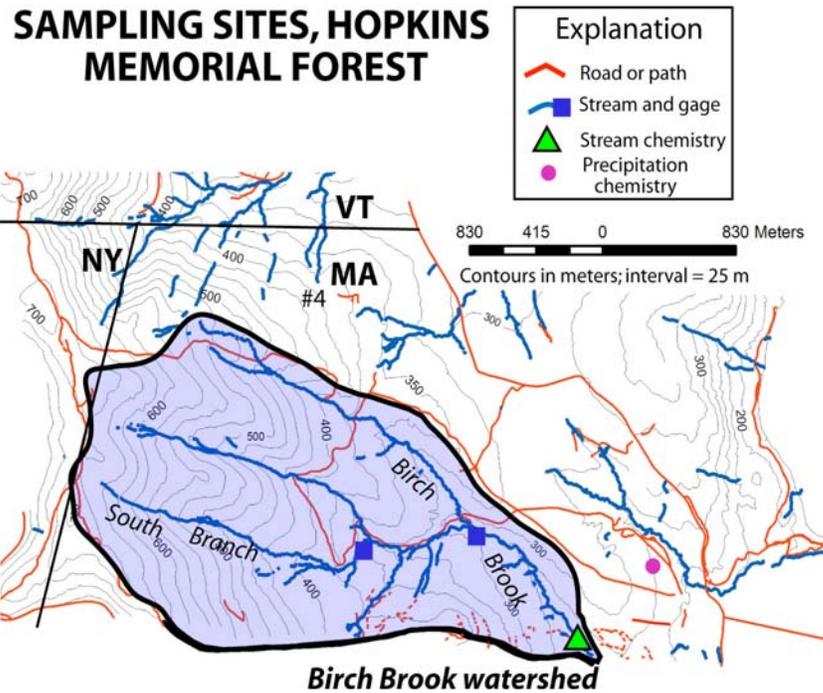


Notes on collection and analysis of bulk precipitation and stream samples, Hopkins Memorial Forest, 1983-2005

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Sampling: Biweekly Bulk samples of precipitation have been collected since June 1983 in the field by Weather Station 1, Hopkins Memorial Forest, Williamstown, Massachusetts, as part of the hydrometeorological monitoring program. Birch Brook samples have been collected monthly since 4/83 upstream from where Birch Brook and Buxton Brook converge along the southern border of the Forest (Fig. 1).

Fig. 1 Hopkins Memorial Forest showing the precipitation and stream collection sites, entirely contained within the Birch Brook watershed.

Bulk precipitation samples are gathered from six funnel-type PET samplers (Fig. 2) every two weeks. Rain falls directly into the funnels and runs through a water loop (to minimize warm-season evaporation) into a 2 L storage bottle.



During the summer, approximately 150 mL from each collector is combined into a composite sample. During the winter season, frozen samples are collected from PET bags that line plastic buckets and are thawed at room temperature overnight as a composite sample in a clean plastic bucket and thawed at room temperature overnight as a composite sample in a clean bucket.

Fig. 2 Bulk precipitation collector. The two-liter storage bottle is contained within the plastic bucket and is not visible in this picture.



Birch Brook sample is hand collected monthly using a clean HDPE or PP sample bottle rinsed at least one time with Birch Brook water (Fig. 3). Drainage area at the collection site is about 4.85 km².

For both Bulk and Birch Brook samples, **sample date** refers to date of collection.

Fig. 3 Birch Brook stream flow.

Analyses

pH is measured (Fig. 4) and alkalinity (HCO_3^-) titrated on unfiltered samples to endpoints of 4.5 and 4.2 using a laboratory Corning Model 12 Research pH meter and Hach digital titrator containing H_2SO_4 . Over the past 23 years the pH of bulk precipitation has risen slightly whereas Birch Brook pH has remained within a relatively narrow range.

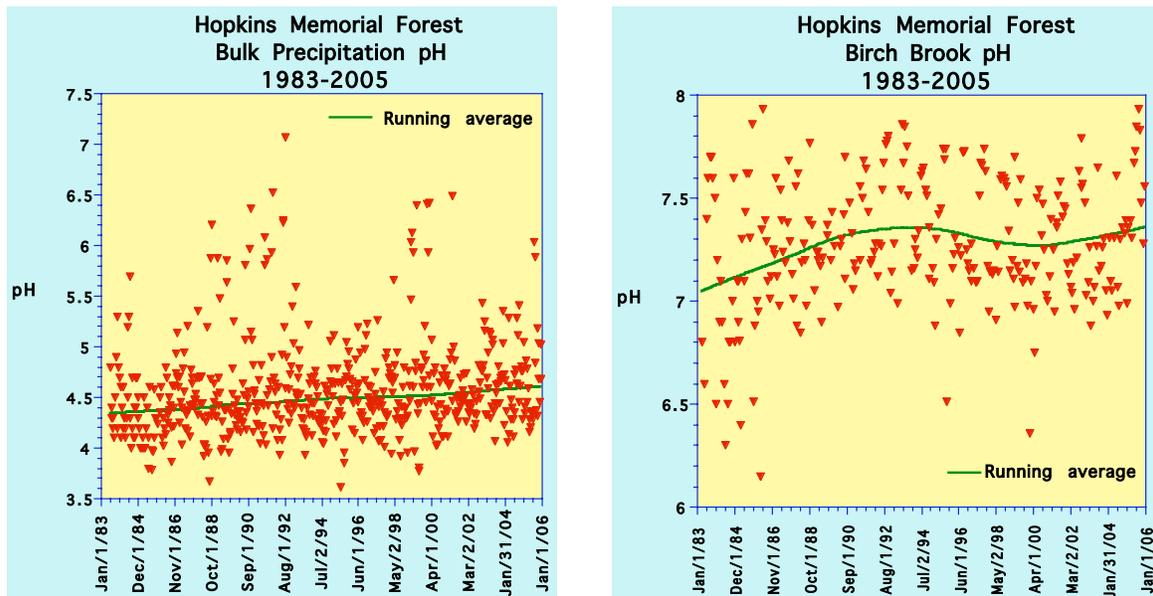


Fig. 4 pH of each Bulk precipitation or Birch Brook stream sample from 1983 through 2005. Nationally rainfall typically has a pH in the range of 4.5 to 5.6 indicating an acid rain condition in HMF.

Each of the following ions are analyzed on 0.45 μm filtered samples (Fig. 5).

Ca^{+2} , Mg^{+2} , Na^+ , K^+ are measured by atomic absorption and emission spectroscopy using a Perkin-Elmer AAS 300. A small amount of either 6% lanthanum chloride (Ca^{+2} , Mg^{+2}) or 5%

cesium chloride (Na^+ , K^+) is added to each aliquot of sample to prevent phosphate interference or ionization of the cation being analyzed.

NH_4^+ is measured on filtered samples using a Technicon Auto-Analyzer using the Berthelot Reaction, a colorimetric analysis in which alkaline phenol and sodium hypochlorite react with ammonium to form indophenol blue.

Cl^- , NO_3^- , PO_4^{2-} , and SO_4^{2-} were measured as follows:

6/83-10/87: Technicon Auto Analyzer

10/87-7/00: Dionex 4000i Ion Chromatograph

7/00-present: Dionex DX600 Ion Chromatograph



Fig. 5 Charles Soucy ('09) preparing a precipitation sample for analysis.

Notes about data quality

Users of these data should note that most samples were analyzed 2 to 4 times using standard QA and QC techniques, but there are still anomalies in the data that must be carefully evaluated.

Missing Data--missing sample values mainly reflect field conditions such as no or low precipitation, storms that overturned all precipitation collectors, or pervasive contamination from bird fecal matter.

Incorrect analyses—sample charge balances that fall outside

a range of 0.80 to 1.20 may include one or more incorrect values, most often for Ca^{+2} or HCO_3^- .

Substitute data—missing pH values for bulk precipitation collection 38 and 79 were filled using $\text{pH} = 4.5$, the mean value for 22 years of samples.

Notes about specific ions in bulk precipitation:

Calcium (Ca^{+2}): Bulk dissolved calcium values are typically <1.0 mg/L, but control the cation balance except in low pH samples. Calcium usually balances bicarbonate anions (HCO_3^-) but when Ca^{+2} values exceed 3 mg/L, they likely represent contamination of some sort.

Magnesium (Mg^{+2}) and Potassium (K^+): These two ions rarely affect the chemical balance and values are generally <1.0 mg/L. Higher K^+ values in the spring likely reflect locally derived pollen. High Mg^{+2} values are probably contamination.

Sodium (Na^+): Na^+ is considered "too high" when its value exceeds 1.0 mg/L, and is a good indicator of contamination.

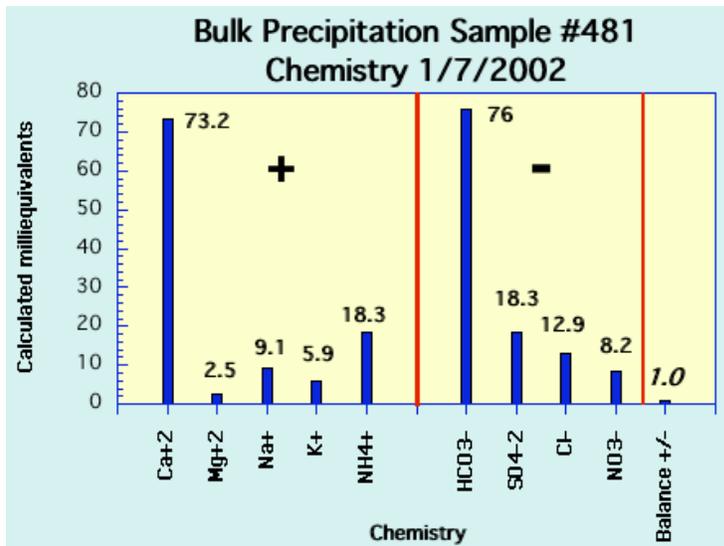


Fig. 6 Graphical comparison of Cations (+) and Anions (-) calculated milliequivalents from Bulk Precipitation sample # 481. Note how all the major ions are accounted for since the charge balance (+/-) equals 1.0.

Ammonium (NH₄⁺): Ammonium significantly affects the overall balance when its values exceed 1 to 2 mg/L. This is a fairly rare occurrence in bulk chemistry and correlates with low pH value.

Bicarbonate (HCO₃⁻): Bicarbonate is only present when sample pH > 4.5. Though bicarbonate should be mainly balanced by Ca²⁺ (Fig. 6); its range is broad. Mistakes in titration are the most frequent sources of error in charge-balance calculations.

Sulfate (SO₄²⁻): strong-acid anions such as sulfate and

nitrate typically have higher concentrations than cations and generally show a positive correlation with {H⁺}. When acid ions are at low values and pH is low, as is sometimes the case with bulk chemistry, the sample may be contaminated. Sulfate values rarely exceed 5 mg/L except during the summer months.

Nitrate (NO₃⁻): Nitrate behaves similarly to sulfate. It can affect the overall balance when it exceeds 4 mg/L. Extremely high nitrate values are linked to bird fecal matter in the collector.

Chloride (Cl⁻): Chloride mainly correlates with Na⁺, but it sometimes exceeds the expected ratio due to contamination, or during the pollen season when Cl⁻ is partly balanced by K⁺.

pH values are generally in the range of 4.0 to 6.0, but individual storms may be slightly higher or lower. pH values >7.0 probably are contaminated.

Notes about specific ions in Birch Brook:

Calcium (Ca²⁺): Birch Brook dissolved calcium values are typically between 2 and 10 mg/L, and usually correlate with bicarbonate values (Fig. 8).

Magnesium (Mg²⁺) and Potassium (K⁺): These two ions rarely affect the chemical balance and values are generally <2.0 (Mg²⁺) or <1.0 (K⁺) mg/L. Higher K⁺ values in the spring likely reflect locally derived pollen. High Mg²⁺ values are probably contamination.

Sodium (Na^+): Na^+ is considered "too high" when its value exceeds 1 mg/L, and is a good indicator of contamination.

Ammonium (NH_4^+): Ammonium is a fairly rare occurrence in Birch Brook chemistry and correlates with low pH value and perhaps season.

Bicarbonate (HCO_3^-): Bicarbonate should be mainly balanced by Ca^{+2} ; its range is broad. Mistakes in titration are the most frequent sources of error in charge-balance calculations.

Sulfate (SO_4^{-2}): Sulfate typically ranges from 4 to 10 mg/L. Values outside of this could be the result of analytical method (colorimetric vs. ion chromatography).

Nitrate (NO_3^-): Nitrate values are usually <1 mg/L and may differ due to analytical method (colorimetric vs. ion chromatography). Values may also be high during stream snowmelt.

Chloride (Cl^-): Values are typically <1 mg/L, higher concentrations are likely due to analytical method (colorimetric pre-1987 vs. ion chromatography) or to road salt application during winter months for a few samples.

pH values are generally >7.1, but individual storms and resulting water flow quantities may cause the pH to be slightly lower.

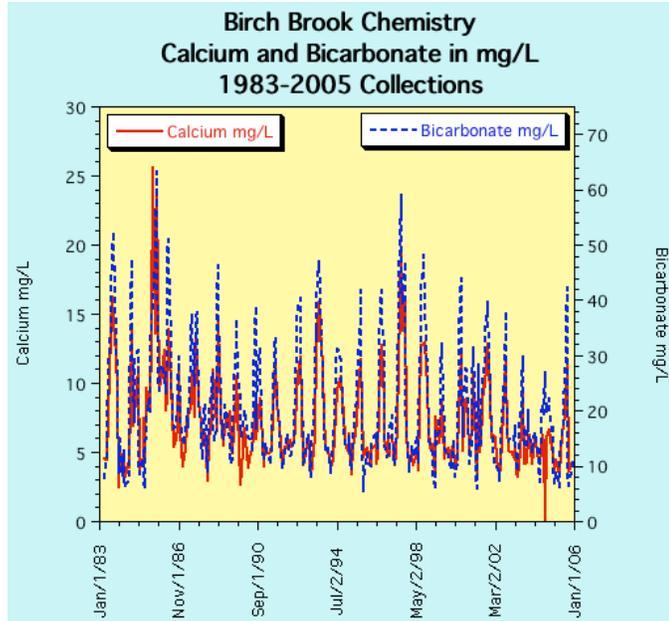


Fig. 7 Comparison of Calcium and Bicarbonate concentrations (mg/L) for each of the Birch Brook samples.

Seasonal trends

Seasonal variation is most evident during late fall and early spring. These periods are often marked by relatively high amounts of ions because airborne pollen (spring) and dead leaves (autumn) influence the ion content of bulk precipitation. Changes in ions also reflect seasonal changes in fossil-fuel combustion upwind of the sampling site and changes in storm tracks.

Statistical trends in the chemistry of bulk precipitation

No detailed analysis of these data has been performed since the 1996 senior Honors Thesis (Mathematics and Statistics) of Teon Edward. According to her analysis of the Hopkins Memorial Forest precipitation data, evidence for temporal trends using the 1983-94 dataset was weak.

Seasonal Kendall Test for Trend: Kendall trend tests compares values from a month to all the values from the same month in subsequent years. For example, January values are compared to all future January values. Seasonal trend values for nitrate and pH may exhibit patterns that may affect the interpretation of any trend established. For both, the values are positive during the winter months, corresponding somewhat to when leaves are off the trees. During the summer months all but one of the values is negative. It was difficult to evaluate the annual cycle of nitrate and pH, but distinct trends may exist for different parts of the year (Edwards 1996: 53-55).

Autocorrelation: Autocorrelation tests whether single data points can be used to predict other data points, allowing detection of possible cycles, seasonality, and trends. In terms of trend, however, the Hopkins Memorial Forest chemical data autocorrelates at a low lag span from relatively large to not significant (Edwards 1996: 88-95). Due to seasonality, which complicates the detection of any trends in the ions, autocorrelation is not a good way to detect trend in the HMF data. However, whether or not seasonality actually exists is not known. The presence of seasonality is strongly suggested by inspection of the original data or their seasonal components, significant differences in results from methods accounting for seasonality and not accounting for seasonality, or autocorrelation plots with apparently seasonal structure. Since a one-year lag suggests seasonality, by including a 1-year lag in the model for Hopkins Forest data, some seasonal effects may be partially removed. However, not all the autocorrelation plots for the HMF data can be one year long.

In addition to these two methods, the Mann-Kendall, Adjacent Mann-Kendall, and the Seasonal Kendall were also applied to the HMF data. The analyses revealed that significant trends in the HMF Bulk chemistry exist for the ammonium, bicarbonate, and pH data.

Miscellaneous notes

These data provided by the Center for Environmental Studies, Williams College -- including HMF precipitation and Birch brook chemistries--are preliminary and subject to revision. Inaccuracies in the data may be present because of instrument malfunctions or database issues. Subsequent review may result in significant revisions to the data. Data users are cautioned to consider carefully the provisional nature of the information before using for decision-making. Information concerning the accuracy and appropriate uses of these and other chemical data from Hopkins Memorial Forest can be obtained from the Technical Assistant, Jay Racela, or from Williams College Geoscience Prof. David Dethier. Contact: jracela@williams.edu, ddethier@williams.edu