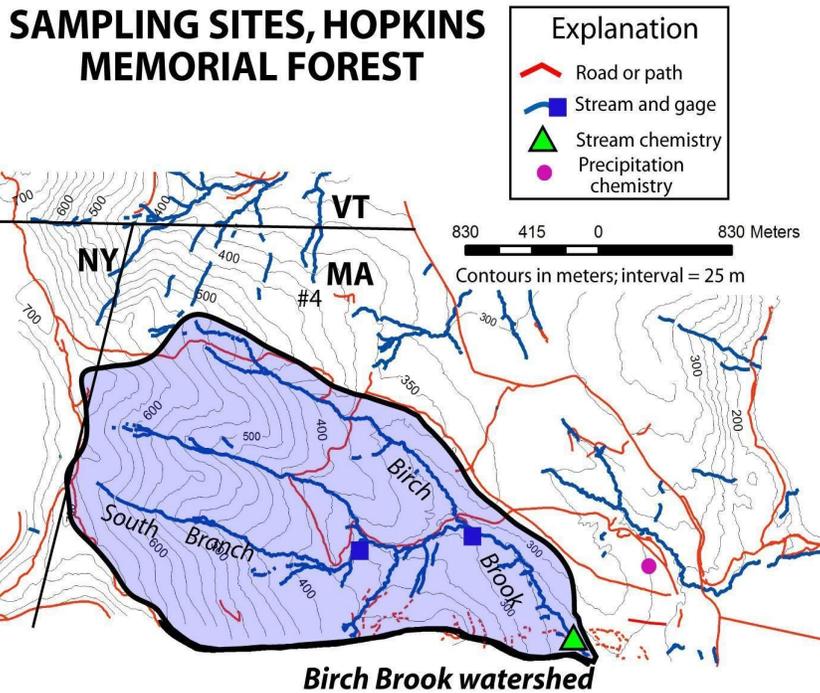


Notes on collection and analysis of bulk precipitation and stream samples, Hopkins Memorial Forest, 1983-2016

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Sampling:
Biweekly bulk samples of precipitation have been collected since June 1983 in an open field (Fig. 1) in Hopkins Memorial Forest, Williamstown, Massachusetts, as part of the

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

hydrometeoro-logical 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). Ford Glen has been sampled monthly since 2007.

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.



Figure 2. Bulk precipitation collector. The two-liter storage bottle is in the plastic bucket and not visible.



Birch Brook samples are 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 (~3.9 km² at the stream gage).

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

Figure 3. Birch Brook weir, looking downstream. Volume flux (discharge) of water has been measured continuously since 1985 using pressure transducers.

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 (1983-2005) or titrated to 4.5 then 3.5 with a Radiometer Analytical Autotitrator (2005-present) with 24 hr of collection. Over the past 35 years the pH of bulk precipitation has risen significantly whereas Birch Brook pH has risen only slightly.

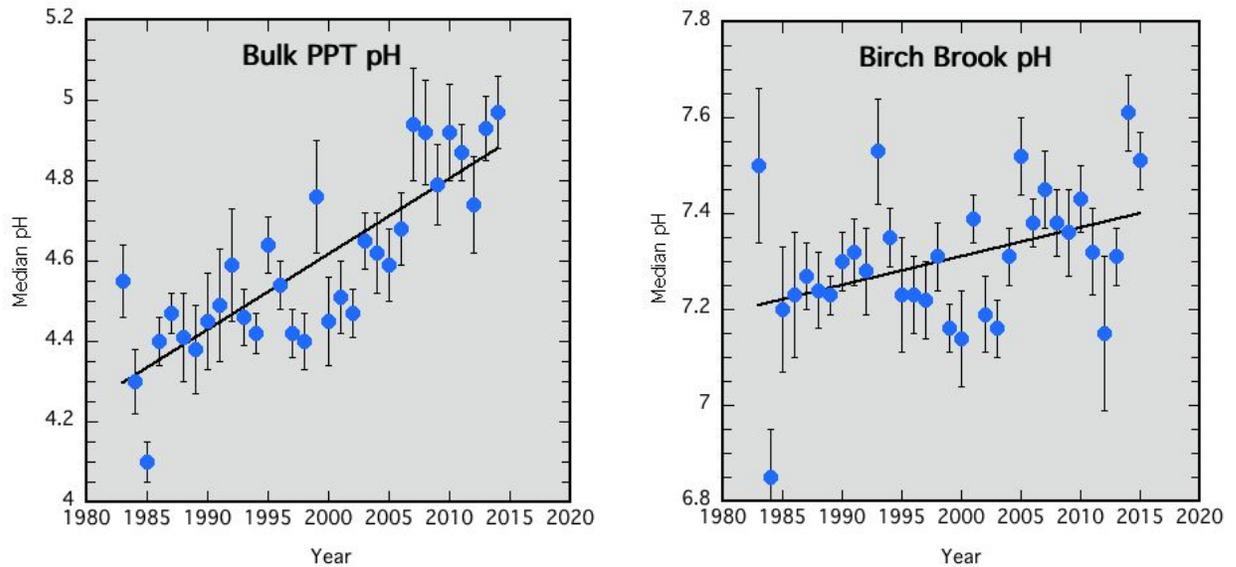


Figure 4. Annual median pH of Bulk precipitation and Birch Brook stream water collections. Bulk PPT $p < 0.0001$; Birch Brook $p < 0.0001$.

Base cations and common anions are analyzed on 0.45 µm filtered samples (nitrocellulose membrane filters) after refrigeration in the dark at 4°C (Fig. 5), generally 3 weeks to 3 months after sample collection.

Ca²⁺, Mg²⁺, Na⁺, K⁺ were measured by Atomic Absorption and emission Spectroscopy:

1983-1989: Perkin-Elmer 403

1989-2000: Perkin-Elmer 1100B

2000-2017: Perkin-Elmer Analyst 300

2017-present: Perkin-Elmer PinAAcle 900H

A small amount of either 5% lanthanum chloride (Ca²⁺, Mg²⁺) or 0.5% cesium chloride (Na⁺, K⁺) is added to each aliquot of sample to prevent phosphate interference or ionization of the cation being analyzed.

NH₄⁺ was 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.

SiO₂ was analyzed on filtered samples with a Technicon Auto-Analyzer utilizing the reduction silicomolybdate to "molybdenum blue" with ascorbic acid. This colorimetric reaction allows for quantitative silica results in the presence of known standards.

Cl⁻, NO₃⁻, PO₄⁻², and SO₄⁻² were measured as follows:

1983-1987: Technicon Auto-Analyzer II

1987-2000: Dionex 4000i Ion Chromatograph

2000-2015: Dionex DX600 Ion Chromatograph

2015-present: Metrohm 883/863 Ion Chromatograph

Notes about data quality

Most samples were analyzed 2 to 4 times but there are still anomalies in the data that should be carefully evaluated. Sample charge balance is used as the initial screen. For individual ions, quality control and quality assurance were performed with commercial standard reference standards and using intra-laboratory comparisons. The standard reference materials were used as a single-blind setup until after results obtained. Using archived samples as intra-laboratory comparisons assured researchers of reproducibility and statistical replication.

Current analyses:

Analysis	Instrument	Detection limit	Run Precision
Calcium (Ca+2)	Perkin-elmer PinAAcle 900H	0.49 µeq/L	0.90 %RSD
Magnesium (Mg+2)	Perkin-elmer PinAAcle 900H	0.41 µeq/L	0.53 %RSD
Sodium (Na+)	Perkin-elmer PinAAcle 900H	0.43 µeq/L	0.55 %RSD
Potassium (K+)	Perkin-elmer PinAAcle 900H	0.26 µeq/L	0.78 %RSD
Ammonium (NH4+)	Technicon Auto-analyzer II	0.56 µeq/L	2.64 %RSD
Silica (SiO2)	Technicon Auto-analyzer II	0.33 µeq/L	1.46 %RSD
Chloride (Cl-)	Metrohm 883/863 IC	0.57 µeq/L	0.28 %RSD
Nitrate (NO3-)	Metrohm 883/863 IC	0.16 µeq/L	0.10 %RSD
Phosphate (PO4-2)	Metrohm 883/863 IC	0.21 µeq/L	0.16 %RSD

Sulfate (SO ₄ -2)	Metrohm 883/863 IC	0.21 µeq/L	0.18 %RSD
pH	Radiometer Analytical TIM840	2 to 12	2 ± 0.02 to 12 ± 0.12
Alkalinity by auto-titrator	Radiometer Analytical TIM840	0.16 µeq/L	0.45 %RSD

Historical analyses:

Analysis	Precision	Accuracy
Cations by Flame Atomic Absorption ¹	0.1mg/L + 0.5 ⁻⁴ to 30mg/L + 0.015	<1mg/L ± 0.01; 1mg/L ± 0.1 ⁻² to 40mg/L ± 0.04
Anions by Auto-Analyzer ²	0.1mg/L ± 0.001 to 25mg/L ± 0.25	0.1mg/L ± 0.001 to 25mg/L ± 0.25
Alkalinity by manual titration ³	0.2 ± 0.002 to 200 ± 2	0.2 ± 0.002 to 200 ± 2

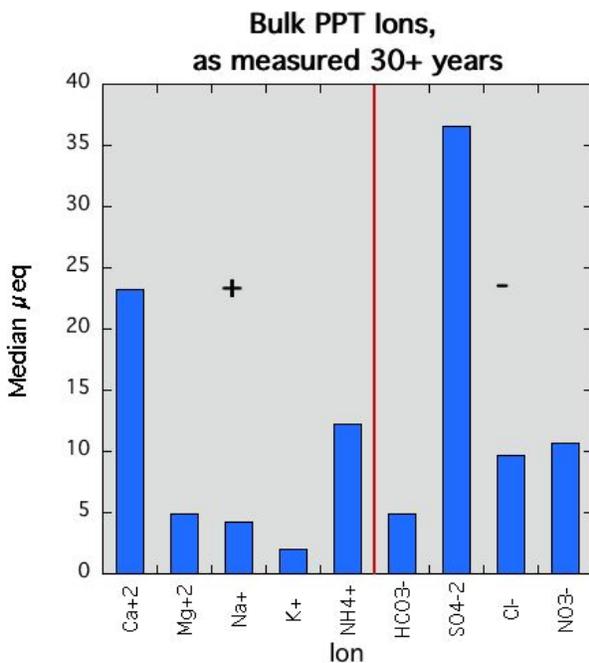
¹ from 1989-2000, ² 1983-1987, ³ 1984-2012

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. They are indicated as a blank field in the data sheet.

“Incorrect” analyses—when sample charge balances fall outside a range of 0.80 to 1.20, analyses may include one or more incorrect values, most often for Ca⁺² or HCO₃⁻.

Substitute data—missing pH values for bulk precipitation collection 38 and 79 were filled using pH = 4.55, the median value for 30+ years of samples.

Notes about specific ions in bulk precipitation



Calcium (Ca⁺²): Bulk dissolved calcium values are typically < 28 µeq/L, but control the cation balance except in low pH samples. Calcium usually balances bicarbonate anions (HCO₃⁻) but when Ca⁺² values exceed 50 µeq/L, they likely represent contamination.

Magnesium (Mg⁺²) and Potassium (K⁺): These two ions rarely affect the chemical balance and values are generally < 10 µeq/L. Higher K⁺ values in the spring likely reflect locally derived pollen. High Mg⁺² values are probably sample contamination.

Figure 5: Median major ion content of bulk precipitation as measured over 30+ years.

Sodium (Na^+): Na^+ is considered "too high" when its value exceeds 15 $\mu\text{eq/L}$, and is a good indicator of cation values that are too high.

Ammonium (NH_4^+): Ammonium significantly affects the overall balance when its values exceed 50 $\mu\text{eq/L}$. This is a fairly rare occurrence in bulk chemistry and correlates with low pH value.

Bicarbonate (HCO_3^-): Bicarbonate is only present when sample $\text{pH} > 4.5$. Though bicarbonate should be mainly balanced by Ca^{+2} (Fig. 6), its range is broad. Errors in titration are the most frequent sources of error in charge-balance calculations.

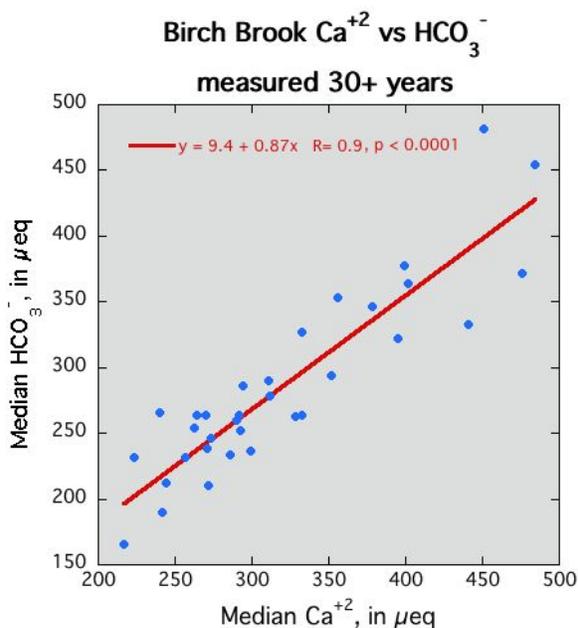
Sulfate (SO_4^{-2}): strong-acid anions such as sulfate and nitrate typically have higher concentrations than cations and generally show a positive correlation with (H^+). When acid ions are at low values and pH is low, as is sometimes the case with bulk chemistry, the sample may be contaminated. Sulfate values rarely exceed 50 $\mu\text{eq/L}$ except during the summer months.

Nitrate (NO_3^-): Nitrate behaves similarly to sulfate. It can affect the overall balance when it exceeds 40 $\mu\text{eq/L}$. 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 spring tree-pollen season when Cl^- is partly balanced by K^+ .

Sample 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 may be contaminated from algal growth in the collection apparatus.

Notes about specific ions and silica in Birch Brook samples



Calcium (Ca^{+2}): Birch Brook dissolved calcium values are typically between 200 and 500 $\mu\text{eq/L}$, and usually correlate with bicarbonate values (Fig. 7).

Magnesium (Mg^{+2}) and Potassium (K^+): These two ions rarely affect the chemical balance and values are generally 100 (Mg^{+2}) or 5 (K^+) $\mu\text{eq/L}$. Higher K^+ values in the spring likely reflect locally derived pollen. Mg^{+2} concentrations are highly correlated with Ca^{+2} . High Mg^{+2} values are probably contamination.

Figure 7. Birch Brook comparison of calcium and bicarbonate over 30+ years of sampling.

Sodium (Na^+): Na^+ is considered "too high" when its value exceeds 50 $\mu\text{eq/L}$, and is a good indicator of overly high cation content.

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 100 to 200 $\mu\text{eq/L}$.

Nitrate (NO_3^-): Nitrate values are usually $<10 \mu\text{eq/L}$ and may reflect, in part, the analytical method (colorimetric vs. ion chromatography) in early samples. Values may also be high during stream snowmelt.

Chloride (Cl^-): Values are typically $< 25 \mu\text{eq/L}$; higher concentrations in a handful of samples are likely due to contamination from acid rinsing of bottles or to road salt application on a nearby road during winter months.

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

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.

Trends in the chemistry of precipitation and streams

Over the 30+ years of data we have collected, we have seen a decrease in acid deposition as bulk precipitation pH has steadily increased. Additionally we have seen a significant decrease in the amount of sulfate in precipitation throughout the study period and a slight decrease in calcium. Nitrate, phosphate, magnesium and sodium have remained relatively unchanged. Birch Brook stream chemistry has somewhat followed suit in that sulfate concentrations have significantly decreased, whereas pH and ANC, and calcium have increased since about 2004. Nitrate, potassium and chloride have remained relatively stable. The calculated flux of Birch Brook and Ford Glen are markedly different, especially for calcium, magnesium and silica despite similar climates, land-use history and bedrock.

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 Lab supervisor, Jay Racela, or from Williams College Geoscience Prof. David Dethier. Contact: jracela@williams.edu, ddethier@williams.edu