latter study also found that chloride was systematically higher in the HBEF bulk collectors with protection screens compared to unscreened bulk and wet-only collectors used from 1965 to 1966 (Fig. 17). This difference may have affected annual chloride input values for the first 3 years of the HBES (see Quality Assurance Procedures).



After the TAA was installed at Cornell University in 1970, the authors conducted chloride analyses on all stored samples of Mirror Lake water and W-1 and W-101 streamwater. The overlap with Fisher's 1970 data for W-2, W-4, and W-6 streamwater and HBEF precipitation confirmed that the new technique was satisfactory. Routine chloride analyses were begun on W-3 and W-5 streamwater samples beginning in June 1971, though some samples from W-5 were tested as early as October 1970. Chloride data for all samples were derived from the TAA method after June 1972. In June 1996, the chloride analysis with TAA was replaced with the IC method. Comparison of chloride values determined (with TAA and IC) from precipitation ( $n = 51$ ) and streamwater samples ( $n = 81$ ) taken over a 1-year period revealed no significant differences ( $p > 0.10$ ; Mann-Whitney rank sum test of group means, paired t-test, and regression analysis).

**Phosphate and Total Phosphorus.** Routine analyses for phosphorus were first attempted by the authors at Cornell University in July 1970 using an automated colorimetric technique on a TAA (Appendix B). We initially focused on samples of Mirror Lake water but later incorporated the ortho-phosphate determination into routine analyses for all precipitation and streamwater samples. By June 1972, the procedure had been modified to increase sensitivity such that it produced consistent values even at the very low levels ( $< 5 \mu\text{g/L}$ ) found in HBEF streamwater. After this time, the phosphate data for all samples were added to the long-term database.

Total phosphorus was determined with the same technique used for phosphate except that the water samples are pre-digested, and until 1998, measurements were made on a nonautomated spectrophotometer (Appendix B). Testing of the method on Mirror Lake and precipitation samples began in June 1971, but routine analysis and database entry for streamwater samples did not occur until June 1972. Apart from precipitation and lakewater samples, only samples from W-6 were measured for total phosphorus. In an examination of weekly data from 1974 to 1991, total phosphorus and phosphate concentrations in HBEF precipitation samples were not significantly different ( $p > 0.10$ ; Mann-Whitney nonparametric rank sum test of median values). Small (e.g., 5 to 10  $\mu\text{g/L}$ ) apparent increases in streamwater phosphate concentrations during 1989 to 1992 may have been due to decreasing sensitivity of the TAA colorimeter. Total phosphorus and phosphate concentrations in streamwater were close to the detection limit (Appendix B) and seldom separated by more than the error of the analysis. On the basis of these findings and the expense of the analytical procedure, analyses for total phosphorus in precipitation and streamwater were discontinued in August 1991. Total phosphorus continues to be measured on a routine basis for all Mirror Lake outlet, inlet, and profile samples.

**Dissolved Silica.** Dissolved silica was measured on W-2, W-4, and W-6 streamwater samples by D.W. Fisher from

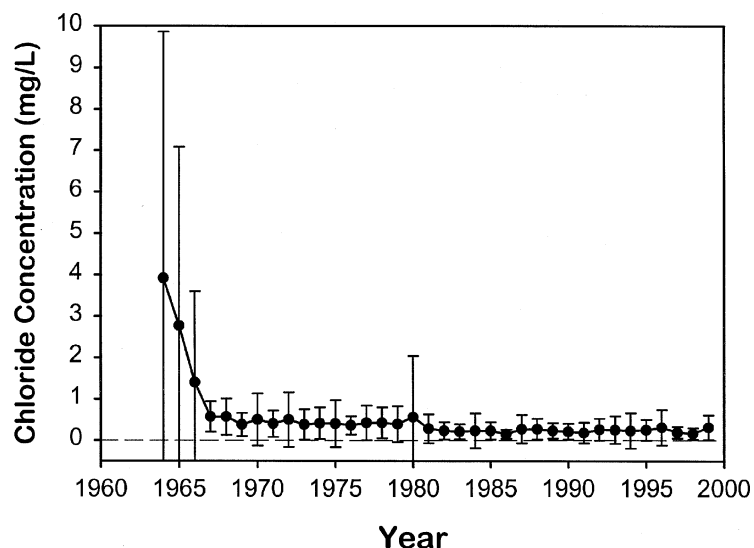


Figure 17.—Arithmetic mean annual chloride concentrations plus or minus one standard deviation for all samples of bulk precipitation from 1964 to 1996, regardless of known contamination.

June 1964 to June 1970 (Appendix B). After several sets of precipitation samples were analyzed and found to have negligible dissolved silica ( $< 0.1 \text{ mg/L}$ ), dissolved silica was no longer measured on a routine basis by Fisher. With the installation of a TAA at Cornell University in 1970, measurements of dissolved silica were conducted on all samples stored since 1967 (preserved with chloroform), including Mirror Lake waters and HBEF streamwater and precipitation. Some streamwater samples had been frozen and required several months of storage at room temperature to return the precipitated silica to solution (Burton et al. 1970). Tests of samples frozen by the authors indicated that this treatment allowed all of the silica to redissolve. Streamwater samples analyzed by Fisher in the spring of 1970 were compared with those analyzed by the automated TAA method. Values were identical within the error of the analyses.

Since June 1984, inductively coupled plasma atomic emission spectroscopy (ICP-AES) has been used to analyze for dissolved silica. In the long-term database, dissolved silica is reported as silicate, though there may be more than one form of dissolved silica in solution (Wetzel and Likens 1991).

**Acid Neutralizing Capacity.** In August 1990, a programmable, potentiometric titrator (Orion model 940/960) was obtained to determine ANC by automated Gran-plot analysis (Gran 1952). Beginning in January 1991, ANC was measured in Mirror Lake inlet, outlet, and profile samples. Since January 1994, ANC has been measured in streamwater samples from W-6. All streamwater samples from the HBEF have been measured for ANC on a routine basis since 1996.

**Table 9.—Arithmetic average ion concentrations and ion balances of Mirror Lake outlet and inlet samples for 1990-95<sup>a</sup>**

Solute	Outlet	NE inlet	NW inlet	W inlet
Calcium	112.8	500.0	108.3	122.3
Magnesium	40.3	178.6	38.7	44.4
Potassium	11.8	37.6	9.0	12.5
Sodium	98.3	1326.8	71.8	100.5
Aluminum	1.0	5.0	1.0	5.0
Ammonium	1.1	1.5	0.9	0.9
Hydrogen ion	0.6	3.5	0.7	0.7
Sulfate	91.7	146.0	107.3	102.8
Nitrate	0.5	0.8	0.3	1.1
Chloride	88.5	1821.7	40.3	71.6
Phosphate	0.1	0.2	0.1	0.2
Bicarbonate	70.5	64.7	70.0	85.7
Dissolved organic carbon	180	510	168	241
Dissolved silica	37	199	122	140
Sum of cations	265.9	2053.0	230.4	286.3
Sum of anions	251.3	2033.4	218.0	261.4
Difference	+14.6	+19.6	+12.4	+24.9
pH	6.22	5.46	6.17	6.14
Calculated ANC	84.0	80.4	81.1	109.4
Measured ANC	70.5	64.7	70.0	85.7

<sup>a</sup>Ion values are in  $\mu\text{eq/L}$ ; DOC and dissolved silica concentrations are in  $\mu\text{mol/L}$ . Aluminum concentrations are based on < 10 samples from each site since 1967; equivalent charge is assumed to be +2.

We define ANC as the ionic sum of the base cations (Ca + Mg + K + Na) minus the sum of strong-acid anions ( $\text{SO}_4 + \text{NO}_3 + \text{Cl}$ ) expressed in microequivalents. Measured ANC matches ( $R^2 > 0.90$ ) with the anion deficit in the ion balance for the NW and West inlets, suggesting a good correlation with bicarbonate concentrations in these circumneutral streams (Table 9). The NE inlet is problematic because of high DOC concentrations, lower pH (< 6), and high total ionic strength (> 5,000  $\mu\text{eq/L}$ ). The lake outlet has a poorer correlation ( $R^2 = 0.50$ ) between ion balance and ANC possibly because of a lack of variability in major ionic species and perhaps the influence of degassing and decompositional processes, i.e., temporary ANC (Wetzel 1975). Using calculated specific conductance (see Specific Conductance), the ANC data applied (as bicarbonate ion) for the lake outlet and NE inlet provide a good fit to the measured conductance, suggesting that the ANC data are reasonably accurate.

Measured ANC values from W-6 streamwater usually are negative (range -5 to -15  $\mu\text{eq/L}$ ), averaging -8.3  $\mu\text{eq/L}$  for the record of measurement (Table 8). This average is higher (less negative) than the calculated ANC (-14.0  $\mu\text{eq/L}$ ) as defined previously. This difference is expected in dilute acidified waters because of the buffering influence of DOC (Munson and Gherini 1993). We found that Gran-plot titration equivalence points, i.e., pH at ANC = 0 (Barnes 1964) range from pH 4.9 for lakewater to pH 5.3 for HBEF streamwater (Fig. 18), and decline with increasing ionic strength.

**Dissolved Organic Carbon.** DOC has been determined for precipitation and streamwater samples from the HBEF during studies that attempted to characterize and quantify ecosystem organic carbon cycles or processes over relatively short periods (Hobbie and Likens 1973; Jordan and Likens 1975; McDowell and Likens 1988; Hedin et al. 1990; Campbell et al. 2000). Monthly paired samples have been analyzed at Syracuse University from W-5 and W-6 since the experimental whole-tree harvest of W-5 in 1982-83 (Lawrence and Driscoll 1988).

Routine weekly analysis of DOC from the Mirror Lake inlets and outlet and from W-6 streamwater began in August 1992. Since June 1995, DOC has been measured for all HBEF streamwater samples on a weekly basis at Syracuse University (W-1, W-2, W-3, W-4, W-5, and W-6) and the Forest Service (W-6, W-7, W-8, and W-9). Because precipitation DOC is highly variable qualitatively and quantitatively (Jordan and Likens 1975; McDowell and Likens 1988) and difficult to characterize chemically (Likens et al. 1983), no effort was made to establish routine monitoring of carbon inputs from bulk-precipitation collectors until recently (Campbell et al. 2000). Since June 1995, DOC has been measured on a weekly basis in samples from RG-11 by the Forest Service.

Cole et al. (1984) and recent studies (unpublished data) have found that DOC is 98 to 100 percent of total organic carbon (TOC) in all samples except Mirror Lake water (Fig.

19), so that currently only lake profile samples are filtered before analysis. More specific research into the processing of particulate and dissolved carbon through ecosystems is underway at HBEF, and we anticipate incorporating filtration into the standard collection procedure for DOC to meet those needs. The long-term database contains DOC values from analyses run at IES (Mirror Lake), Syracuse (W-6), and the Forest Service (Mirror Lake, W-7, W-8, W-9, and RG-11).

**Dissolved Inorganic Carbon.** Interest in DIC at the HBEF began with investigations into decomposition processes in Mirror Lake in the late 1970's and early 1980's (Jordan and Likens 1975; Cole and Likens 1979; Cole 1985). The DIC analysis was based on Stainton's (1973) technique using a Fisher-Hamilton Gas Partitioner Model 29 (Fisher Scientific 1970). This instrument was replaced by a Shimadzu Gas Chromatograph model GC-8A in 1985 (Shimadzu Corp. 1985; Appendix B). For the most part, the only samples measured for DIC during these years were from periodic profiles of Mirror Lake. These were collected primarily to support short-term experiments until August 1990 when systematic, routine sampling of Mirror Lake was established with rigid protocols (see Field Procedures: Mirror Lake Collections).

A study involving the direct measurement of the partial pressure of carbon dioxide (Appendix B) required weekly DIC measurements of Mirror Lake surface water beginning in May 1992 (Cole et al. 1994). Routine samples of W-6 streamwater were added to this effort in July 1992, and weekly samples of the Mirror Lake inlets and outlet were first taken in August 1993. Beginning in January 1994, W-1 through W-6 streamwaters were sampled for DIC routinely; by May 1995, all streamwater sites at W-1 through W-9 were included in the regular weekly DIC analyses.

**Specific Conductance.** Conductance was measured by D.W. Fisher on all routine samples of precipitation and streamwater (including samples stored since June 1964) from June 1965 through June 1970. The instrument used is uncertain, but the USGS had well-established protocols and Wheatstone bridge-type instruments that were fabricated specifically for analyses of dilute waters (Rainwater and Thatcher 1960). These values have been included in the long-term database.

Continuous measurements of specific conductance in W-4 streamwater with a battery-operated, circular-chart recorder (Industrial Instruments Type RQ1) were established by the authors in 1965 but discontinued in 1977 when it was found that the accuracy of the instrument was close to the variability of the streamwater conductance. Whitney underwater conductivity meters were used to test Mirror Lake water in the field from July 1967 to October 1971; these data were entered into the long-term database for the lake profiles.

After 1969, the authors measured the conductance of precipitation, stream, and lake inlet water with a Beckman

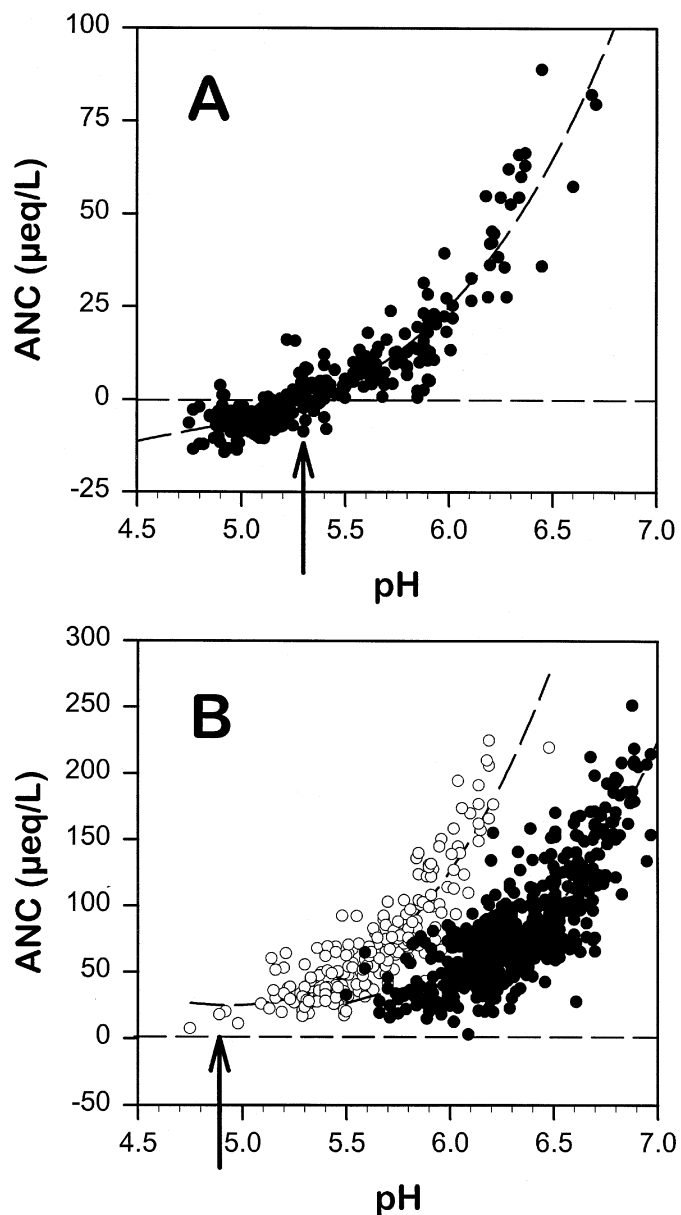


Figure 18.—Relationships between acid neutralizing capacity, pH, and equivalence point (→) in (A) HBEF streamwater and (B) in Mirror Lake outlet and NW and West inlets combined (●), and NE Inlet (○).

Instruments model analog meter in the HBES facilities at Cornell University (Appendix B).

When the responsibility for determination of pH was assigned to personnel stationed at the HBEF in June 1972, operation of the conductance meter was transferred there also. The conductance of lakewater samples has been measured by the authors with battery-operated field meters (Whitney or YSI) or the laboratory benchtop meter since January 1972. The Beckman meter was replaced by a YSI Model 32 digital meter in March 1990. Comparisons of field and laboratory meters showed that their precision is within 5

percent. Measured conductance approximates theoretical conductance for most of the samples collected at the HBEF (Fig. 20), though there are distinct, site-dependent differences (see Quality Assurance Procedures).

## Data Management

### History and Development of HBES Database

**1963 to 1982.** Prior to the availability of personal computers and computer peripherals that are now in common use, the authors used tabular accounting ledgers to track solute concentration values and daily precipitation input and streamwater output data applicable to these chemical samples. We edited, interpolated, and calculated daily discharge from original stream-gauge charts for several of the gauged watersheds until Forest Service personnel assumed complete management of the hydrologic data collection in 1965. Daily inputs/outputs were compiled into monthly values that were converted to annual (water year) figures using manual, analog calculators (see Data Calculations). After these first chemical budgets were published (Fisher et al. 1968; Johnson et al. 1968; Likens et al. 1967), we entered data on punch-tape terminals in batches of cations or anions for separate watersheds and single years, and used programs written in Basic on a mainframe computer at Dartmouth College to calculate daily and monthly inputs/outputs. The calculated values were stored as computer printouts. Analytical data were calculated from hand-drawn standard curves. Similar procedures were followed when HBES analytical facilities were relocated to Cornell University in 1969 except that the new computer facility required the transfer of the raw data to IBM-type punch cards, and programs were written in Fortran.

Printed copies of the analytical worksheets containing sample dates, instrument readouts, and conversions to concentrations, as well as standard-curve reductions used for all chemical analyses since 1963, are archived at IES or the HBEF. These original documents have been of great value in interpreting the accuracy of the analyses in the early years of the HBES. There are no known copies of the original worksheets generated by D.W. Fisher except for typed data sheets forwarded to the authors during Fisher's tenure with the HBES (1964-72).

Between 1969 and the relocation of the authors to IES in 1982, computer programs were added to examine the chemistry data for individual samples and to assist in the creation of standard curves. The quality control subroutines included programs for determining ion balance, converting pH to hydrogen ion, estimating sea salt contribution, and calculating theoretical conductance (see Specific Conductance). These were programs written in Basic that ran on desktop computer-calculators (e.g., Tandy TRS-80 and Wang terminals). The chemical data had to be

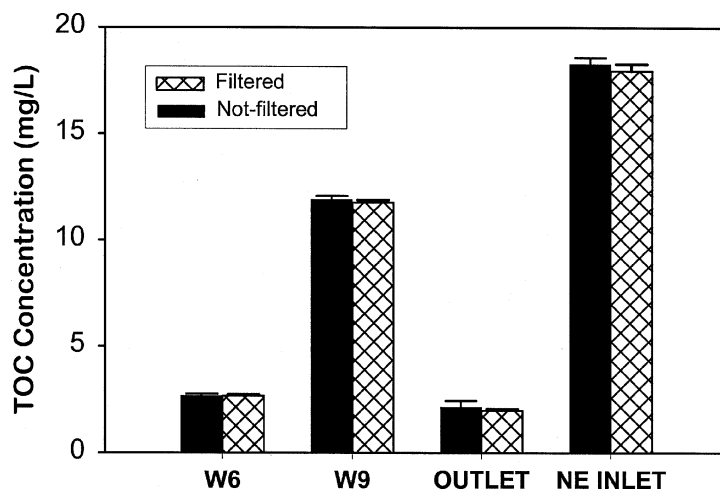


Figure 19.—Comparison of filtered and unfiltered streamwater samples from W-6, W-9, Mirror Lake outlet, and NE Inlet analyzed for total organic carbon. Each column represents the mean of 10 samples plus one standard deviation as the error bar.

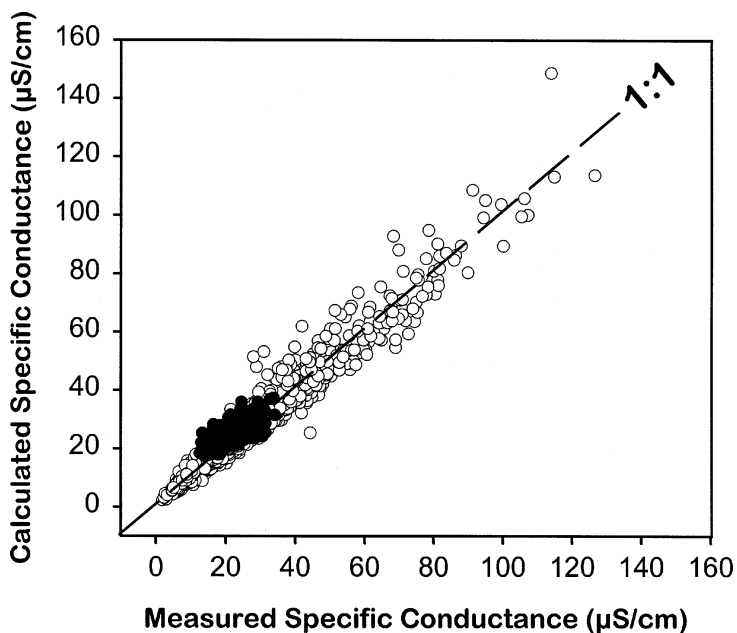


Figure 20.—Relation between measured and calculated specific conductance for samples of bulk precipitation (°) and W-6 streamwater (•).

keypunched into the required format for each program one sample at a time. This labor-intensive technique made quality control tedious. The authors spent considerable time and effort upgrading the analytical instrumentation during that period, but were unable to dedicate similar resources to computer equipment due to funding constraints.

**1983 to 1988.** With the establishment of the HBES analytical facilities at IES in 1983, the project began a rapid transition to the use of personal computers and software-based data management systems. In 1983, all of the HBES chemical

data were transferred from IBM punch cards to ASCII files on floppy disks (CP/M format) that are archived at the HBEF. In 1984, J.S. Eaton and D. Richardson developed a data management system consisting of: 1) a full array of weekly solute data for each sample site for each water year (1 June to 31 May) in flat ASCII file format; 2) a series of Basic programs to calculate daily and monthly inputs and outputs for each site from each ASCII file; and 3) final output files (as monthly or water-year solute import or export for all sites combined) in dBase II format. In 1987, the ASCII sample data on disk were converted to MS-DOS format and coded for a series of quality control descriptors. In addition, the platform for storage and query of calculated monthly or annual data was upgraded to dBase III. It was at this time that J.S. Eaton's health deteriorated and progress was slowed on the development of a integrated quality assurance and database management system.

**1989 to the Present.** Momentum was regained in 1990 when the raw chemistry dataset was recompiled from ASCII into dBase IV format. This represented an enormous improvement over individual water-year ASCII files in several ways: 1) each collection could be screened in its entirety and from the first to most recent samples; 2) quality control procedures could be developed that did not require external programs to run; and 3) data could be exported to graphics or statistical software rapidly and with complete control over user-selected criteria. Once loaded to dBase, the original files from 1963 were reviewed line by line using field notes and analytical worksheets to check collection data, and processed through a series of dBase screening programs designed to identify problems related to quality control (see Quality Assurance Procedures). Most of these problems were identified as keypunching errors, but this comprehensive screening also resulted in the rejection of several previously acceptable samples based on the violation of uniformly applied, highly conservative contamination criteria with evidence from field notes (see Field Procedures and Appendix C). An embedded system of codes was developed to flag contaminated samples or identify unusual collection conditions.

At this time, under the supervision of D.C. Buso, an IES team consisting of I. Lin, L. Coelho, and T. Miller developed a master program written in dBase that calculated monthly, volume-weighted concentrations and inputs/outputs for each solute from each collection within the parent dBase IV system. This program eliminated the need for the Basic programs written to handle the ASCII files used previously. All data entry, storage, and calculations are now in dBase (version 5.0 for Windows). Data are exported to SigmaPlot (version 5.0 for Windows) for graphical analysis or to SigmaStat (version 2.0 for Windows) and Systat (version 8.0 for Windows) for statistical analysis.

### Recalculation of Import and Export Values

After the master dBase program was created in 1990, all precipitation deposition and streamwater export values were recalculated using the updated concentration files in

**Table 10.—Nonparametric p-values (Mann-Whitney rank sum test) for comparison of median values of monthly precipitation data (pair A) and monthly streamwater data (pair B) calculated prior to 1987 and recalculated in 1990<sup>a</sup>**

Solute	p value	
	Pair A	Pair B
Calcium	0.596	0.942
Magnesium	0.444	0.759
Potassium	0.167	0.872
Sodium	0.890	0.603
Ammonium	0.452	0.516
pH	0.822	0.151
Sulfate	0.445	0.969
Nitrate	0.404	0.925
Chloride	0.161	0.972
Monthly water amount	0.860	0.983

<sup>a</sup>P values < 0.10 indicate significant difference in medians between original and recalculated data sets.

conjunction with hydrologic data that also had undergone a comprehensive quality review by the Forest Service (Federer et al. 1990). Because of alterations in both chemistry and hydrology and corrections to the date of collection, the recalculated values are slightly different from those published earlier (Likens et al. 1977). We compared the old and new data using the monthly, volume-weighted average (VWA) concentrations of all solutes from precipitation and streamwater samples collected at W-6 from 1963 to 1987. We applied the nonparametric Mann-Whitney test of group medians because most monthly concentrations were not distributed normally. This test indicated that the differences between the medians of the paired calculated monthly VWA concentrations were not significant for any solute, including pH, in precipitation or streamwater (Table 10).

We also used linear regression analysis to examine the relationship between paired VWA concentrations in precipitation and streamwater (Table 11, Fig. 21). For the paired precipitation data, the correlation was poorest for monthly VWA concentrations of potassium ( $R^2 = 0.70$ ) and chloride ( $R^2 = 0.25$ ); these comparisons were heavily influenced by outliers in the original dataset (Fig. 21). Some monthly concentrations of potassium and chloride in the original precipitation data were high due to individual weekly samples identified as contaminated based on the new dBase screening procedures and review of field notes. These values were eliminated from the recalculation. Much of the general scatter between the monthly VWA deposition data was due to recompilation of the daily precipitation data or to collection-date corrections, rather than to editing of the weekly chemistry. Because precipitation chemistry is highly variable on an event basis, small changes in hydrologic data or simple mistakes in the collection date can have a significant impact on monthly VWA concentrations.

**Table 11.—Linear regression statistics comparing monthly precipitation chemistry calculated prior to 1987 and recalculated in 1990, and streamwater chemistry calculated prior to 1987 and recalculated in 1990<sup>a</sup>**

Solute	slope	Y-intercept	R <sup>2</sup>	p value
Paired Precipitation				
Calcium	0.90	0.61	0.85	<0.001
Magnesium	0.94	0.19	0.95	<0.001
Potassium	0.67	0.47	0.70	<0.001
Sodium	0.80	0.88	0.77	<0.001
Ammonium	0.90	1.42	0.83	<0.001
pH	0.92	0.33	0.88	<0.001
Sulfate	0.91	6.43	0.86	<0.001
Nitrate	0.85	4.47	0.79	<0.001
Chloride	0.25	5.95	0.32	<0.001
Paired Streamwater				
Calcium	1.00	0.11	0.98	<0.001
Magnesium	0.86	3.60	0.87	<0.001
Potassium	1.03	0.07	0.98	<0.001
Sodium	0.96	1.07	0.94	<0.001
Ammonium	0.93	0.13	0.98	<0.001
pH	0.71	1.41	0.69	<0.001
Sulfate	0.99	0.76	0.98	<0.001
Nitrate	1.01	0.01	0.99	<0.001
Chloride	1.01	0.04	0.96	<0.001

<sup>a</sup>Calculated from concentrations in µeq/L; p values < 0.10 indicate correlation between calculated results is significant.

The old and new streamwater data correlated well ( $R^2 > 0.90$ , slopes near 1.0) except pH and magnesium (Table 11, Fig. 21). Several monthly VWA pH values (< 2 percent) tended to skew the regression lines. These monthly values, driven by spurious sample pH's that the quality control/quality assurance (QC/QA) subroutines had detected, resulted from keypunching errors (see Quality Assurance Procedures). Unlike the situation with precipitation, corrections to sampling dates had a negligible influence on the assignment of the daily water values and subsequent volume-weighting of pH because of the weak relationship of pH to discharge (linear regression of pH with instantaneous flow has a slope = -0.0021;  $R^2 = 0.03$ ). The scatter in paired monthly VWA concentrations of magnesium (Fig. 21) was attributed to a single weekly streamwater sample that was improperly analyzed or grossly contaminated in the laboratory (see Quality Assurance Procedures).

## File Management

**Structure and Function of Data Files.** Laboratory values and codes are keypunched into dBase files specifically labeled for "new" data but formatted and structured identically to the archived database files. The final storage files are not used for preliminary data entry to avoid errors that would corrupt the permanent records. The "new" files are appended to archived files only after completion of

quality control procedures (see Quality Assurance Procedures). There are three types of files and each has a specific structure. Modifications of these file structures is undertaken carefully as data can be lost due to changes in format.

**Data Entry.** Prior to receipt of analytical laboratory results from IES, preliminary field data (date, time, temperature, etc.) are entered onto each "new" file for each sample site. This file includes all data derived from the analyses at the Pierce Lab, as well as applicable field codes (Appendix C).

Chemical analyses (in mg/L) are received by the HBEF from the IES laboratory on "summary sheets" for keypunching. A complete analytical record usually is available within 2 months of the sample date, but the printed copy is delayed to compile at least 10 new weekly records and to allow the laboratory to conduct its own QC/QA tests, and reanalyze samples if necessary. The summary sheets are examined for obvious outliers as soon as they are received, and requests for reanalyses are made immediately. The IES laboratory holds 3 to 4 months of samples before preserving them with chloroform and returning them to the HBEF for permanent storage. This delay allows sufficient time for the "new" data to be run through the QC/QA protocols, and/or requests for reanalyses (see Quality Assurance Procedures).

After quality assurance criteria are met, each new dBase file is appended to its associated final storage file. The storage file is checked for continuity at the appending date; the backup file is overwritten if no problems are discovered. The harddrive data on all three IES owned personal computers at the HBEF are backed up weekly by 100-MB removable cartridges (internally mounted Iomega Zip Drives). The weekly zip disks are removed from the lab each night by the IES Manager of Field Research at the HBEF. Annual backup cartridges are sent to IES for archiving.

### Quality Assurance Procedures

**Quality Assurance Goals.** The goals of our quality assurance procedures are to:

- 1) Provide the most representable sample possible to ensure the accuracy of ecosystem input and output calculations.
- 2) Maintain the integrity of the long-term record.
- 3) Detect and correct procedural errors.

Errors in the chemical database tend to fall into three categories: keypunching mistakes, contamination, and analytical error (in descending order of frequency). We believe that our quality assurance procedures have eliminated all serious errors in data entry.

Contamination is a difficult and challenging problem that requires extreme caution in the application of quality assurance procedures. Precipitation samples are particularly sensitive to contamination because of the low concentrations of many solutes; these samples also are highly variable (see Precipitation Collections: Contamination). A procedure that results in the rejection of extreme values without corroborative field evidence for contamination will bias the dataset. We believe that our procedures avoid serious bias while excluding grossly contaminated samples in the long-term database.

Extreme analytical error is not common but readily detected and relatively easy to correct. Less easily corrected is long-term bias due to changes in methodology or inaccuracy. By applying our procedures uniformly over the entire dataset from its inception to the present, we believe that we can at least detect—if not correct—such problems. At a minimum, the users of suspect data can be made aware of the situation.

We have not developed fixed acceptability criteria for quality assurance based on concentration extremes, ion balance,

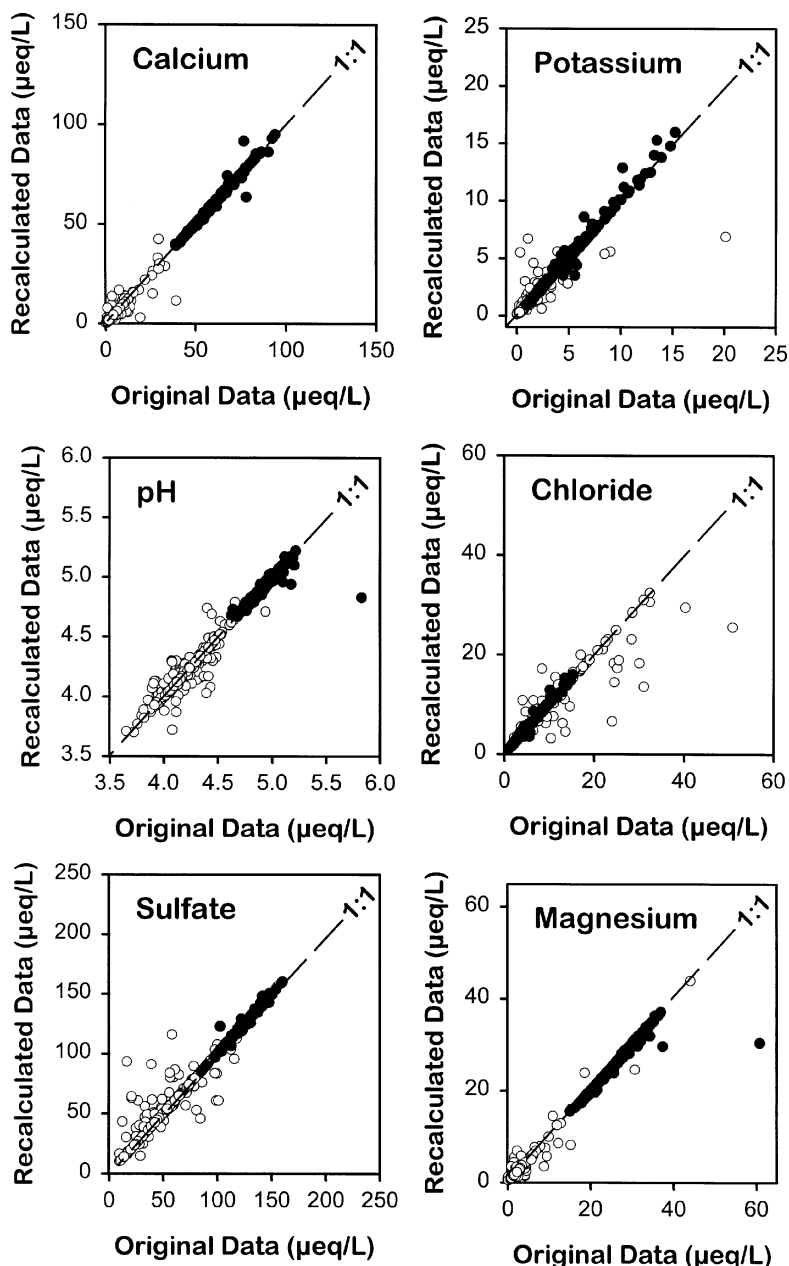


Figure 21.—Comparison of monthly volume-weighted average concentrations calculated prior to 1987 and recalculated in 1990 for bulk precipitation (○) and W-6 streamwater (●); see Table 11.

ion error, and calculated conductance. We use these measurements as guides to help identify problems, provide a semiquantitative assessment of the degree of the problem, and help choose a course of action. For example, our rejection of any sample for “natural” contamination usually begins at the time we collect and examine the sample. When there are no obvious signs of gross field contamination, we retain the record. In the case of laboratory contamination (including washing acids) or analytical error, only the strongest evidence from the quality assurance programs allows rejection. Without a plausible explanation for this

condition, the sample remains in the database and is used in the calculation of imports/exports. We believe that this systematic approach strikes a reasonable balance between ignoring obvious quality problems and “filtering” the data to fit predetermined standards.

**Quality Assurance Programs.** Upon completion of keypunching and coding, each “new” file (see Structure and Function of Data Files) is run through four dBase programs that assist in identifying problems.

Program 1 consists of a series of procedures that code sample records on the database for missing concentration data and analytical zeros, and flags samples already identified as suspicious based on a field code entered during initial keypunching.

Prior to 1990, the HBES chemical dataset contained zeros (0) for values below the analytical limits for each measured species, though theoretically no solute concentration is at zero. However, the use of zeros “left-censors” the database by removing values at the lowest range of the analysis; this results in lower means and increased standard deviations within each field (Newman et al. 1989). For the HBES chemical dataset before 1990, a zero indicated that the value was below the minimum reportable concentration (MRC). The MRC for any solute is an empirical compromise between operator experience and a calculated limit of quantification (defined as 10 times the standard deviation of a blank). For example, analyses conducted by the authors prior to the availability of data processing software and personal computers relied more heavily on analyst experience and thus MRCs were often slightly different from a calculated method detection limit (MDL). With the advent of more precise determinations near the MDL using these new software tools, the MRC was typically the same as the MDL. After much discussion and sensitivity analysis using our long-term database, it was decided in 1990 to replace all analytical zeros with a value equal to one-half the MRC applicable to the period of analysis. Small increases in unweighted average concentrations of substances, often at the limit of analytical resolution in precipitation and streamwater, were noted. However, the impact of inserting one-half MRC in the raw chemistry files on the VWA monthly or annual concentrations or calculated fluxes was negligible.

Program 2 is used to scan the “new” data for extremes in concentration, defined as concentrations in excess of the long-term (past 10 years) mean concentration plus 10 standard deviations (for precipitation), or 3 standard deviations (for streamwater and lakewater). A sample with a solute that exceeds these values is flagged in a “QA\_code” field (or column) for examination later. This program is particularly helpful in identifying errors in data entry.

Program 3 is used to compute and enter cation and anion sums, ion balance, and percent ion error, defined as the ion balance divided by one-half the sum of all ions. Ion balances are useful in identifying problems in streamwater and lakewater samples at the HBEF. Anion excesses for

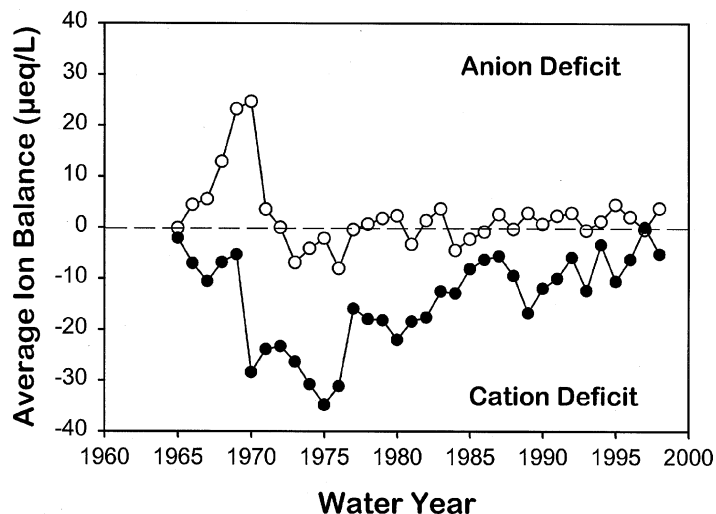


Figure 22.—Annual, volume-weighted average ion balance for precipitation (○) and W-6 streamwater (●). Aluminum equivalence not applied; complete ion balances prior to 1965 not available.

streamwater samples with a pH < 5 usually correlates with total aluminum, given a best estimate of aluminum charge (see aluminum analysis). Alternatively, cation excesses for samples with a pH > 6 correlate with +ANC, suggesting bicarbonate as the unmeasured anion (see Acid Neutralizing Capacity). Average ion balances calculated from 1967 to 1971 and from 1991 to 1995 are acceptable for precipitation, streamwater, and lakewater samples (Tables 8-9). VWA annual streamwater and precipitation ion balances are reasonable (i.e., differences can be explained). From 1968 to 1970, the precipitation VWA ion balance has an anion deficit; from 1970 to 1976, the streamwater VWA ion balance has a cation deficit (Fig. 22; see Resolving Analytical Problems).

Program 4 is used to calculate and enter the theoretical conductance of each sample based on measured ion concentrations. These data are used to test for complete ion analyses or to grossly confirm pH values (Fig. 23) based on the theoretical equivalent conductances of each ion in solution (Gambell and Fisher 1966; Miller et al. 1988). Agreement is excellent for bulk-precipitation samples (linear regression slope = 0.99,  $R^2 = 0.95$ ), which can vary over a wide range of conductance (Fig. 23). For streamwater samples from W-6, the relationship between measured and calculated conductance is much weaker (slope = 0.72;  $R^2 = 0.73$ ), probably because of the narrow range in ionic strength, the presence of unmeasured, charged organic radicals, and the difficulty of assigning a charge to aluminum. For Mirror Lake outlet, inlet, and profile samples, the measured conductance is regularly 10 to 20 percent less than the calculated values, possibly because of greater opportunities for organic complexation, which effectively reduces free ion activity (Miller et al. 1988).

The ancillary data generated by the dBase programs are inserted automatically into specific dBase fields (columns) in each chemistry file to become part of the permanent record



for that sample. No records of sample analyses are deleted. Samples rejected by the calculation programs are marked by hand using a pass/fail conditional field in the database (see Structure and Function of Data Files). When the problem can be resolved by reanalysis and the samples are at the IES laboratory, such a request is made. Samples already preserved or shipped to the HBEF for storage are not reanalyzed for quality assurance purposes, though they are available for other analyses (e.g., see aluminum analysis).

### Resolving Analytical Problems

After running all the original, uncensored weekly precipitation chemistry data (from 1963 to 1987) through these automatic procedures in 1990, 163 of 1,254 precipitation samples (13 percent) failed the quality assurance protocols. About 75 percent of these samples already had been coded by J.S. Eaton for contamination in the field and rejected for use in calculations before 1987 based on the presence of gross amounts of particulate material, or high, unbalanced concentrations of chloride. The remaining samples that failed (3 percent) were attributed to keypunching or analytical errors, particulate and salt contamination, or residue from washing acid.

Streamwater and lakewater samples taken before 1987 seldom failed (< 1 percent) procedures applied since 1990, and none was rejected. Certain solute analyses were suspicious, but since timely reanalysis was not possible, the records were coded rather than rejected (see Resolving Analytical Problems).

**Precipitation Samples.** The ionic concentration of precipitation samples (more than 1,800 records by year 2000) averages 211  $\mu\text{eq/L}$  (107  $\mu\text{eq/L}$  cations and 104  $\mu\text{eq/L}$  anions) but ranges widely from 8 to 1,623  $\mu\text{eq/L}$ . Outliers in the precipitation chemical database are common and ion balance and percent ion error are highly variable.

The first step in identifying samples with potential contamination or analytical error is comparison with duplicate collections (see Precipitation Collections: Contamination). There is a good correlation between precipitation pH (hydrogen ion activity) and specific conductance, and between total ionic charge and specific conductance (Fig. 23,  $R^2 = 0.77$  and  $0.73$ , respectively). Values for pH and specific conductance between all of the bulk collectors at the HBEF do not differ from the expected error of measurement, so confirmation of a grossly contaminated sample is relatively straightforward. However, where there are modest differences between samples in these initial tests, or if uncertainty exists, the sample is analyzed. Differences in ion balance then can be used to identify contaminants.

The following examples indicate how problems with precipitation data are detected and how decisions regarding these data are handled.

On several occasions in June and July 1968, an original, clean precipitation sample was poured off into a storage bottle with a plastic cap liner that apparently leached chloride

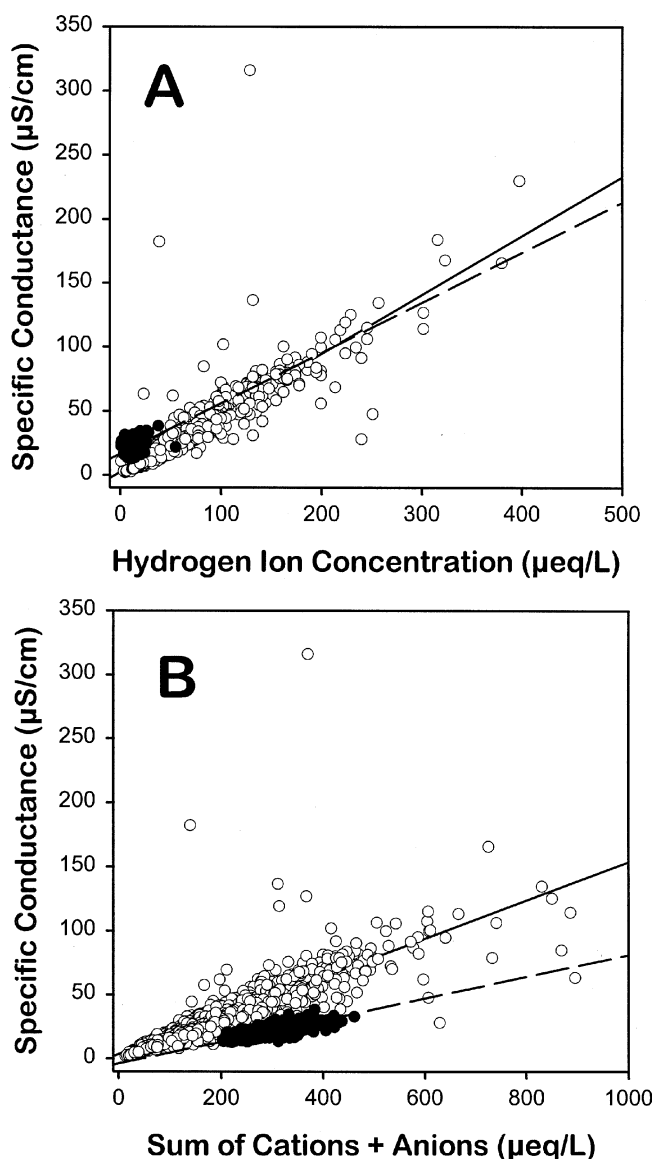


Figure 23.—Relationships between (A) specific conductance and hydrogen ion concentration and (B) specific conductance and the sum of all ions in bulk precipitation ( $\circ$ ) and W-6 streamwater ( $\bullet$ ).

into the original solution during storage or shipment. Laboratory analyses indicated the presence of hydrochloric acid in otherwise dilute and well-balanced samples. All of these samples were rejected (but not discarded from the record). We have not used bottles with cap liners since August 1968.

In another incident in the 1970's, the equivalence values of potassium and chloride in precipitation samples were more than 10 times normal and nearly equal, i.e., the ion balances were excellent. However, the original field conductance was far below the calculated theoretical conductance. The only reasonable explanation for this type of precipitation

chemistry was contamination by laboratory salts (e.g., pH meter electrode filling solution) apparently resulting in contamination of the precipitation samples following collection and initial testing. In this case, the affected database records were coded for contamination and excluded from calculations of deposition (though the records were retained). A similar case involving contamination by sodium chloride (probably from spillage of laboratory salts near a snow barrel after collection) occurred in January 1980. The concentrations of sodium and chloride at RG-11 were equivalent, and more than 20 times those at RG-22 (collected concurrently). The chemical records were coded but not used for VWA calculations. The large impact on the annual arithmetic average for sodium and chloride for all samples regardless of contamination indicated the potential for distortion of the long-term data.

Between 1964 and 1966, when bulk-precipitation collectors were fitted with plastic and aluminum screens, chloride was a frequent contaminant (Juang and Johnson 1967). Samples with obvious chloride contamination ( $> 10$  mg/L) were identified readily by ion balance inequity and excluded from calculations of deposition. However, because there was no systematic database screening system in 1967, it is apparent that some of the less extreme samples were retained, and that these were among the 40 samples detected and coded by outlier, ion balance, and conductance programs when the long-term data were reviewed in 1990.

Because of concerns about contamination by washing acid prior to changes in protocol in 1974 (see Sample Equipment Preparation), special attention was paid to detecting problems from residual HCl. We screened all analytical records from that period (448) for chloride concentrations that were  $> 1$  mg/L and low in sulfate and nitrate but balanced by high hydrogen ion ( $\text{pH} < 3.5$ ), suggesting the presence of hydrochloric acid. Chloride balanced by other cations (e.g., sodium) was not considered a contaminant unless indicated by other sources such as field notes. Few of these samples had a low pH. Samples with potential HCl contamination were easily identified because of the unique chemical signature and because they tended to be clustered by dates (e.g., 3 weeks in October and November 1970). This clustering was attributed to brief periods when washing protocols were not followed by student assistants. These samples were coded and allowed to remain in the database (seven sample records or 1.6 percent) but not used in calculating deposition.

After 1973, the entire apparatus used to collect precipitation at HBEF was washed and tested for cleanliness before use at the Pierce Lab (see Sample Equipment Preparation). This procedure eliminated incidents of HCl contamination. Field blanks have been tested periodically to ensure the quality of the DIW rinsing system and the chemical inertness of precipitation collection gear.

Annual VWA chloride concentrations in bulk precipitation dropped in water year 1981. This nearly coincided with the time when the large Rubbermaid snow barrels were replaced with plastic buckets (February 1982; see Field Procedures).

Subsequently, a study of collector leaching was conducted by IES and Forest Service (unpublished data). It showed that the barrels tended to leach small amounts of chloride (5 to 15  $\mu\text{eq/L}$ ) into standing DIW over a 3-week period. No other ions were present in greater than trace quantities, so the chloride may have originated from organic plastizers rather than washing acids. However, since bulk collectors are not left in the field longer than 1 week and the sample usually is frozen (snow) during this time, this was an extreme test. The same six barrels were tested against three other types of bulk collector (15 collectors total) using natural precipitation leaching for 3 weeks. There was no difference (beyond the error of each analysis) between collectors for any measured solute, though one of the six snow barrels had slightly elevated (3  $\mu\text{eq/L}$  above average) chloride.

In fact, a careful examination of weekly chloride data revealed systematically lower chlorides during the summer when funnel-bottle equipment was in use and before the barrels were replaced. Wet-only collectors operated over the same time period by the HBES and NADP show similar declines in chloride. No changes in analytical techniques were made by either group. Although the original snow barrels might have been sources of trace amounts of chloride, they did not have a significant influence on the large changes in chloride inputs documented during the early 1980's.

Because particulate material can be captured in bulk collectors, we used funnel screens (1964 to 1966) and multiple sites to collect precipitation (Appendix A). It is not possible to eliminate the collection of all fine particulates, though we do reject samples with high levels of fine material. While our goal is to collect the cleanest possible precipitation samples to properly quantify ecosystem imports, we also have an extensive database on dirty samples (see Precipitation Collection Procedures). Therefore, we can identify most natural contamination at the HBEF. Precipitation samples containing bird feces, large amounts of particulates, or insect fragments have a higher pH and a lower conductance than concurrent clean samples (organic debris may absorb or complex ionic solutes). In ion analyses, bird feces is expressed as highly elevated concentrations of ammonium and phosphorus. The presence of insect or leaf fragments usually increases potassium concentrations (leaching from intact insects is negligible). The presence of pollen has no apparent effect on pH, conductance, or solutes except for potassium and phosphate, and even these ions are not always correlated with pollen.

**Streamwater Samples.** Unlike precipitation samples, outliers are not common in the streamwater chemical database, and ion balances vary little. To date, no entire record of streamwater chemistry has been rejected. When an outlier is detected by the program, the ion balance is compared to the suspicious solute concentration. If there is a match, the record is flagged. When discharge data do not indicate a large change in flow (e.g., a threefold increase) associated with this sample, the specific solute data are deleted and replaced with a code that alerts the calculation program (see Data Calculations). This approach allows the

application of “hydrologic horse sense” to eliminate what typically are keypunching mistakes, or, more rarely, errors in laboratory procedures.

For example, after all data were screened in 1990, a set of samples from W-1 through W-6 collected in September 1980 returned flagged data files with magnesium concentrations in excess of the long-term average concentration plus three times the standard deviation (Fig. 21; see Quality Assurance Programs). There were no other matching anion equivalencies. All other analyses, including calcium, pH, and conductivity, reflected typical values that suggested laboratory error. Because these samples could not be reanalyzed, only the magnesium data were struck from the record and replaced with a code indicating removal. The remainder of the sample record was retained in the database (see Recalculation of Import and Export Values).

**Methodological Changes.** Samples are measured for several months or more to obtain comparative data to assess the effects of changes in methodology. This careful approach is an essential part of the long-term trend analysis for all the solutes measured at the HBEF, since abrupt changes (dilution or concentration of specific solutes) can occur, particularly with respect to watershed manipulations. However, it should be noted that some trends are evident only in hindsight and long after the analyses are complete.

The record for the nitrate analyses is a good example. A twofold increase in streamwater nitrate that developed in 1969 remained high until about 1977 and then decreased gradually. This 6-year period of elevated nitrate caused an equal offset in the streamwater ion balance (Fig. 22) that corresponded to an unmeasured cation. Since these effects occurred around the time the nitrate methods were switched from D.W. Fisher’s responsibility to Cornell University (see Nitrate Analysis), the analytical record was examined to determine whether this effect was an artifact of methodology. We found that only streamwater samples from untreated HBEF watersheds showed elevated nitrate levels even though samples from precipitation, experimentally treated watersheds, and Mirror Lake inlets were analyzed concurrently. There were no other errors with a measured cation, pH, or other anion that might have balanced the nitrate in streamwater. Further, the overlapping analyses conducted on the samples when methods were changed (1970 to 1972 and 1975 to 1976) confirmed the high nitrate values. Annual VWA pH, based on Fisher’s data, declined by about 0.1 unit (to 4.8) at the beginning of that period. While the data were not used in calculations of annual pH averages, the duplicate streamwater pH’s determined by the authors were significantly lower than Fisher’s from 1966 to 1970 (Figs 14-15).

Thus, we hypothesize that aluminum and hydrogen were mobilized with the nitrate, and that the charge on the aluminum ion increased at lower pH values to match the nitrate (see aluminum analysis). Unfortunately, aluminum was not measured on a routine basis during most of this period, and reanalysis for nitrate is problematic after long storage (see Sample Preservation). Because of the careful

records of analytical overlap, we are confident that the change in technique did not affect the nitrate values. There are similar examples for other solutes, including ammonium, pH, and chloride, primarily for the early part of the record (see Analytical Methods).

## Data Calculations

### Hydrology Data

**HBEF Water-Year Data.** From the outset of the HBES it was decided to compile all annual input or output values in water years, that is, from 1 June to 31 May (see Federer et al. 1990). This timing was designed to capture all outputs resulting from each winter’s snowmelt, which usually occurs by mid-May. This protocol also ends the water year when streamflow begins to decrease due to evapotranspiration as deciduous trees break dormancy. In this way, the increases in precipitation inputs and resulting re-wetting of soils after leaf fall in October and November can be included with the hydrologic period most likely to be influenced by these changes (Likens et al. 1977; Likens and Bormann 1995; Federer et al. 1990).

The Forest Service stores HBEF hydrology data as annual files (calendar year) of daily precipitation (entire watershed, or single rain gauge) or streamflow (entire watershed) as areal mm/d in flat ASCII file format. These data are available on the HBES homepage ([www.hbrook.sr.unh.edu](http://www.hbrook.sr.unh.edu)).

The hydrology files must be modified to remove superfluous headers, spaces, and monthly and annual sums that make direct uploading to dBase format impossible. An editing program (EDIX) is used to strip each file to a bare minimum. From this abridged ASCII file data are appended to our daily hydrology files in dBase format. These files are upgraded every 6 months as data become available, and only after the Forest Service certifies their accuracy through its stringent quality assurance programs.

**Mirror Lake Water Data.** Hydrology data from the USGS stream gauging stations on the Mirror Lake outlet and the NE, NW, and W inlets have been compiled annually since 1981 (Winter 1985). The USGS records streamflow as daily average stage (in feet) at each site in spreadsheet format (Microsoft Excel). Stage data are available approximately 1 year after collection. These values are obtained as ASCII files, loaded to a spreadsheet (Lotus 123 or Excel), and rearranged or converted as needed prior to appending to the primary archive dBase file. Data are maintained in the storage and calculation dBase files as average daily flow in liters.

### Calculation Program

The selection (by J.S. Eaton) of dBase as the format for storage of the long-term data in 1984 was fortuitous. This decision has made routine query of the data easy and provides security for archival purposes. Conversely, it is complicated to generate values for chemical budgets with the master dBase program. However, much time has been spent

testing and modifying the program so we have confidence in its operation. dBase as it is currently configured may not be flexible enough to handle future collections and new analyses, so other software platforms (e.g., Microsoft Access) are being tested for their applicability.

The master dBase program was written to use HBES chemical data and Forest Service or USGS daily water data and to create a permanent file of monthly data, in VWA concentration (mg/L), and monthly input or output (g/ha-month). Annual (water year or calendar year) files are created from separate subroutines. The files, procedures, and dBase programs used to create and maintain the HBES chemical database are described in our Data Management Operating Procedures Manual which is maintained at the HBEF and IES.

## Precipitation Inputs

**Calculating Algorithm.** The amount of daily precipitation for the period of collection (in mm/ha-day) is multiplied by concentration data (mg/L) for each substance analyzed at the end of the period. Calculation periods are typically 1 week (7 days  $\pm$  1) unless there has been no precipitation. As a rule, the precipitation collectors are not retrieved during an event but after precipitation stops, usually the next dry day. Regardless of catch, the collector is replaced each week (see Collection Procedures and Equipment). Samples coded for contamination in the database are ignored by the program; the next uncontaminated sample is then used to provide chemistry for the entire period.

**Precipitation Calculation Results.** The resulting daily deposition values (g/ha-day) for each collection are summed to provide the mass inputs for each month (g/ha-month). Daily values are not retained. The monthly data are summed for water-year or calendar-year annual input. Input flux values are comparable for watersheds of different sizes because they are normalized by areal amount of precipitation (Likens et al. 1967). VWA concentrations are back-calculated from the total mass input and the total precipitation input for the monthly and annual databases.

## Streamwater Outputs

**Calculating Algorithm.** Streamflow data (in mm/ha-day) for each sample date are multiplied by the concentration (mg/L) for each substance analyzed in that sample. For the dates between samples, the average of the beginning and ending concentration values is applied to the daily flow. Calculation periods are typically 1 week, though intermediate samples are taken during episodes of high flow (see Event Sample Protocol).

**Streamwater Calculation Results.** As with daily deposition values, the resulting daily export values (g/ha-day) for each

collection are summed to provide the mass output for each month (g/ha-month). Daily values are not retained. The monthly data are summed for water-year or calendar-year annual output. Output flux values are normalized by areal amount of streamflow. VWA concentrations are back-calculated from the total mass export and the total streamflow output for the monthly and annual databases.

## Lake Inlets and Outlet Fluxes

**Nutrient Flux Algorithm.** Flow data (L/day) for each sample date are multiplied by the concentration (mg/L) for each substance analyzed in that sample. For the dates between samples, the average of the beginning and ending concentrations is applied to the daily flow. Calculation periods are typically 1 week, though intermediate samples are taken during episodes of high flow (see Event Sample Protocol).

**Lake Inlets and Outlet Calculation Results.** As with the precipitation and streamwater data, the resulting daily export values (g/day) for each lake site are summed to provide the mass output for each month (g/month). Daily values are not retained. The monthly data are summed for water-year or calendar-year annual input. VWA concentrations are back-calculated from the total mass export and the total flow for the monthly and annual data bases. Note that for the estimates of lake nutrient budgets (mass inputs and mass outputs) we have not normalized the USGS hydrology data on an areal basis for individual subwatersheds. To obtain areal values for comparing subwatersheds, total hydrologic outputs for each day must be divided by the watershed area above each stream gauging site (Winter et al. 1989).

## Conclusion

The chemical record of the Hubbard Brook Ecosystem Study now spans 36 years. Much effort has been expended to preserve the integrity of this complex record and to avoid artifacts due to changes in personnel, procedures, and analytical equipment. New procedures and methods were adopted when improvements in analytical accuracy or efficiency were deemed significant, and when adequate funds became available to apply them. Tests were conducted to evaluate the effects of these procedures on the long-term record. These efforts reflect a commitment to established principles of ecosystem investigation, as well as a willingness to learn better ways to conduct experiments and measure their impact. It is hoped that this account will assist in the interpretation of the HBES chemical record, and provide valuable instruction in the development of other studies. We are confident that the long-term chemical record described here for the HBES is as accurate and consistent as available technology and human care would allow.

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## Appendix A

### Precipitation Site Locations and Dataset Sources

The following is a record of each time the primary site of precipitation collection has been relocated, or the source from which the primary precipitation chemical data were derived has changed. The first priority in the early years of the HBES was to collect the cleanest possible (least contaminated) precipitation samples from several several combinations of bulk and wet-only collectors and sites.

June 1963 to April 1966: average of chemical data from three bulk collectors, analyzed separately, located on an elevational gradient near W-6 at RG-9, RG-10, and RG-11.

May 1966 to May 1967: chemical data from two possible sites: bulk collector at RG-11; or automatic, wet-only collector (Wong Laboratories, mark IV type) at the R.S. Pierce Ecosystem Laboratory (known then as HBEF Station) if the bulk collector was contaminated.

June 1967 to October 1967: average of chemistry, analyzed separately, from uncontaminated precipitation collections from four sources: RG-11 bulk collector; bulk collector at HBEF Station; Wong wet-only collector at HBEF Station; and USGS automatic, wet-only collector at HBEF Station.

October 1967 to November 1967: average of chemistry, analyzed separately, from uncontaminated samples from RG-11 and HBEF Station bulk collectors, and from USGS wet-only collector at HBEF Station.

November 1967 to April 1968: average of chemistry, analyzed separately, from uncontaminated samples from four sources: bulk collector and Wong wet-only collector at RG-11; a bulk collector and USGS wet-only collector at HBEF Station.

April 1968 to May 1969: average of chemistry, analyzed separately, from uncontaminated samples from three sources: bulk collector at RG-11; a bulk collector and USGS wet-only collector at HBEF Station.

June 1969 to November 1972: uncontaminated chemistry from bulk collector at RG-11.

April 1973 to May 1983: average of chemistry, analyzed separately, from bulk collector at RG-11 and bulk collector near RG-8, approximately April to November each year. Collector was discontinued at RG-8 during the snow season (December to April), so chemistry for each winter period is from RG-11 bulk collector only.

June 1983 to May 1990: same as 1973 to 1983 except that the bulk collector near RG-8 was moved to RG-1 (near W-1).

May 1990 to present: an average of uncontaminated RG-1 and RG-11 bulk samples, analyzed separately, collected year round.

## Appendix B

### Analytical Methods

**Definitions.** The following definitions are provided for a clear understanding of the quality control terms applied to the long-term chemical record and used in these appendices:

Precision over range (POR): the closeness of agreement among a number of consecutive measurements of the same sample under the same analytical conditions expressed as a percentage of the upper range of typical values; synonymous with repeatability.

Method detection limit (MDL): the lowest concentration value at which the analysis can discriminate between a standard concentration and the background signal of the instrument; equal to three times the standard deviation of the average analytical blank. Listed as a range because this value has varied over time with changes in sample matrices, analyst experience and mechanical proficiency.

Minimum reportable concentration (MRC): the lowest concentration value that is practical and routinely achievable with confidence over the expected range based on long-term experience. Analogous to the MDL since 1990 (see Quality Assurance Programs).

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Calcium, Magnesium, Potassium, Sodium

Period of application: June 1963 to present.

Analysts: the authors at Dartmouth, Cornell and IES.

Range encountered: typically < 5 mg/L calcium and sodium, < 2 mg/L magnesium, and < 1 mg/L potassium for uncontaminated precipitation, and untreated streamwater and lakewater. Mirror Lake NE inlet samples affected by contamination with road salt require dilution for sodium, which exceeds 50 mg/L on occasion.

Method:

Flame Atomic Absorption Spectrophotometry (FAAS) with air/acetylene mixture (Perkin-Elmer 1968; Slavin 1968; Skougstad et al. 1978); lanthanum-oxide hydrochloric acid buffer added to samples and standard solutions to prevent dampening of absorbance by other solutes.

Instruments used: Perkin-Elmer models 303, 403, 503, and 2380; AAnalyst 300.

POR: 1 percent for streamwater to 5 percent for precipitation.

MDL: 0.01 to 0.02 mg/L.

MRC: 0.01 mg/L for all four ions.

Comment: Other than upgrading FAAS equipment and variations in the approach used to generate calibration curves (i.e., absorbance vs. concentration modes), there have been few changes in these analyses. Dissolved aluminum, nitrate, sulfate, and/or silica may have interfered with calcium determinations in streamwater samples from first 2 years of analyses (Skougstad et al. 1978). However, corrections were made (Likens et al. 1967; Johnson et al. 1968) and lanthanum addition has been used since 1965 without exception. Currently, POR is higher for precipitation because base cation concentrations approach the MDL in most samples. Methods and specifications for AAnalyst 300 instrument are similar to Perkin-Elmer equipment.

Aluminum

Period of application: June 1964 to June 1970; June 1976 to present.

Analysts: D.W. Fisher (1964-70) in Washington, DC; the authors (1976 to present) at Cornell and IES; and Northeastern Research Station's Forestry Sciences Laboratory at Durham, New Hampshire (1995 to present).

Range encountered: typically 0.1 to 0.5 mg/L aluminum in streamwater; always at detection limits in precipitation.

Methods:

## Total Aluminum

1) spectrophotometric: ferron orthophenanthroline method (Fisher et al. 1968; Rainwater and Thatcher 1960) 1964 to 1970.

Instrument used: Spectrophotometer, Beckman model B.

POR: 10 percent (estimated).  
MDL: 0.01 mg/L.  
MRC: 0.01 mg/L.

2) same method, 1976 to present (Skougstad et al. 1978) on all W-6 streamwater samples and precipitation samples from RG-1 and RG-11.

Instrument used: Spectrophotometer, dual-beam: Coleman PE model 55, or Shimadzu model 160.

POR: < 5 percent.  
MDL: 0.005 to 0.01 mg/L.  
MRC: 0.01 mg/L.

## Monomeric Inorganic Aluminum

3) colorimetric, automated, pyrochatecol-violet chelation method, following resin-column fractionation into organic and inorganic monomeric forms (Driscoll 1984; McAvoy et al. 1992), on streamwater samples from W-7, W-8, and W-9, 1995 to present.

Instrument used: Technicon AutoAnalyzer II.

POR: < 5 percent.  
MDL: 0.01 mg/L.  
MRC: 0.01 mg/L.

Comment: Improvements in spectrophotometry have increased precision and accuracy of method 2 (Skougstad et al. 1978). Dissolved iron could interfere with this analysis. However, more than 100 analyses for iron in W-6 streamwater measured concurrently with aluminum (since 1976) indicate that iron is present at an order of magnitude below threshold necessary to have impact. The Forest Service laboratory at Durham uses method 3 on streamwater samples from W-7, W-8, W-9, and other sites.

## Ammonium

Period of application: June 1964 to present.

Analysts: D.W. Fisher (1964-72) in Washington, DC; the authors (1970 to present) at Cornell and IES.

Range encountered: typically < 1 mg/L ammonium in precipitation, streamwater, and lakewater, and often at detection limits in streamwater and lakewater year round. Up to 2 mg/L ammonium have been measured in uncontaminated samples of precipitation.

### Methods:

1) spectrophotometric: distilled as ammonia from buffered solution and reacted with Nessler's reagent (similar to EPA method No. 350.2; Fisher et al. 1968; Rainwater and Thatcher 1960), 1964 to 1972.

Instrument used: Spectrophotometer, Beckman model B.

POR: 5 percent (estimated).  
MDL: 0.01 mg/L (method).  
MRC: 0.01 mg/L (estimated).

2) colorimetric, automated (Keith 1996: EPA method No. 350.1), indophenol-blue (phenol-sodium hypochlorite) method, 1970 to present.

Instruments used: Technicon AutoAnalyzer (TAA) I and II (Technicon Instruments 1971: methods No. 98-70W and 154-71W); since March 1993, Alpkem Flow Solution III automated analyzer (Alpkem Corp. 1991: phenate method No. 578, similar to EPA No. 350.1).

POR: < 5 percent in precipitation, up to 20 percent in streamwater.

MDL: 0.005 to 0.02 mg/L.

MRC: 0.01 mg/L.

Comment: Reported accuracy for the analysis in the first 4 years of application was  $\pm 0.1$  mg/L (Fisher et al. 1968) while the method was documented to be accurate to  $\pm 0.01$  mg/L in Rainwater and Thatcher (1960). The technique and precision for the Alpkem Corp. instrument are essentially the same as for the TAA. POR in streamwater is greater due to extremely low concentrations.

## pH

Period of application: June 1964 to present.

Analysts: D.W. Fisher (1964-72) in Washington, DC; the authors (1963 to present) at Dartmouth, Cornell, and HBEF.

Range encountered: pH 2.5 to 7.5 for samples of precipitation, streamwater, and lakewater.

Method: potentiometric, paired-glass pH and reference electrodes, air equilibrated, without stirring.

Instruments used: Beckman analog meter (Zeromatic or model N) prior to 1972, Orion analog meters (models 401, 407A) 1972 to 1996, Orion digital meters (models 710A and 940), 1996 to present.

POR: 0.1 to 0.01 pH unit.

MDL: not applicable.

MRC: not applicable.

Comment: Recommended USGS method from 1963 to 1972 was to measure with minimum aeration and agitation (Barnes 1964; Fisher et al. 1968; Rainwater and Thatcher 1960). It is likely that D.W. Fisher used two buffers of pH 7.0 and 4.0 to span the range encountered, as reported by Gambell and Fisher (1966).

The authors determine pH within 1 or 2 days of collection. Meters are calibrated with analytical-grade, NBS-certified buffers at pH 7 and 4, accurate to  $\pm 0.01$  with temperature correction. Low-ionic strength buffers of pH 6.97 and 4.10 (Orion Research 1997), and DIW are tested to document electrode accuracy and speed of response, but these data are not used for calibration. Precision of measurement improves with increasing ionic strength and decreasing pH. Nernst slope corrections usually are 95 percent or better. The standard electrode system consists of a glass pH electrode paired with a KCl-filled, high-flow (Ross-type) reference electrode, or research-grade combination pH/reference electrode (Orion Research 1997). Samples are measured at room temperature (15-20°C) in 30-mL plastic cups, without constant stirring or gas purging, or addition of KCl stabilizers to increase electrolyte strength (Galloway et al. 1976, 1979; Orion Research 1997). In addition to the operational instructions applicable to each meter, the current protocol for calibration and measurement, including copious rinsing with DIW between steps, is:

- 1) Measure weak HCl solution (pH ~3).
- 2) Equilibrate in DIW (pH ~5.6).
- 3) Calibrate with standard pH 7 and pH 4 buffers.
- 4) Equilibrate in DIW (pH ~5.6).
- 5) Test each sample aliquot twice; soak electrode in first aliquot for about 5 minutes; record second reading when stable or after no more than 5 additional minutes.
- 6) Check and recalibrate with pH 7 and pH 4 buffers 3 to 5 times during the analysis of the full suite of weekly samples (see Appendix C).

Electrodes are replaced semiannually or whenever calibration is unstable or electrode response sluggish. Data from ANC titrator (Orion 940) with similar electrodes are compared to data from the 710A meter for each sample when volume is sufficient. Only data from the 710A are used in the chemical budget calculations.

## Sulfate

Period of application: June 1964 to present.

Analysts: D.W. Fisher (1964-72) in Washington, DC; the authors (1970 to present) at Cornell and IES.

Range encountered: typically < 20 mg/L sulfate in precipitation, streamwater, and lakewater, but seldom near detection limits.

### Methods:

1) spectrophotometric: barium-chloride titration with thordin endpoint indicator, concentrated fivefold to increase sensitivity (Fisher et al. 1968; Rainwater and Thatcher 1960), 1964 to 1972.

Instrument used: Spectrophotometer, Beckman model B.

POR: < 5 percent (method).

MDL: 0.1 mg/L (estimated).

MRC: 0.1 mg/L (estimated).

2) colorimetric, automated, barium-sulfate formation and methylthymol-blue indicator (Keith 1996; EPA method No. 375.2), adjusted for low-range (0.5 to 30 mg/L) samples (Technicon Instruments 1971: methods No. 375.1 and 375.2; Gales et al. 1968; Lazarus et al. 1968), 1970 to 1976.

Instrument used: Technicon AutoAnalyzer (TAA) I and II.

POR: 10 percent > 1 mg/L, 20 percent < 1 mg/L.

MDL: 0.5 mg/L improving to 0.1 mg/L.

MRC: 0.2 to 0.1 mg/L.

3) ion chromatography (Keith 1996; EPA method No. 300.0) concurrently with analyses for nitrate (Small et al. 1975; Tabatabai and Dick 1983), 1976 to present.

Instruments used: Dionex model 14 (prior to 1986), model 2000i (after February 1986) and model DX500 (after February 1994) chromatographs, using a Dionex AS4A separator column.

POR: 5 percent above 1 mg/L.

MDL: 0.1 mg/L prior to 1986; 0.01 to 0.02 mg/L currently.

MRC: 0.2 mg/L prior to 1986; 0.01 mg/L currently.

Comment: D.W. Fisher recorded sulfate concentrations on worksheets to 2 decimal places but reported sulfate to 1 decimal place (Fisher et al. 1968). All of the analyses apparently are least accurate at low concentrations. However, sulfate concentrations < 0.3 mg/L are rare in precipitation samples (<1 percent of records), and sulfate values below 3 mg/L have not been detected in streamwater or lakewater. Upgrading the TAA analytical equipment in May 1972 apparently improved sensitivity of the method from  $\pm 0.5$  to  $\pm 0.2$  mg/L. Improvements in IC data acquisition software reduced MDL, especially after purchase of Dionex 500 in 1994.

## Nitrate

Period of application: June 1964 to present.

Analysts: D.W. Fisher (1964-72) in Washington, DC; the authors (1970 to present) at Cornell and IES.

Range encountered: typically < 10 mg/L nitrate in precipitation, untreated streamwater, and lakewater, and often at detection limits in streamwater during growing season. Up to 82 mg/L nitrate have been measured in experimentally manipulated watersheds at HBEF; these samples require dilution before analysis.

### Methods:

1) spectrophotometric: phenoldisulfonic acid technique (Fisher et al. 1968; Rainwater and Thatcher 1960), 1964 to 1972.

Instrument used: Spectrophotometer, Beckman model B.

POR: 5 percent (estimated).

MDL: 0.005 mg/L (reported).  
MRC: estimated 0.01 mg/L

2) colorimetric, automated (Keith 1996: EPA method No. 353.2), copper/cadmium reduction with sulfanilimide to produce a colored diazo complex (Technicon Instruments 1971: methods No. 33-69W and 100-70W; Brewer and Riley 1965; Kamphake et al. 1967), 1970 to 1976.

Instrument used: Technicon AutoAnalyzer I and II.

Precision over range: < 10 percent.

MDL: 0.01 to 0.02 mg/L.  
MRC: 0.02 to 0.01 mg/L.

3) ion chromatography (Keith 1996; EPA method No. 300.0) concurrently with analyses for sulfate (Small et al. 1975; Tabatabai and Dick 1983), 1976 to present.

Instrument used: Dionex model 14 (prior to 1986), model 2000i after February 1986, and model DX500 (after February 1994) chromatographs using a Dionex AS4A separator column.

POR: < 5 percent.  
MDL: 0.005 to 0.02 mg/L.  
MRC: 0.01 to 0.02 mg/L.

Comment: The authors tested other methods in the early 1970's (e.g., spectrophotometric brucine method; Jenkins and Medsker 1964) to measure nitrate with greater accuracy below 1.0 mg/L, but these methods required sample dilution more frequently or were sensitive to interferences (e.g., chloride). Method 2 measured both nitrate and nitrite, though nitrite is essentially absent from HBEF streams, which usually are well oxygenated.

#### Dissolved Organic Nitrogen

Period of application: June 1995 to present.

Analyst: Northeastern Research Station's Forestry Sciences Laboratory at Durham, New Hampshire.

Range encountered: typically < 1 mg/L dissolved organic nitrogen (DON) in streamwater or precipitation.

Method:

High-temperature catalytic oxidation (HTCO) of sample followed by determination of total dissolved nitrogen (TDN) as metastable nitrite (Merriam et al. 1996).

Instrument used: Shimadzu TOC-5000 carbon analyzer furnace coupled with an Antek chemiluminescent nitrogen detector.

POR: < 5 percent  
MDL: 0.03 mg/L  
MRC: 0.03 mg/L

Comment: DON is calculated by subtracting ammonium-nitrogen and nitrate-nitrogen (see Ammonium and Nitrate analyses) from TDN.

#### Chloride

Period of application: June 1964 to present.

Analysts: D.W. Fisher (1964-72) in Washington, DC; H.T.F. Juang and N.M. Johnson 1965-66 at Dartmouth; the authors (1970 to present) at Cornell and IES.

Range encountered: typically < 5 mg/L chloride in precipitation, streamwater, or lakewater. Reaches 130 mg/L in NE inlet of Mirror Lake.

Methods:

1) spectrophotometric: ferric ion-mercuric thiocyanate method (Fisher et al. 1968; Juang and Johnson 1967; Iwasaki et al. 1952), 1964 to 1972.

Instrument used: Spectrophotometer, Beckman model B or model DU.

POR: < 5 percent (estimated).  
MDL: 0.01 mg/L (estimated).  
MRC: 0.01 mg/L (estimated).

2) colorimetric, automated, ferric ion-mercuric thiocyanate method (Keith 1996: EPA method No. 325.1; Technicon Instruments 1971: method No. 99-70W; Zall et al. 1965; O'Brien 1962), 1970 to 1996.

Instrument used: Technicon AutoAnalyzer I and II.

POR: < 5 percent for samples < 10 mg/L.  
MDL: 0.01 mg/L.  
MRC: 0.01 mg/L.

3) ion chromatography (Keith 1996; EPA method 300.0) run concurrently with analyses for sulfate and nitrate (Tabatabai and Dick 1983), 1996 to present.

Instrument used: Dionex model DX500 chromatograph with a Dionex AS4A separator column.

POR: < 5 percent for samples < 10 mg/L.  
MDL: 0.01 to 0.02 mg/L.  
MRC: 0.01 mg/L.

Comment: Blanks, standards, and unknowns compared by Fisher and Juang in 1966 agreed within 3 percent (Juang and Johnson 1967). NE inlet of Mirror Lake contaminated with road salt since 1971; these samples require dilution: precision is about 5 percent.

#### Ortho-Phosphate and Total Phosphorus

Period of application: June 1972 to present.

Analysts: the authors (1970 to present) at Cornell and IES.

Range encountered: typically < 100 µg/L ortho-phosphate in uncontaminated precipitation, streamwater, or lakewater at HBEF, and usually near detection limits in most samples. Ortho-phosphate usually is about 90 percent of total phosphorus in lakewaters.

Methods:

##### 1) Ortho-Phosphate

Colorimetric, automated, phosphomolybdenum-blue, ascorbic acid method (Keith 1996: EPA method No. 365.1; Technicon Instruments 1971: method No. 2-68W; Murphy and Riley 1962; Alpkem 1991: method No. 580) 1970 to present.

Instruments used: Technicon AutoAnalyzer I, and since November 1992, Alpkem Flow Solution III automated analyzer.

POR: < 5 percent at < 100 µg/L; up to 20 percent for samples < 10 µg/L.  
MDL: 1 to 2 µg/L.  
MRC: 1 µg/L.

##### 2) Total Phosphorus

Spectrophotometric: high-temperature, persulfate digestion of sample aliquots prior to (nonautomated) application of the phosphomolybdenum-blue method (Strickland and Parsons 1968).

Instrument used: Spectrophotometer, dual beam.

POR: < 5 percent at < 100 µg/L; up to 20 percent for samples < 10 µg/L.  
MDL: 1 to 2 µg/L.  
MRC: 1 µg/L.

Comment: Ortho-Phosphate can be defined operationally as soluble-reactive phosphorus (SRP; expressed as phosphate) because of the possibility that polyphosphates and organic phosphorus

compounds may hydrolyze in contact with reagents. Results of both methods are expressed as phosphate because a potassium phosphate standard is used. Digestion of wetted reagent blanks prior to addition of remaining DIW volumes was added in 1997 to improve precision and sensitivity of total phosphorus analysis. Highly sensitive methods employing organic extractants (Meyer and Likens 1979) have been used periodically to determine low concentrations of phosphorus. The technique and precision for the Alpkem Corp. instrument are essentially the same as for the TAA.

#### Dissolved Silica

Period of application: June 1964 to present.

Analysts: D.W. Fisher (1964-70) in Washington, DC; the authors (1970 to present) at Cornell and IES.

Range encountered: typically < 20 mg/L silica in streamwater or lakewater, at or near detection limit in uncontaminated precipitation.

#### Methods:

1) spectrophotometric: hetero-poly molybdenum blue method method (Fisher et al. 1968; Rainwater and Thatcher 1960), 1964 to 1970.

Instrument used: Spectrophotometer, Beckman model B.

POR: < 5 percent (estimated).

MDL: 0.05 mg/L (estimated).

MRC: estimated 0.1 mg/L (estimated).

2) colorimetric, automated, silicomolybdate-blue method (Technicon Instruments 1971: method No. 105-71W), 1970 to 1984.

Instrument used: Technicon AutoAnalyzer I and II.

POR: 10 percent.

MDL: 0.1 to 0.5 mg/L

MRC: 0.1 mg/L.

3) inductively coupled plasma atomic emission spectroscopy (ICP-AES) 1984 to present.

Instrument used: Perkin-Elmer ICP-AES model P400 (Perkin-Elmer 1993)

POR: 5 percent.

MDL: 0.1 to 0.2 mg/L.

MRC: 0.1 mg/L.

Comment: Freezing of samples while in temporary storage or during winter season collection is avoided to prevent precipitation of dissolved silica. Should freezing occur, samples are analyzed after a month or more at room temperature to redissolve the silica (Burton et al. 1970).

#### Dissolved Organic Carbon

Period of application: 1971 to present.

Analysts: the authors at Cornell, HBEF, and IES, J.J. Cole at IES (1990-1994), C.T. Driscoll at Syracuse University (1990 to present), and the Northeastern Research Station's Forestry Sciences Laboratory at Durham, New Hampshire (1995 to present).

Range encountered: typically < 20 mg/L DOC in uncontaminated precipitation, streamwater or lakewater. Highly variable in bulk precipitation.

#### Methods:

1) gas chromatography: glass-fiber filtration (ashed Whatman GF/F; 0.45- m pore), helium gas purging to remove carbon dioxide, and persulfate digestion (Menzel and Vaccaro 1964) followed by acidified syringe-stripping and detection as carbon dioxide by thermal conductance (Stainton 1973; McDowell et al. 1987), 1971 to 1984.

Instrument used: Fisher-Hamilton Gas Partioner model 29.



POR: 10 percent.  
MDL: 0.05 mg/L .  
MRC: 0.1 mg/L.

2) infrared detection, following UV-enhanced persulfate digestion and acidified, helium gas sparging (Keith 1996: EPA method No. 415.2; Small et al. 1986), 1990 to present, for samples from Mirror Lake and W-1 through W-6.

Instrument used: Dormann or Astro Carbon Analyzer.

POR: 10 percent.  
MDL: 0.1 mg/L.  
MRC: 0.1 mg/L.

3) automated, UV and heat-enhanced, persulfate digestion and colorimetric carbon dioxide detection for samples from W-7, W-8, and W-9, 1990 to 1995 (Technicon Instruments method no. 451-76W; Cauwet 1984).

Instrument used: Technicon AutoAnalyzer II.

POR: 5 percent.  
MDL: 0.1 mg/L.  
MRC: 0.1 mg/L.

4) infrared carbon dioxide detection, following acidification, nitrogen gas sparging, and high temperature catalyst-enhanced combustion (Shimadzu 1995), 1996 to present, for samples from Mirror Lake, W-6, W-7, W-8, and W-9.

Instrument used: Shimadzu model 5000A TOC Analyzer.

POR: 2 percent.  
MDL: 0.05 mg/L.  
MRC: 0.1 mg/L.

Comments: Method 1 was run at HBEF; method 2 at IES or Syracuse. Method 3 was used by the Forest Service on other stream sites in New England from 1990 to 1995 after which the analyses were conducted using method 4. Correlation between methods 3 and 4 is excellent (slope = 1.04,  $R^2 = 0.99$ ), though method 3 has a -0.17 mg/L DOC bias, suggesting systematically incomplete digestion with this technique (J.Campbell, USFS; unpublished data).

#### Dissolved Inorganic Carbon

Period of application: 1974 to present.  
Analysts: the authors at HBEF.

Range encountered: typically 30 to 100  $\mu\text{mol/L}$  DIC in streamwater and 50 to 1,000  $\mu\text{mol/L}$  in lakewater. Currently, precipitation is not analyzed.

Method:

Collected similar to a sample for dissolved oxygen (Wetzel and Likens 1991), avoiding entraining bubbles or unnecessary agitation. Gas chromatography: acidified syringe-helium stripping and detection as carbon dioxide by thermal conductance (Stainton 1973).

Instrument used: Shimadzu model GC-8A with a Supelco MS5A column filled with PoraPak Q media.

POR: 5 percent  
MDL: 1  $\mu\text{mol/L}$ .  
MRC: 5  $\mu\text{mol/L}$ .

Comment: High-density, polyethylene (HDPE) sample bottles were compared to glass sample bottles (BOD-type) to determine whether significant amounts of gas were lost in storage. Within the normal lag time (< 24 hours) between sampling and analysis, there was no difference in DIC determined from samples in either container. Due to loss of glass bottles that broke in transport, streamwater DIC

samples now are collected in 60-mL HDPE bottles that are filled to the top, sealed with air bubbles removed, and refrigerated. Lake profile water samples continue to be collected in standard, 300-mL BOD bottles. To provide values for the partial pressure of carbon dioxide gas from an aqueous sample, a water sample is collected and injected with a fixed volume of ambient air, shaken to equilibrate, and analyzed by direct injection after the headspace air has been removed. This sample is compared to concurrent ambient air carbon dioxide, carbon dioxide gas standards, and aqueous extraction DIC measurement (Cole et al. 1994).

#### Acid Neutralizing Capacity

Period of application: 1990 to present.

Analysts: the authors at HBEF.

Range encountered: typically -50 to +1000  $\mu\text{eq/L}$  ANC in streamwater or lakewater. Not measured in precipitation.

#### Method:

Automated Gran plot analysis (Gran 1952) from a potentiometric titration with dual electrodes, using NBS standardized 0.1 N HCl in a sample of 50.0 mL volume.

Instrument used: Orion model 960 autotitrator.

POR: 5 percent.

MDL:  $\pm 1$   $\mu\text{eq/L}$ .

MRC: not applicable

Comments: The methods currently stored on the autotitrator are designed to allow titrations to proceed between pH 4.5 and 3.5 (Driscoll and Bisogni 1983). Depending on the initial pre-titration pH and previous experience, the sample is automatically pre-dosed with a fixed amount of HCl titrant to force the analysis to proceed within that pH range.

#### Specific Conductance

Period of application: 1964 to present.

Analysts: D.W. Fisher (1964-70) in Washington, DC; the authors (1970 to present) at Cornell and HBEF.

Range encountered: 0.5 to 500  $\mu\text{S/cm}$ ; typically 15 to 25  $\mu\text{S/cm}$  for most precipitation and streamwater samples. NE inlet of Mirror Lake has been affected by road salt since 1971; these samples usually range from 100 to 300  $\text{S/cm}$ .

#### Method:

Before 1990, conductance was determined on the sample and corrected to 25°C using a standard theoretical formula for a KCl solution (Am. Public Health Assoc. 1998) based on measured sample temperature (usually room temperature). The instrument used after 1990 has an attached temperature probe (thermistor; precision  $\pm 0.1^\circ\text{C}$ ) that allows for automatic compensation to 25°C.

Instrument used: Beckman Instruments analog model with a tube null-indicator until March 1990 and then with Yellow Springs Instrument digital model 32, both with a low-volume, glass conductivity cell with dual platinum electrodes at a cell constant of 1.0/cm.

POR: 5 percent.

MDL: 0.1  $\mu\text{S/cm}$ .

MRC: 0.5  $\mu\text{S/cm}$ .

Comment: Cells are mounted on a laboratory stand so that they can be lifted vertically in and out of an empty 10-mL plastic syringe barrel clamped to the same stand. Samples are poured into the sealed syringe barrel and the cell is immersed in the solution. Volume used usually is < 20 mL for both rinses. Sample aliquots are tested twice; the second reading is recorded. Cells are rinsed between samples with DIW and stored in same. Calibration with known KCl solutions is checked weekly based on dilute NADP test solutions ( $\sim 75$   $\mu\text{S/cm}$ ; NADP 1990), and occasionally with commercially available test solutions ( $\sim 1000$   $\mu\text{S/cm}$ ; Yellow Springs Instrument 1990).

# Appendix C

HUBBARD BROOK ECOSYSTEM STUDY

## FIELD NOTES

FROM: **MONDAY** \_\_\_\_\_ TO: **SUNDAY** \_\_\_\_\_

<b>GENERAL INFORMATION</b>
----------------------------

(compiled by: \_\_\_\_\_)

Day	Date	Weather	TEMP°F		Precip (inches)	
			High	Low	Station	PVFarm
MON	_____	_____				
TUE	_____	_____				
WED	_____	_____				
THR	_____	_____				
FRI	_____	_____				
SAT	_____	_____				
SUN	_____	_____				

HUBBARD BROOK ECOSYSTEM STUDY

**SAMPLE NOTES**

**PRECIPITATION SAMPLES**

Conversion Factors

10 in. Bulk Rain Funnel: NET divided by 51.1 = catch  
N/A if Overfilled

12 in. Bulk Snow Bucket: NET divided by 69.3 = catch

Date Collected: \_\_\_\_\_

	Volumes Collected			
	RG-22	RG-11	RG-1	RG-19
Gross g	_____	_____	_____	_____
Tare g	_____	_____	_____	_____
Net g	_____	_____	_____	_____

SITE	COLLECTOR VOLUME (mL)	CATCH (mm)	SRG CATCH (mm)	Coll. EFF (%of SRG)
RG-11	_____	_____	_____	_____
RG-1	_____	_____	_____	_____
RG-19	_____	_____	_____	_____

CONTAMINATION  
 (0 = none; 1 = low -----> 5 = high)  
 Fine PM Coarse PM Insects Bird FECEs Color GB Ring

SITE	CONTAMINATION		FIELD Collector's Initials	dBASE FIELD Code?	SAMPLE REJECTED @LEVEL =	Database CODES checked?
	Fine PM	Coarse PM				
RG-22	_____	_____	_____	_____	_____	_____
RG-11	_____	_____	_____	_____	_____	_____
RG-1	_____	_____	_____	_____	_____	_____
RG-19	_____	_____	_____	_____	_____	_____

ADDITIONAL COMMENTS: \_\_\_\_\_

Applicable dBASE FIELD Codes: 970 = Obvious Contamination; Sampled REJECTED  
 (See SOP Manual) 969 = Possible Contamination; Check Return Analyses  
 955 = QNS: Quantity Not Sufficient for all analyses (<100 mL NET catch)

**STREAMWATER SAMPLES**

Date Collected: \_\_\_\_\_

dBASE  
FIELD  
Code?

SITE      TIME (EST)      TEMP (deg C)      GAGE HT.      HYDROG. L/R/P/F      FLOW (0=none; 1=low .....> 5=high)      COLOR      SEDIMENT      REMARKS

WS-1	_____	_____	_____	_____	_____	_____	_____	_____	_____
WS-2	_____	_____	_____	_____	_____	_____	_____	_____	_____
WS-3	_____	_____	_____	_____	_____	_____	_____	_____	_____
WS-4	_____	_____	_____	_____	_____	_____	_____	_____	_____
WS-5	_____	_____	_____	_____	_____	_____	_____	_____	_____
WS-6	_____	_____	_____	_____	_____	_____	_____	_____	_____
Hubbard Bk	_____	_____	_____	_____	_____	_____	_____	(monthly)	_____
[      ]	_____	_____	_____	_____	_____	_____	_____	(ad lib)	_____

ADDITIONAL COMMENTS: \_\_\_\_\_

dBASE  
FIELD  
Code?

**MIRROR LAKE SAMPLES**

Date Collected: \_\_\_\_\_

OUTLET	_____	_____	_____	_____	_____	_____	_____	_____	_____
NE INLET	_____	_____	_____	_____	_____	_____	_____	_____	_____
NW INLET	_____	_____	_____	_____	_____	_____	_____	_____	_____
WEST INL	_____	_____	_____	_____	_____	_____	_____	_____	_____
SEEP	_____	_____	_____	_____	_____	_____	_____	(monthly)	_____

ADDITIONAL COMMENTS: \_\_\_\_\_

Applicable dBASE FIELD Codes: 911 = High Flow Event in Progress; 912 = Drought Conditions: Syringed from Standing Pool

# FIELD ANALYSES

DATE RUN: \_\_\_\_\_ RUN By: \_\_\_\_\_

Meter CALIBRATION: See Calibration form for Standard Procedure

Conductivity Correction Factor = \_\_\_\_\_ x at: \_\_\_\_\_ °C Lab Temp.

SAMPLES:	DATE COLLECTED	710 Meter pH	SpCond @25 °C	REMARKS Codes?	ORION 960		ANC end pt. pH
					pH	ANC	
<b>Precipitation</b>							
STATION	_____	_____	_____	_____		n/a	
RG-11	_____	_____	_____	_____			
RG-1	_____	_____	_____	_____			
RG-19	_____	_____	_____	_____			
<b>Streamwater</b>							
WS-1	_____	_____	_____	_____			
WS-2	_____	_____	_____	_____			
WS-3	_____	_____	_____	_____			
WS-4	_____	_____	_____	_____			
WS-5	_____	_____	_____	_____			
WS-6	_____	_____	_____	_____			
HUBBARD BK**	_____	_____	_____	_____			
( )	_____	_____	_____	_____			
<b>Mirror Lake Samples</b>							
OUTLET	_____	_____	_____	_____			
NE INLET	_____	_____	_____	_____			
NW INLET	_____	_____	_____	_____			
WEST INLET	_____	_____	_____	_____			
SEEP **	_____	_____	_____	_____			

ADDITIONAL COMMENTS: \_\_\_\_\_

(\*\*= monthly samples)

# HBES pH METER Calibration

DATE:

INITIAL CALIBRATION of _____ METER by _____							
EST	HCl Boot pH	DIW Soak pH	pH 7 Buffer initial -->	pH 7 Buffer set	pH 4 Buffer initial -->	pH 4 Buffer set	Slope %

Check or Recalibrate	EST	pH 7 Buffer check-->	pH 7 Buffer reset	pH 4 Buffer check-->	pH 4 Buffer reset	Slope %

Check or Recalibrate	EST	pH 7 Buffer check-->	pH 7 Buffer reset	pH 4 Buffer check-->	pH 4 Buffer reset	Slope %

Check or Recalibrate	EST	pH 7 Buffer check-->	pH 7 Buffer reset	pH 4 Buffer check-->	pH 4 Buffer reset	Slope %

Check or Recalibrate	EST	pH 7 Buffer check-->	pH 7 Buffer reset	pH 4 Buffer check-->	pH 4 Buffer reset	Slope %

Check or Recalibrate	EST	pH 7 Buffer check-->	pH 7 Buffer reset	pH 4 Buffer check-->	pH 4 Buffer reset	Slope %

INITIAL CALIBRATION of _____ METER by _____							
EST	HCl Boot pH	DIW Soak pH	pH 7 Buffer initial -->	pH 7 Buffer set	pH 4 Buffer initial -->	pH 4 Buffer set	Slope %

Check or Recalibrate	EST	pH 7 Buffer check-->	pH 7 Buffer reset	pH 4 Buffer check-->	pH 4 Buffer reset	Slope %

Check or Recalibrate	EST	pH 7 Buffer check-->	pH 7 Buffer reset	pH 4 Buffer check-->	pH 4 Buffer reset	Slope %

Check or Recalibrate	EST	pH 7 Buffer check-->	pH 7 Buffer reset	pH 4 Buffer check-->	pH 4 Buffer reset	Slope %

Check or Recalibrate	EST	pH 7 Buffer check-->	pH 7 Buffer reset	pH 4 Buffer check-->	pH 4 Buffer reset	Slope %

Check or Recalibrate	EST	pH 7 Buffer check-->	pH 7 Buffer reset	pH 4 Buffer check-->	pH 4 Buffer reset	Slope %

cal-frm2.wk4

## Conversion Factors

solute	mg/L to $\mu\text{eq/L}$	mg/L to $\mu\text{mol/L}$	
Calcium	x 49.90	x 24.95	
Magnesium	x 82.29	x 41.14	
Potassium	x 25.57	x 25.57	
Sodium	x 43.50	x 43.50	
Aluminum	x 111.19	x 37.06	at valence = +3; pH < 5
Ammonium	x 18.04	x 18.04	
pH	$10^{-\text{pH}} \times 10^6 = \text{hydrogen ion in } \mu\text{eq/L or } \mu\text{mol/L}$		
Sulfate	x 20.82	x 10.41	
Nitrate	x 16.13	x 16.13	
Chloride	x 28.21	x 28.21	
Phosphate	x 31.56	x 10.53	
Dissolved Silica	-----	x 16.64	not ionic
Dissolved Organic Carbon	-----	x 83.33	pH dependent charge



Buso, D.C.; Likens, G.E.; Eaton, J.S. 2000. **Chemistry of precipitation, streamwater, and lakewater from the Hubbard Brook Ecosystem Study: a record of sampling protocols and analytical procedures.** Gen. Tech. Rep. NE-275. Newtown Square, PA: U.S. Department of Agriculture, Forest Service, Northeastern Research Station. 52 p.

The Hubbard Brook Ecosystem Study (HBES), begun in 1963, is a long-term effort to understand the structure, function and change in forest watersheds and associated aquatic ecosystems at the Hubbard Brook Experimental Forest in New Hampshire. Chemical analyses of streamwater and precipitation collections began in 1963, and analyses of lakewater collections began in 1967. This publication documents these collection methods, sites, and analytical techniques, providing a complete record to ensure the integrity of HBES data.

**Keywords:** ecosystems; streamwater; precipitation; lakewater; chemical analyses; quality assurance; collection procedures; New Hampshire





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**Headquarters of the Northeastern Research Station is in Newtown Square, Pennsylvania. Field laboratories are maintained at:**

**Amherst, Massachusetts, in cooperation with the University of Massachusetts**

**Burlington, Vermont, in cooperation with the University of Vermont**

**Delaware, Ohio**

**Durham, New Hampshire, in cooperation with the University of New Hampshire**

**Hamden, Connecticut, in cooperation with Yale University**

**Morgantown, West Virginia, in cooperation with West Virginia University**

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