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The biogeochemistry of chlorine at Hubbard Brook, New Hampshire, USA

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Abstract. Chlorine is a minor constituent of most rocks and a minor (although essential) element in plants, but it cycles rapidly through the hydrosphere and atmosphere. In forest ecosystem studies, chloride ion (Cl^-) is often thought to be conservative in the sense that the sources and sinks within the ecosystem are assumed negligible compared to inputs and outputs. As such, Cl^- is often used as a conservative tracer to assess sources and transformations of other ions. In this paper we summarize research on chloride over the course of 36 years (1964–2000) at the Hubbard Brook Experimental Forest (HBEF) in central New Hampshire, USA. Evidence presented here suggests that in the 1960s and 1970s the dominant source of atmospheric Cl^- deposition was from pollutant sources, probably coal burning. In the 1970s the Cl^- inputs in bulk deposition declined, and the lower Cl^- deposition in the last two decades is dominated by marine sources. Between 1964 and 2000 there was no significant trend in Cl^- export in stream flow, thus the net hydrologic flux (NHF = bulk deposition inputs − streamflow outputs) has changed over this period. Early in the record the NHF was on average positive, indicating net retention of Cl^- within the system, but since about 1980 the NHF has been consistently negative, indicating an unmeasured input or source within the ecosystem. Dry deposition can account for at least part of that unmeasured source, and it appears that release of Cl^- from mineralization of soil organic matter (SOM) may also play an important role. We believe that accumulation of Cl^- in vegetation during the 1960s and 1970s offset the unmeasured source and resulted in net ecosystem retention. Accumulation of vegetative biomass has ceased since about 1982, leading to the apparent net export (negative NHF) since that time. Although we have no direct measurements of Cl^- accumulation in vegetation, our estimates suggest that an aggrading forest could sequester about 32 mol Cl ha^{-1} $year^{-1}$, or about a third of the annual average bulk deposition flux to this ecosystem. Experimental additions of Cl^- to the forest floor cause increases in Cl^- concentration in foliage, throughfall, and soil solution. Manipulations of vegetation also affect the Cl^- cycle. Harvesting or devegetation of watersheds causes an increase in the Cl^- concentration and flux in stream water for several years after the disturbance. This period of release is followed by a period of reaccumulation of Cl^- that may last more than 15 years. In this respect, the behavior of Cl^- after disturbance parallels that of NO_3^-, for which export increases after disturbance due to reduced plant nitrogen uptake and mineralization of nitrogen from detritus, rather than SO_4^{2-}, for which export decreases after disturbance due to pH-dependent adsorption onto mineral soils. The interannual pattern of Cl^- export from the system primarily reflects the atmospheric inputs, but the net retention and cycling of Cl^- within the system appears to be largely under biological, rather than geochemical, control.

Introduction

In research on terrestrial biogeochemistry, chlorine (Cl) is often measured but seldom studied. Biogeochemical studies frequently measure chlorine concentrations (primarily as the chloride ion Cl^-) in natural waters to complete an ion balance, but rarely focus attention on the behavior of the ion. Though some Cl compounds are very reactive in the atmosphere, the Cl^- ion is generally thought to be unreactive in soils and only minimally taken up by plants. Consequently, Cl^- is often considered an inert tracer that can be used to interpret transport of other ions. Nonetheless, Cl^- is an essential plant nutrient (Marschner 1995), albeit a minor one, and may not be as inert as is generally assumed. In this paper we present a summary of findings about the biogeochemistry of Cl^- from the Hubbard Brook Experimental Forest (HBEF) in New Hampshire, USA. The HBEF has been the site of the long-term Hubbard Brook Ecosystem Study, and an excellent database on Cl^- cycling has been accumulated from various studies during the 36 years of the study summarized here.

Biogeochemistry of chlorine

Chlorine (AW 35.45) is a member of the halogen family of elements (F, Cl, Br, I and At) that is characterized by small bond energies and high electron affinities. Chlorine ranks 18th of the 92 natural elements in its overall abundance on Earth (Graedel and Keene 1996), but it comprises only 0.064% of the Earth's upper crust on average (Wedepohl 1995), and is a minor constituent of igneous, sedimentary and metamorphic rocks, with the exception of the evaporites (Bowen 1966; Graedel and Keene 1996). Typical concentrations of Cl in igneous rocks, shales, sandstones and limestones are 130, 180, 10, and 150 mg/kg, respectively (Bowen 1966). Although the mantle and crust hold the largest reservoirs of Cl globally, fluxes of Cl into and out of mantle and crust pools are very small (from volcanic emissions and weathering, respectively) and by far the most active pool of Cl is in the oceans (Graedel and Keene 1996). Chlorine is the most abundant element in seawater other than hydrogen and oxygen. Fluxes between the oceans and the atmosphere dominate global cycling of Cl, and oceanic Cl^- is the source of most of the Cl^- cycling through terrestrial and freshwater ecosystems (Graedel and Keene 1996).

In the troposphere, Cl exists both as particles derived from sea spray and terrestrial dust, and as reactive gases, including hydrochloric acid (HCl), chloromethane (CH_3Cl), and several others. Wave generation of aerosols is by far the largest source of Cl to the troposphere, and redeposition of those aerosols to the sea and land by wet and dry deposition processes is the largest sink (Graedel and Keene 1996). Natural sources of the gaseous species include volatilization from sea salt, volcanic emission, marine biological processes, and biomass combustion, while anthropogenic sources include coal combustion, municipal and industrial waste incineration, and various industrial processes (Keene et al. 1999). Chloromethane can also be produced via abiotic processes in live and senescent plant material (Hamilton et al. 2003). In the United States, most of the anthropogenic emission of Cl is from coal combustion (McCulloch et al. 1999). The Cl content of coals can reach as high as 1%, and nearly all of it is released during coal combustion; however, if flue-gas desulfurization is used most of the Cl in these emissions is removed along with the sulfur (McCulloch et al. 1999). Because the emitted Cl compounds are highly reactive in the troposphere, only a small portion of the Cl from these sources is transported to the stratosphere.

Chlorine compounds tend to be highly soluble in water and mobile in soils, so atmospheric deposition and transport through terrestrial ecosystems is rapid if hydrologic flow is occurring. Most of the Cl^- deposited on land returns to the sea by this route. In arid areas Cl^- can accumulate in salt beds, the mining of which provides the primary source of nearly all the Cl^- used commercially (Graedel and Keene 1996). Irrigation and so-called 'dryland farming' in arid and semi-arid areas can lead to greatly increased concentrations of various salts, including NaCl, in surface waters and surface soils. This process is referred to as salinization and is becoming increasingly widespread (Williams 1987). Wind-dispersed aerosols from these salinized surfaces can be transported long distances, thus affecting sites well downwind of the salinized area.

Although Cl concentrations in most rocks are low, rock weathering (especially of sandstones and shales) is the source of most of the Cl^- in rivers globally (Graedel and Keene 1996). Nonetheless, many small-watershed studies assume that weathering of Cl^- is negligible compared to atmospheric deposition (e.g., Juang and Johnson 1967; Hedin et al. 1995; Lockwood et al. 1995; Peters and Ratcliffe 1998). Chloride does not participate in any significant degree in the formation of secondary minerals, and is generally thought to be only poorly adsorbed to soils (Mott 1981).

Chlorine is an essential element in plants and animals. The function of chloride in both plants and animals is thought to be primarily electrolytic, and in plants it may be involved in the water-splitting step of photosynthesis (Kramer and Kozlowski 1979). Chloride is highly mobile in plants, being readily taken up by root systems and leached from foliage (Tukey 1970; Lovett and Hubbell 1991). However, measurements of the concentration of Cl^- in plant tissues are uncommon in ecological studies, probably because it is rarely limiting to plant growth. Organochlorine compounds are also present in many plants, but at concentrations much smaller than that of inorganic chloride (Oberg 2003). Likewise, a large number of bacteria and fungi in soils can produce organochlorine compounds, some of which are retained within the organism (such as pigments or hormones) and some of which are excreted as waste products or defensive compounds (Oberg 1998). There is evidence that some microorganisms produce exoenzymes that form reactive chlorinated compounds that may aid in the degradation of plant material (Asplundh et al.

1993; Oberg 1998; Ortiz-Bermudez et al. 2003). It has been shown that organochlorine compounds are formed during degradation of organic matter, and they may be the dominant form of Cl in decomposing plant material in soils (Öberg et al. 1996; Myneni 2002).

In forest ecosystems, Cl^- is often thought to be conservative in the sense that the sources and sinks within the ecosystem are assumed negligible compared to inputs and outputs (e.g., Neal and Kirchner 2000). As such, Cl^- is often used as a conservative tracer to assess sources and transformations of other ions (e.g., Hedin et al. 1995; Lockwood et al. 1995; Peters and Ratcliffe 1998; Hall et al. 2002) and residence time of water (Kirchner et al. 2000).

Chloride cycling in northeastern forests

In one of the first input–output budgets developed in the Hubbard Brook Ecosystem Study, Juang and Johnson (1967) reported the Cl^- budget for two watersheds of the HBEF in New Hampshire. They noted an excess of stream water output over precipitation input of Cl^- totaling 37 mol ha^{-1} $year^{-1}$ for the period September 1965–August 1966. They attributed the imbalance to unmeasured dry deposition inputs of Cl^-. However, Likens et al. (1977) reported that on average for the period 1963–1974, Cl^- inputs exceeded outputs from HBEF watersheds. Peters (1991) reported that Cl^- outputs exceeded inputs by 39 and 14 mol ha^{-1} $year^{-1}$ in a study of two watersheds in the Adirondack Mountains of New York. Peters attributed the imbalance not to dry deposition, but to mineral weathering, particularly of hornblende. At both the HBEF and in the Adirondack Mountains, throughfall and stemflow fluxes were greater than precipitation fluxes of Cl^-, indicating Cl^- leaching from the canopy or washoff of dry deposition (Eaton et al. 1973; Peters 1991). However, the results of these studies were called into question by Norton et al. (1996), who noted that the colorimetric assay used in both of these studies is subject to substantial positive interference from dissolved organic carbon (DOC) in solution. If the throughfall or surface waters were more enriched in DOC than the precipitation (which is generally true) then the interference would give the appearance of a net release of Cl^- from the canopy and from the watershed.

Vitousek and Reiners (1975) reported little difference in Cl^- export between previously logged and unlogged watersheds in New Hampshire, which they interpreted as indicating that retention of Cl^- in biomass was minimal.

Thus, while many biogeochemical studies interpret the behavior of Cl^- to be conservative or nearly so, there are many known processes of interaction of Cl with plants and soil that would contradict this interpretation. Our main purpose in this paper is to use the many studies at Hubbard Brook to understand the processes that dictate the dynamics of Cl in a watershed ecosystem, and to determine the trends in those processes over the 36 years of study from 1964 to 2000.

Methods

The Hubbard Brook experimental forest

The HBEF (43°56′N, 71°45′W) comprises most of the Hubbard Brook Valley in the White Mountain National Forest of central New Hampshire (Figure 1). Details about the forest ecosystem and general procedures and analytical methods used in our studies are summarized in Likens et al. (1994, 1998, 2002), Likens and Bormann (1995) and Buso et al. (2000).

The eastern portion of the HBEF (including experimental watersheds 1–6 and 9) is underlain by a complex assemblage of meta-sedimentary and

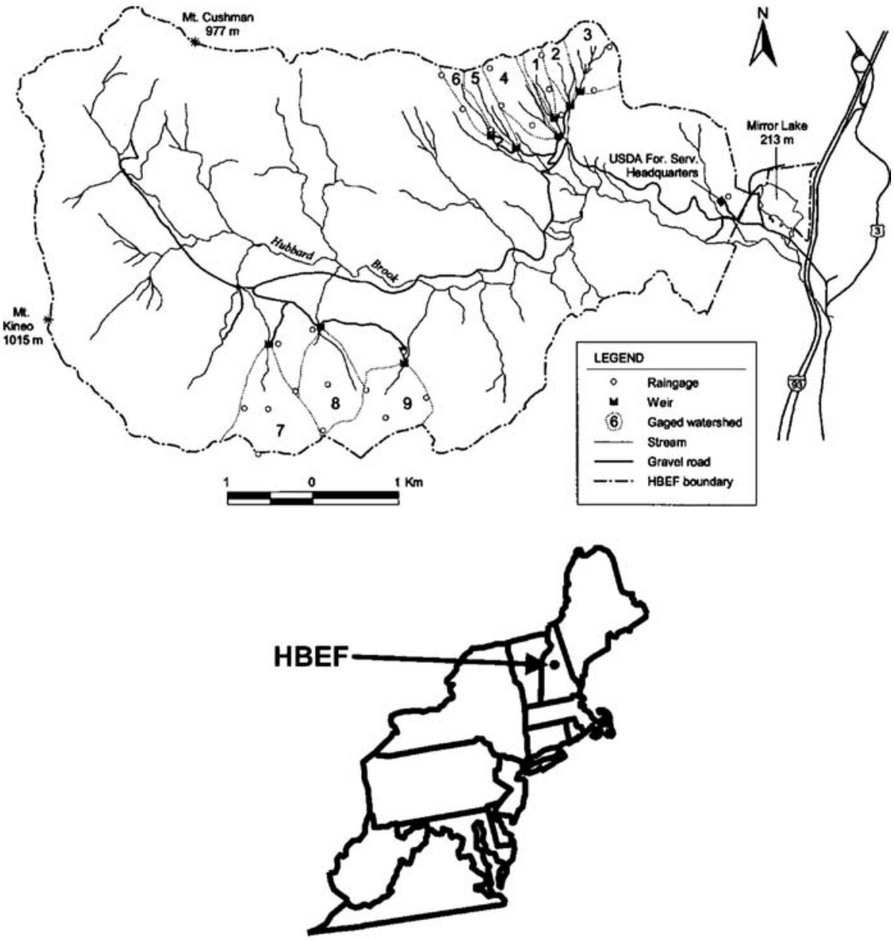

Figure 1. Map of the Hubbard Brook valley. The inset shows the location of the HBEF in the eastern US.

igneous rocks. The major map unit is the Silurian Rangeley Formation, consisting of quartz mica schist and quartzite interbedded with sulfidic schist and calc-silicate granulite. The western portion of the forest (including portions of watersheds 7 and 8) is underlain by the Devonian Kinsman Granodiorite, a foliated granitic rock with megacrysts of potassium feldspar. The retreat of the continental glacier ~14,000 years ago left a mantle of till 0–3 m thick. Soils are primarily acidic, well-drained Haplorthods formed from this till.

The HBEF is vegetated primarily by forests of the northern hardwood association dominated by sugar maple (*Acer saccharum* Marsh), American beech (*Fagus grandifolia* Ehrh.) and yellow birch (*Betula alleghaniensis* Britt.). Spruce–fir forest, including red spruce (*Picea rubens* Sarg.), balsam fir (*Abies balsamea* (L.) Mill) and paper birch (*Betula papyrifera* var. *cordifolia* Regel Fern.), dominates above 730 m elevation.

Mean annual precipitation at the HBEF is 1423 mm (SD = 187, range 1107–1824 mm in the period 1964–2000) with 25–33% of the total occurring as snow (Federer et al. 1990; A.S. Bailey et al. 2003). Mean annual streamflow is 917 mm (SD = 218, range 574–1479 mm). Mean annual temperature (1955–2000) at 450 m elevation is 5.6 °C (− 8.3 °C in January and 18.7 °C in July) (A.S. Bailey et al. 2003).

Field methods

In this paper we summarize a large number of studies from the Hubbard Brook Ecosystem Study, and the procedures for these studies are detailed in the individual papers cited. General field and analytical procedures for the Hubbard Brook Ecosystem Study are reported in Buso et al. (2000). We include below a brief summary of field procedures for the data sets that are central to this paper. Bulk deposition is collected weekly in open polyethylene funnels draining to polyethylene bottles in the summer, and in plastic barrels or buckets in the winter (Buso et al. 2000). Precipitation amount is measured with a network of rain gauges throughout the Hubbard Brook Valley (Likens and Bormann 1995). Stream chemistry is measured on weekly grab samples from the streams draining the various small watersheds used in the study (Buso et al. 2000). Water discharge in these streams is measured with a combination of V-notch weirs and flumes (Likens and Bormann 1995). Throughfall was measured from 1989 to 1992 during the growing season with 18 funnel-bottle collectors distributed among three sites along the elevational gradient near Watershed 6 (W6), the biogeochemical reference watershed (Lovett et al. 1996). Soil solution is collected monthly from zero-tension lysimeters in three soil horizons at these same sites (Driscoll et al. 1988).

The long-term, weekly stream and precipitation chemistry data are weighted by volume and averaged by water-year (June 1–May 31). Because soils are generally saturated at the HBEF on June 1 (prior to budbreak), using the water-year averaging minimizes the change in soil water storage term in the hydrologic mass balance (Federer et al. 1990). We report calendar-year averages only when comparing these data to other calendar-year data. In this paper, annual averages are for water-years unless specifically noted otherwise.

Analysis of Cl^- in water samples

Until recently, the standard analysis for Cl^- in water samples used a colorimetric method involving the ferric thiocyanate reagent (Technicon Industrial Systems 1976). However, because of the DOC-induced interference discussed above (and in Norton et al. 1996), most recent analyses for Cl^- reported in the literature have been done using ion chromatography, which is free from the DOC interference.

In the Hubbard Brook Ecosystem Study we used the colorimetric analysis of Cl^- for the bulk deposition and streamwater samples from the beginning of the record in 1964 through June of 1996. Before 1972, the analysis was done manually, and after 1972 it was automated with the Technicon Autoanalyzer (Technicon Industrial Systems 1976). From June 1995 to June 1996 both the colorimetric and the ion chromatographic analyses were done on all bulk deposition and stream samples (Buso et al. 2000). There was little or no difference between the methods for the bulk deposition samples, which tend to have very low DOC (mean = 100 μmol l^{-1}) (Figure 2). For the stream samples, all of which had DOC concentrations <200 μmol l^{-1}, there was a slight bias towards higher concentrations in the colorimetric analysis (Figure 2). Disturbance in the watershed appears to have little effect on DOC concentrations in stream water – the complete devegetation of watershed 2 produced no significant response in DOC (McDowell and Likens 1988). After June 1996, only the ion chromatograph was used for Cl^- analysis. Because the two methods differed by a maximum of 5% for these samples, and the average difference was $<1\%$, the prior Cl^- analyses in the data set were not adjusted. However, prior data from the HBEF (and elsewhere) in which Cl^- was analyzed colorimetrically in high-DOC waters should be interpreted with caution due to the possible bias. For instance, the Eaton et al. (1973) throughfall study at the HBEF used the colorimetric method on throughfall and stemflow, which can have high DOC concentrations. More recent studies of throughfall (Lovett et al. 1996) and soil water (Driscoll et al. 1988) at the HBEF used ion chromatography for Cl^- determinations.

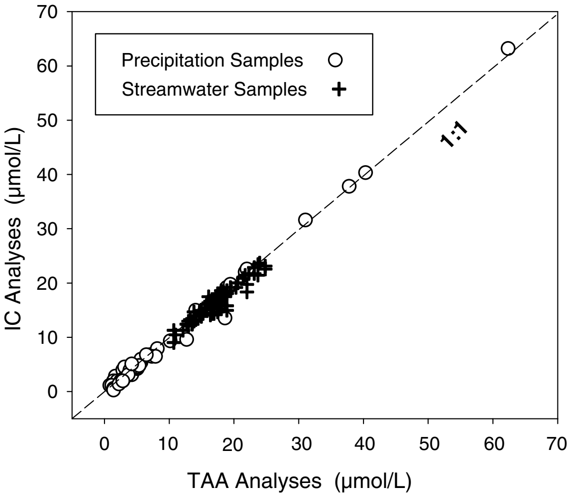

Figure 2. Comparison of Cl^- concentration in stream and bulk deposition samples analyzed by automated wet chemistry (Technicon Autoanalyzer [TAA]) versus ion chromatography (IC).

Cl^- contamination from bulk deposition collectors

Between 1964 and 1966, when summer bulk precipitation collectors were fitted with plastic and aluminum screens, Cl^- was a frequent contaminant (Juang and Johnson 1967; Buso et al. 2000). After 1966 the screens were no longer used. Consequently precipitation samples prior to 1967 were not used in this analysis, and our precipitation record starts in 1967, while the stream water record starts in 1964.

Prior to 1982, winter bulk deposition was collected in acid-washed vinyl barrels. In 1981, laboratory tests indicated the possibility of Cl^- contamination from these barrels. When deionized water was allowed to stand in these barrels for 3 weeks, Cl^- concentrations increased from below detection levels to an average of 10.8 μmol l^{-1}. In a similar 3-week test using a real precipitation event that was allowed to stand in the barrel, no change in Cl^- concentration was detected. These are severe tests of contamination, because in our normal collections precipitation stands in the collector for a maximum of one week, and in winter that precipitation is usually in a frozen, rather than liquid, form. Nonetheless, in February 1982, winter bulk deposition collectors were switched from the vinyl barrels to polyethylene buckets, and the buckets have remained in use since then. In the laboratory leaching tests, no contamination was observed from either these polyethylene buckets or the funnels, tubing and bottles that are used to collect summer bulk deposition at the HBEF. Thus there is a small possibility of Cl^- contamination in winter bulk deposition collected before February 1982. The magnitude of the contamination is unknown, but is thought to be small, and no correction for it has been made in the data set (Buso et al. 2000).

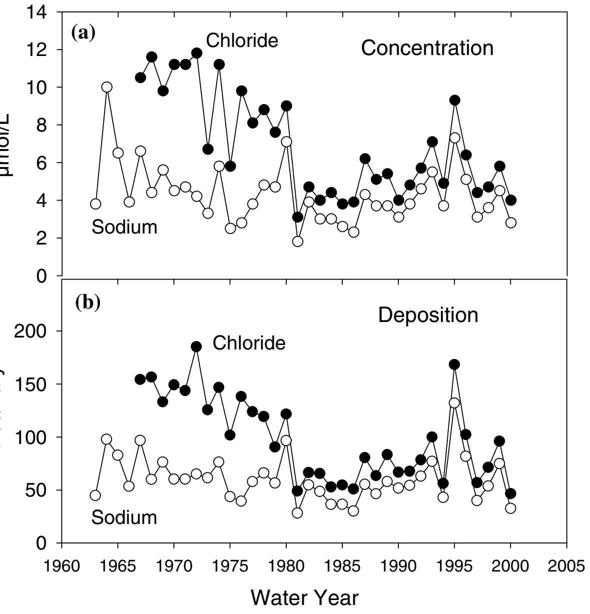

Figure 3. Concentration (a) and flux (b) of Cl^- and Na^+ in bulk deposition at the HBEF.

Flux and cycling of Cl^-

Atmospheric inputs

Bulk deposition and wet deposition

Annual input of Cl^- in bulk deposition has changed dramatically over the course of this study. Concentration of Cl^- in bulk precipitation declined from the beginning of the record in 1967 until 1981 (Figure 3). Since then, the concentration has increased slowly, though it has not regained the levels observed in the late 1960s. Even more interesting is the fact that early in the record, Cl^- and sodium (Na^+) concentrations in bulk deposition were poorly correlated ($r^2 = 0.05$, 1967–1980), and Cl^- concentrations were substantially greater than Na^+ concentrations (Figure 4). After 1981, Cl^- and Na^+ concentrations were more nearly equal and highly correlated ($r^2 = 0.98$, 1981–2000) (Figure 4). The Cl^- to Na^+ molar ratio in bulk deposition averaged around 2.3 prior to 1975, peaked at a value of about 3.5 in 1976, and fell sharply through 1981. Since that time, the ratio has fluctuated slightly above the seawater ratio of 1.2 (Figure 5). Concentration of Cl^- in wet-only precipitation from the National Atmospheric Deposition Program (NADP) site at the HBEF has closely matched the bulk deposition concentrations (Figure 6) (Martin et al. 2000). The bulk deposition collector is continuously open, as opposed to the automatic closure of the NADP collector during dry periods,

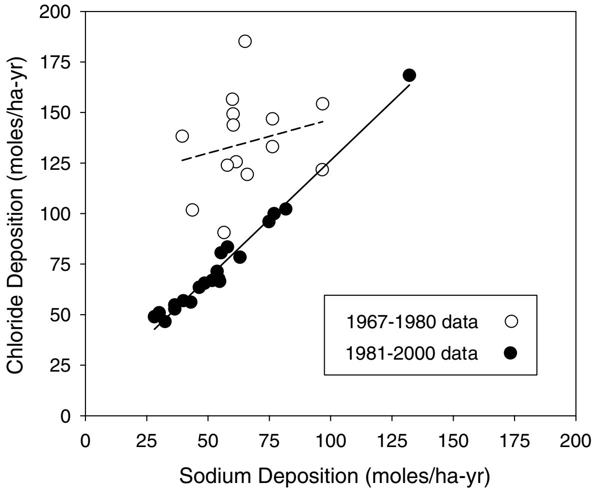

Figure 4. Bulk deposition of Na^+ versus Cl^- for two periods, 1967–1980 and 1981–2000.

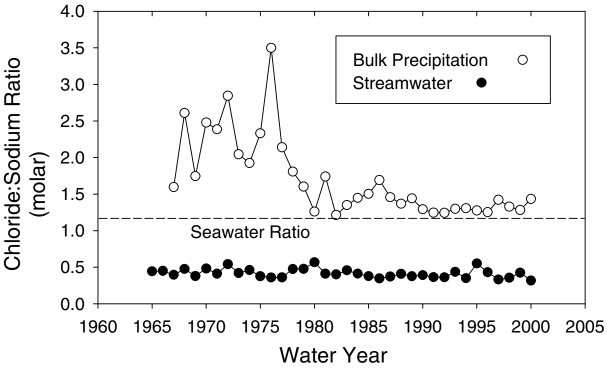

Figure 5. Molar ratio of Cl^-:Na^+ in bulk deposition and stream water. Dashed line is sea salt ratio.

and the collection of particulate and gaseous material during dry periods probably accounts for the slightly higher concentrations in the bulk collector. The NADP collection site is also about 300 m lower in elevation and closer to heavily traveled roads than the bulk collector in Figure 6. We attributed the very high Cl^- concentration reported for the NADP site for 1978 to contamination from the collector's O-ring in the first years of the NADP program (Martin et al. 2000), and we did not include that year in our comparison of bulk and wet-only deposition (Figure 6).

The concentration of Cl^- in bulk deposition decreased sharply from water-year 1980 to 1981 (Figure 3). When calculated on a calendar-year basis, this

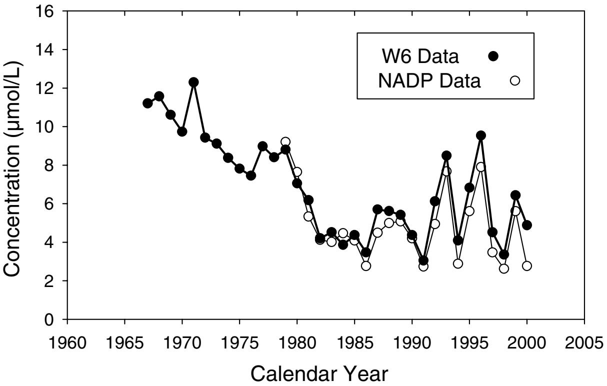

Figure 6. Concentration of Cl^- in bulk deposition (W6) and in wet-only precipitation collected by the NADP at the HBEF. Points are annual volume-weighted means on a calendar-year basis.

decrease is seen to be part of a multiple year decline from 1979 to 1982, and the same decline is observed in the NADP precipitation data (Figure 6). Rather than the anomalously steep drop that appears in 1980–1981 in the water-year data, the calendar year data show this to be consistent with the decline in Cl^- concentrations that had been ongoing since the late 1960s. The difference between the water-year and calendar-year summations occurs largely because the highest monthly Cl^- deposition ever measured at the HBEF, 51 mol/ha, occurred in February 1981, which is part of calendar year 1981 but water year 1980.

There is no strong seasonal pattern in either the concentration or deposition of Cl^- in bulk deposition, though there is a tendency for lower concentrations in the summer (Figure 7). Likewise, precipitation amount at this site is relatively evenly distributed throughout the year (Figure 7). Summertime concentrations of Cl^- in bulk deposition declined sharply until about 1981, and they have remained lower and less variable than concentrations in the winter (Figure 8). Winters in New Hampshire entrain two elevated sources of atmospheric Cl^-: (1) an increase in the frequency of coastal storms that bring maritime air to the site (Likens and Bormann 1995) and (2) an increase in the use of salt as a road de-icer. Road salt is not used within the HBEF, but is used heavily in the surrounding area and could be transported to the HBEF as dust. However, we do not believe that road salt is responsible for the trends in atmospheric deposition of Cl^- that we observe in the long-term record, because road salt usage increased dramatically after an interstate highway was constructed across the lower part of the Hubbard Brook valley (downstream of the HBEF) in 1970 (Bormann and Likens 1985; Rosenberry et al. 1999). Thus, the Cl^- deposition at the site was declining at the same time road-salt usage was increasing (Figure 3).

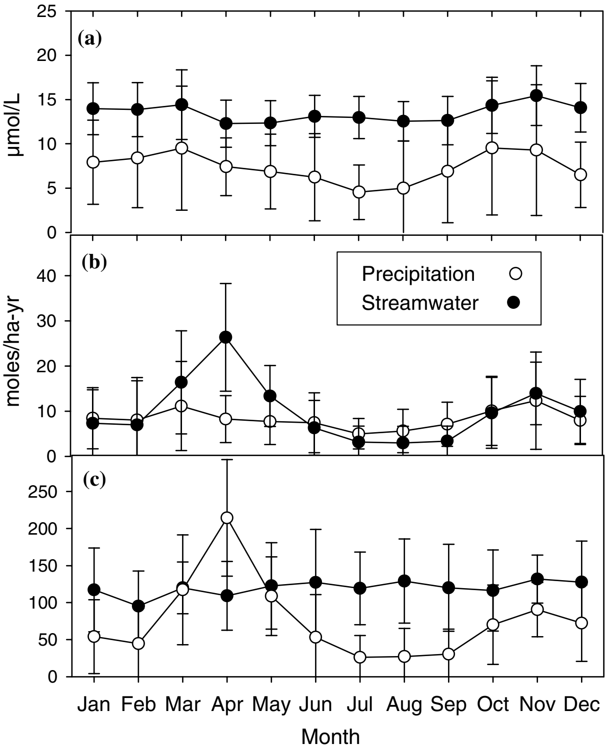

Figure 7. Mean monthly concentrations (a) and flux (b) of Cl$^-$ in bulk deposition and streamwater. (c) Monthly mean precipitation and streamflow amounts.

Dry deposition

Dry deposition of Cl$^-$ is likely because Cl$^-$ occurs in the atmosphere both as reactive gases and as particles large enough to have substantial deposition rates from gravitational settling and inertial impaction (Graedel and Keene 1996). Dry deposition is difficult to measure, however, and we have no direct measurements for the HBEF. We do have three lines of evidence that indicate there is measurable dry deposition at this site, however.

First, in a side-by-side comparison of bulk deposition and wet-only precipitation collectors from 1979 to 1989, the concentration of Cl$^-$ in the bulk deposition was about 12% higher than in wet-only precipitation, although the difference between the collectors was not significant (Martin et al. 2000). Measurements of water amounts indicated there was no evaporation from the bulk deposition collector, so the difference in concentration between the collectors suggests dry deposition of Cl$^-$ into the continuously open bulk collector. Given the configuration and composition (i.e. non-reactive polyethylene) of bulk deposition collectors, this dry deposition is likely to be

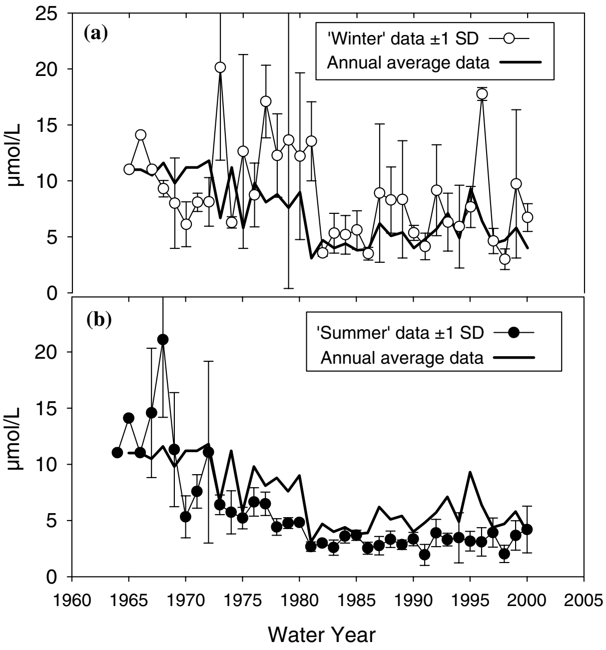

Figure 8. Trends in Cl^- concentration in bulk deposition in (a) winter (December, January and February) and (b) summer (June, July and August). Gray line in both panels is annual mean.

primarily from particles large enough to settle under the influence of gravity (Lovett 1994).

Second, throughfall fluxes of Cl^- were greater than bulk deposition fluxes of Cl^- for the period 1989–1992 (Lovett et al. 1996, and see throughfall section below), suggesting an external input of Cl^- to the canopy in excess of that measured by bulk deposition collectors. An alternative explanation is leaching of Cl^- from the canopy, but since Cl^- is in low concentration in the foliage, Cl^- leaching is often thought to be minimal from non-halophytic plants (Lovett and Hubbell 1991).

Third, in our recent measurements, the streamwater output fluxes of Cl^- were greater than the bulk deposition inputs, suggesting an unmeasured source of Cl^- for the watershed. This source could be dry deposition, as suggested by Juang and Johnson (1967). There are other possible explanations for this apparent net source, however, and we will return to this subject in Discussion.

Measurements of Cl^- in atmospheric particulates at the HBEF were made from 1974 to 1976 using a modified two-stage Lundgren impactor with after filters (Eaton and Likens 1978). The mean concentration of particulate Cl was 53 ng m^{-3}, less than a third the concentration of particulate Na (168 ng m^{-3}). The size distribution of Cl did not resemble that of Na, nor that of the primarily pollution-derived element sulfur (S), but rather that of the crustally

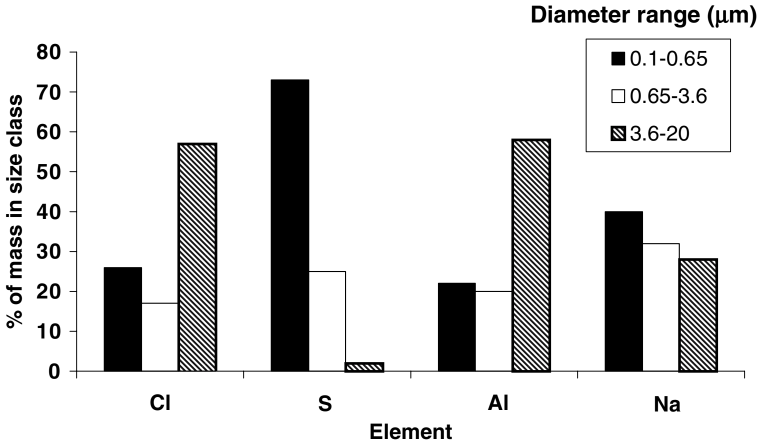

Figure 9. Size class distribution of particulate Cl$^-$, SO$_4^{2-}$, Al^{3+}, and Na$^+$ sampled with an Lundgren impactor at Hubbard Brook, 1974–1976. Data from Eaton et al. (1978).

derived element aluminum (Al) for which the bulk of the mass is in the largest size class (Figure 9). These results are difficult to interpret, but perhaps suggest that gaseous HCl emitted from coal combustion reacted with alkaline particles in the atmosphere to produce particulate Cl$^-$, as can happen with other acidic gases (Lovett et al. 2000). If we estimate deposition velocities for the three particle size classes in Figure 9, we can calculate Cl$^-$ particle dry deposition. Assuming deposition velocities (in cm/s) of 0.1 for the 0.1–0.65 μm diameter class, 0.1 for the 0.65–3.6 μm class, and 0.5 for the 3.6–20 μm class (Likens et al. 1994), we estimate a total Cl$^-$ particle dry deposition of 1.5 mol ha^{-1} year^{-1}. This value is quite low compared to bulk deposition (average 99 mol ha^{-1} year^{-1}) but does not include dry deposition of gaseous Cl compounds, which may be substantial.

Weathering inputs

Small amounts of Cl$^-$ may substitute for hydroxyl ion in several common minerals in soil and bedrock in the central New Hampshire area, including hornblende, biotite, and apatite. However, estimates of Cl$^-$ release by mineral weathering have not been previously attempted and analyses of Cl$^-$ in minerals, rock, and soil in the region are very limited. Whole rock chemical analyses from the White Mountain region show a range of Cl$^-$ concentrations, varying from < 100 mg/kg for schists (including the Rangeley formation, which is the principal bedrock underlying the HBEF), 100–400 mg/kg in granites and 600–3500 mg/kg in syenites (Billings and Wilson 1964). The rocks with the highest concentrations (1200–3500 mg/kg) all contained sodalite, a mineral that includes Cl^- as an essential component. However, no syenite or sodalite-bearing rocks are present in the bedrock at the HBEF. Also, no syenite is present in the region north and west of HBEF, suggesting that this lithology does not contribute to glacial till (Bailey and Hornbeck 1992), the parent material of soil at the HBEF. This conclusion is confirmed by stone counts from glacial till samples taken across the HBEF experimental watersheds (S.W. Bailey et al. 2003).

We can make a rough estimate of Cl^- weathering flux if we assume the ratio of Cl:Na weathering is the same as their ratio in the bulk soil. As the soil at the HBEF is derived from a mixed schist–granite till with no syenite (S.W. Bailey et al. 2003), 100–200 mg kg^{-1} Cl^- may be a reasonable concentration in glacial till. Given a mean Na weathering flux for W6 of 250 mol ha^{-1} $year^{-1}$ (Likens and Bormann 1995; S.W. Bailey et al. 2003), and an average Na^+ concentration in till of 15,000 mg kg^{-1} (S. Bailey unpublished data), we estimate a Cl^- weathering flux of 1.7–3.4 mol ha^{-1} $year^{-1}$. This method relies on the assumption that Cl^- and Na^+ weathering fluxes are in the same ratio as their concentration in the soil. If different minerals dominate weathering of Cl^- versus Na^+, and if these minerals differ greatly in their contribution to weathering flux, then this assumption is not valid.

An alternative approach is to estimate the weathering flux of individual minerals. Deer et al. (1963) compiled chemical analyses for specific minerals from worldwide sources. Typical Cl^- concentrations reported are 5300 mg kg^{-1} in hornblende, 2400 mg kg^{-1} in biotite, and 5000 mg kg^{-1} in apatite. At the nearby Cone Pond Research Watershed, Hyman et al. (1998) estimated hornblende and biotite weathering flux at 3.4 and 11 mol ha^{-1} $year^{-1}$ respectively. Using these flux estimates with the typical Cl^- concentrations reported by Deer et al. (1963) yields 0.45 mol Cl ha^{-1} $year^{-1}$ released by hornblende and 0.33 mol Cl ha^{-1} $year^{-1}$ released by biotite. Blum et al. (2002) hypothesized that apatite weathering may contribute 35% of the Ca in stream water at HBEF. Based on the HBEF streamwater Ca flux (Likens et al. 1998) and typical apatite compositions (Deer et al. 1963), we estimate apatite weathering to release 2.0 mol Cl ha^{-1} $year^{-1}$. Thus total Cl weathering flux from these three minerals is estimated at 2.8 mol Cl ha^{-1} $year^{-1}$.

The strength of the second approach is that it deals directly with the weathering fluxes of the actual minerals thought to contribute to Cl^- weathering at HBEF. The weaknesses are: (1) the weathering fluxes from biotite and hornblende at Cone Pond may not be valid for HBEF, although because they are based on similar till provenance, this site separation may not be a problem (Bailey and Hornbeck 1992; S.W. Bailey et al. 2003), (2) the proposed apatite weathering flux at HB is based on a controversial interpretation of Sr geochemistry, and may be too high, and (3) the typical Cl^- content of the minerals reported by Deer et al. (1963) may not be appropriate to HBEF.

Table 1. Mean concentrations of Cl, Ca, and Al in sugar maple foliage and in throughfall solution in plots treated with $CaCl_2$, $AlCl_3$, and control plots

			Foliar concentrations (mg g^{-1})			Throughfall (mmol$_c$ m^{-2})	
Year	Treatment	Cl$^-$ applied (mmol$_c$ m^{-2})	Cl	Ca	Al	Cl$^-$	Ca^{2+}
1996	Control	0	0.37	4.67 a	0.045	2.35	9.16 b
	$CaCl_2$	250	0.54	6.03 b	0.039	2.72	8.13 ab
	$AlCl_3$	200	0.41	4.20 a	0.045	2.28	7.34 a
1997	Control	0	0.40 a	5.09 a	0.039 a	2.65 a	9.62
	$CaCl_2$	250	0.85 b	6.24 b	0.039 a	3.47 b	9.07
	$AlCl_3$	300	0.59 ab	4.71 a	0.052 b	4.38 c	9.01
1998	Control	0	–	–	–	2.67 a	9.03
	$CaCl_2$	0	–	–	–	3.84 b	9.98
	$AlCl_3$	0	–	–	–	4.02 b	8.22

Modified from Berger et al. (2001). Letters next to data represent statistical differences among means using Scheffe's multiple range test. Within any year, means in the same column sharing the same letter are not statistically different ($p \geq 0.05$). If no letters are present, there were no statistically significant differences.

In any case, both estimates give similar results. If they are accurate, the weathering flux of Cl$^-$ is insignificant to the overall budget, representing only 1–2% of the average export in stream water.

Intrasystem cycling

Biological uptake and cycling in organic matter

Although Cl is an essential element for plants, its concentration is not commonly measured in plant tissue or other forms of organic matter. We have few measurements of Cl in key organic matter pools at the HBEF, including live plant tissue, detritus, and soil organic matter (SOM). In one study, total Cl concentrations in sugar maple foliage near W6 averaged 0.37 mg g^{-1} in 1996 and 0.40 mg g^{-1} in 1997 (Table 1; Berger et al. 2001). (We report Cl concentrations in biomass in units of mass/mass because that is the unit typically given in the literature. For comparison with our other data, note that 1 mg g^{-1} = 28.2 μmol g^{-1}.) Kaufmann et al. (2003) reported inorganic Cl$^-$ concentrations in roots of red pine (*Pinus resinosa)* at HBEF to be 0.293–0.308 mg g^{-1}. (These data are from plants grown in a mesocosm experiment; red pine is not a common species at the HBEF.) There are very few other data in the literature on Cl concentration in trees. In non-halophytic species, concentrations of Cl are expected to be low. Holmes and Baker (1966) report concentrations of inorganic Cl$^-$ in sugar maple foliage to be 0.5 mg g^{-1} for a site in Massachusetts. Lobert et al. (1999) reviewed Cl concentrations in several types of vegetation, and reported concentrations (in mg g^{-1}) ranging from 0.009 to 0.185 in wood, 0.037 to 0.170 in bark, and 0.009 to 2.50 in foliage of temperate-zone forests.

Throughfall and stemflow

Eaton et al. (1973) measured throughfall and stemflow concentrations and fluxes near W6 during the growing season of 1969. They reported substantial increases in throughfall Cl^- fluxes as rainwater passed through the canopy, suggesting a significant amount of washoff of dry deposited Cl^-, or of Cl^- leaching from the foliage. However, the throughfall and stemflow measurements may have been overestimated because of the colorimetric assay that was used (see above).

Lovett et al. (1996) measured throughfall concentrations (using ion chromatography) and fluxes of Cl^- during the growing seasons of 1989–1992 at several locations near W6. For all sites, fluxes of Cl^- in throughfall exceeded those in bulk deposition, indicating washoff of dry deposition or leaching from the canopy (Figure 10). The net throughfall flux (NTF = throughfall − bulk deposition) was more positive for the mature hardwood stands than for smaller-statured successional stands dominated by pin cherry (*Prunus pennsylvanica*). The mean NTF for the mature hardwood stands was 12.5 mol Cl^{-1} ha^{-1} for the June–September growing season, about half the bulk deposition flux of 25.1 mol ha^{-1} for the same period.

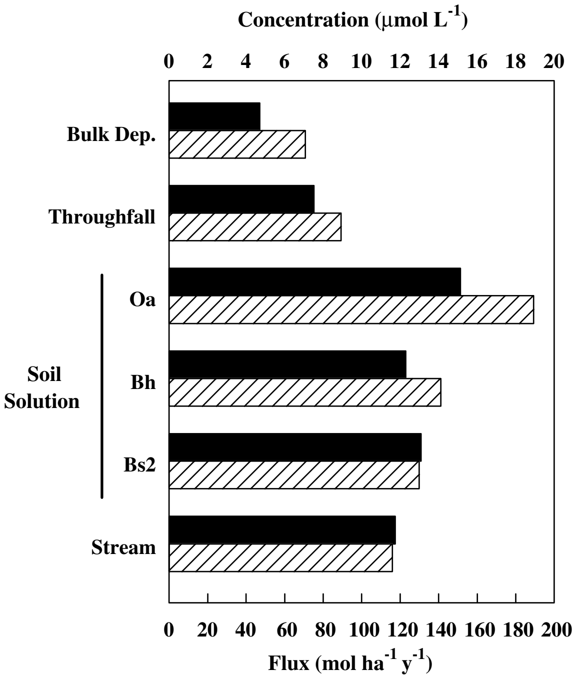

Figure 10. Mean Cl^- concentrations (black bar) and flux (striped bar) in bulk deposition, throughfall, soil solution (Oa, Bh, and Bs horizons) and stream water for 1989–1992. Data are means of the 4 calendar years. Concentrations are volume-weighted.

Soil solution

Chloride concentrations and fluxes tend to increase as solutions pass through the canopy and into the organic horizons of the soil. Both concentration and flux profiles show maxima in the Oa horizon leachate (Figure 10), and the flux profile shows a slight decline as the water moves down through the mineral soil and into the stream. This pattern suggests a source of Cl^- in the organic soil horizons, perhaps leaching from decomposing litter, and a sink in the lower soil horizons, perhaps soil adsorption or plant uptake. Because the data shown in Figure 10 are from 1989 to 1992, a period when Cl^- concentrations in soil solution and stream water were declining, one would expect to observe desorption rather than adsorption of Cl^- from the mineral soil (see discussion under 'Soil Chemical Processes' below). Thus, we interpret the decrease in Cl^- fluxes as water percolates through the soil to be primarily a result of plant uptake. Plants must take up enough Cl^- from soil solution to replace the Cl^- lost by litterfall and foliar leaching plus the amount in accumulating biomass. As we discuss below, accumulation of forest biomass was minimal during the period covered by these soil solution data (1989–1992), but uptake of Cl^- must have been occurring to balance the litterfall losses.

Elevational patterns of soil solution Cl^- concentrations are evident across the forested hill slopes at the HBEF. Concentrations of Cl^- in soil solutions were highest at a 750 m site in the high elevation spruce–fir–paper birch zone. Mean concentrations ($\pm$SD) were 18.0 ± 12.9 μmol l^{-1} (1984–1998) in forest floor leachate and decreased slightly in the lower mineral soil (14.6 ± 8.2 μmol l^{-1}). Soil solution concentrations decreased slightly, but not significantly, with decreases in elevation along the slope, but the same vertical pattern in the soil horizons was evident at all sites. At the low elevation hardwood zone (600 m) mean soil water concentrations were 16.4 ± 16.0 μmol l^{-1} draining the Oa horizon and values decreased somewhat in the mineral soil (Bs horizon 14.0 ± 5.6 μmol l^{-1}). This elevational pattern is consistent with longitudinal patterns in stream Cl^- concentrations (see 'Hydrologic losses and input–output budgets').

Soil solution Cl^- concentrations have decreased consistently over the monitoring period (-0.12 to -0.14 μmol/l-year; 1984–1998), but not significantly ($p > 0.1$, seasonal Kendall Tau procedure, Hirsch and Slack 1984). The lack of statistical significance was probably due to the relatively high variability in soil water measurements. The variability of solution measurements decreases from forest floor solutions to mineral soils solutions to stream water.

Soil chemical processes

Chloride, along with nitrate, is often considered to be 'non-specifically' adsorbed to soils, through electrostatic mechanisms that are completely reversible (Mott 1981). This contrasts with ions such as PO_4^{3-} and SO_4^{2-} that are 'specifically' adsorbed through mechanisms that involve covalent bonding with soil oxides, and may not be completely reversible. However, research on B horizon soils at the HBEF has shown that anions do not fit easily into these

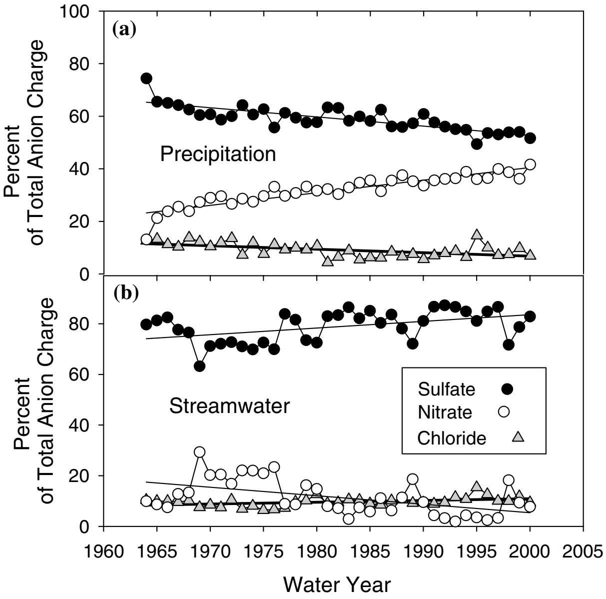

Figure 11. Percent contribution of NO_3^{2-}, SO_4^{2-}, and Cl^- to the sum of the three anions in precipitation (a) and stream water (b).

two classes, and in fact show a gradient of affinity for these soils in the order $PO_4^{3-} > F^- > DOC > SO_4^{2-} > Cl^- \gg NO_3^-$ (Nodvin et al. 1986). Thus Cl^- shows an anion adsorption capacity that is not as high as SO_4^{2-} but much higher than NO_3^-. Adsorption isotherms described by the commonly used Langmuir and Freundlich equations did not fit the behavior of anions in these soils as well as did a simple linear function of the initial mass of the anion added to the soil (Nodvin et al. 1986). The reversibility of the Cl^- adsorption was not examined by the Nodvin et al. study. Nonetheless, if Cl^- behaves like SO_4^{2-}, some retention of Cl^- can be expected on iron and aluminum oxides in the mineral soils at the HBEF.

Unfortunately, we do not have direct measurements of adsorbed soil Cl^- pools for the HBEF. To estimate changes in the pool of soil adsorbed Cl^-, we calculated the partitioning of Cl^- with soil using the model PnET-BGC (Gbondo-Tugbawa et al. 2001) based on the Cl^- partitioning parameters measured for HBEF soil by Nodvin et al. (1986). In calculating changes to the adsorbed pool over time, we assumed completely reversible sorption. These calculations suggest that soil pools have decreased at the HBEF since the early 1960s in response to decreases in atmospheric deposition of Cl^-. We estimate the soil adsorbed Cl^- pool to have been 150 mol ha^{-1} in the mid-1960s. Model-predicted values decreased though the 1960s and 1970s, stabilizing at a mean value of 38 mol ha^{-1} since 1982. This value appears to be at near steady-state with respect to the relatively constant inputs that have been observed during the last 20 years. The decrease in the adsorbed pool (112 mol ha^{-1} decline from 1965 to1982) yields an average Cl$^-$ desorption rate of 6.6 mol ha^{-1} year^{-1} for that period.

We have not measured organic chlorine compounds in HBEF soils, although they probably occur, given their nearly ubiquitous occurrence in other forest soils (Oberg 1998; Oberg 2003; Rodstedth et al. 2003). Microorganisms appear to mediate both the formation of soil organic matter containing Cl and the mineralization of Cl during decomposition (Oberg 1998). The formation and mineralization of organochlorine compounds has been observed in laboratory soil column studies (Rodstedth et al. 2003). Thus, retention and release in SOM are a potential net sink and source for Cl within the ecosystem that we have not quantified.

Chloride contribution to total anions in solution

Chloride currently contributes a small amount of the total anionic charge (SO_4^{2-} + NO_3^- + Cl$^-$) in bulk deposition, but that percentage has declined significantly since the beginning of the record, from about 12% in the mid-1960s to 8% in 2000. (Figure 11a). Over the same period, the contribution of SO_4^{2-} has also declined, while the contribution of NO_3^- has increased. These patterns reflect trends in emissions of the precursors of these ions in the eastern US (Likens et al. 2001). In stream water, however, while the concentrations of both SO_4^{2-} and Cl$^-$ have declined, their contributions to the anion charge have increased, because the contribution of NO_3^- has declined even more strongly Figure 11b). The cause of the high NO_3^- concentrations in stream water in the 1970s and the very low values in the early 1990s are not completely understood, but may have to do with the long-term ramifications of a prolonged drought in the 1960s (Aber et al. 2002; Goodale et al. 2003).

The contribution of Cl$^-$ to anion charge changes only slightly as solutions percolate through the ecosystem. Chloride constitutes about 8% of the anionic charge in bulk deposition and throughfall, increasing to about 9–10% in soil solution and stream water.

Hydrologic losses and input–output budgets

Streamflow represents the only significant mechanism for loss of Cl$^-$ from the watersheds at the HBEF. At the gauging station at the bottom of W6, Cl$^-$ concentration in stream water has been measured weekly since 1964. There is little seasonal variation in the concentration of Cl$^-$ in stream water, but the streamwater export flux of Cl$^-$ increases during the high-flow period of spring snowmelt (Figure 7). Annual streamwater export of Cl$^-$ is also correlated with annual stream flow Figure 12b).

Elevational patterns in stream Cl$^-$ concentrations parallel those observed in soil solutions. Monthly sampling along the length of the stream draining W6

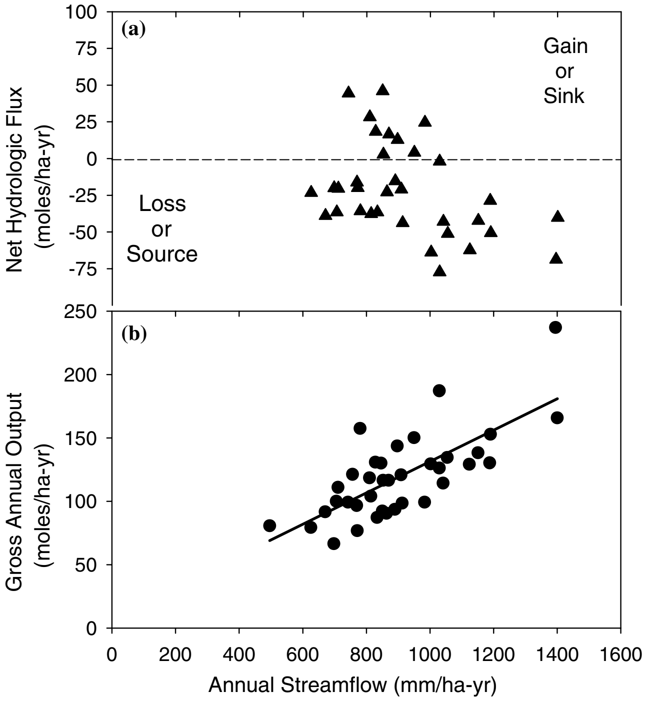

Figure 12. NHF (a) and stream export (b) of Cl^- versus annual stream flow.

for the period 1982–2000 showed that concentrations were highest and most variable at the highest elevation site in the spruce–fir–paper birch zone (750 m; 14.7 ± 8.3 μmol l^{-1}). Concentrations of Cl^- decreased and were less variable as stream water flowed from the spruce–fir–paper birch zone through the upper hardwood zone to the lower elevation hardwood zone (<730 m; 4 sites; 12.1 ± 4.1 μmol l^{-1}).

In general, interannual variations in streamwater Cl^- concentrations have reflected those of Cl^- concentration in precipitation (Figure 13a). However, the decline in atmospheric deposition in the 1970s and early 1980s was not accompanied by an equivalent decline in stream export (Figure 13b) and consequently the net balance of Cl^- in the watershed has changed substantially (Figure 13c). To quantify this input–output balance, we define the net hydrologic flux (NHF) as bulk deposition inputs minus stream water outputs (Likens et al. 2002). A positive NHF indicates an unmeasured sink or output of Cl^-, while a negative NHF indicates an unmeasured source or input.

Prior to WY 1979, the NHF for individual years varied from positive to negative, ranging from +46 to −40 mol ha^{-1} $year^{-1}$. The mean for the period 1967–1979 was positive (+11 mol ha^{-1} $year^{-1}$). Since 1979, however, the NHF has been consistently negative, and the 1979–2000 period has a mean

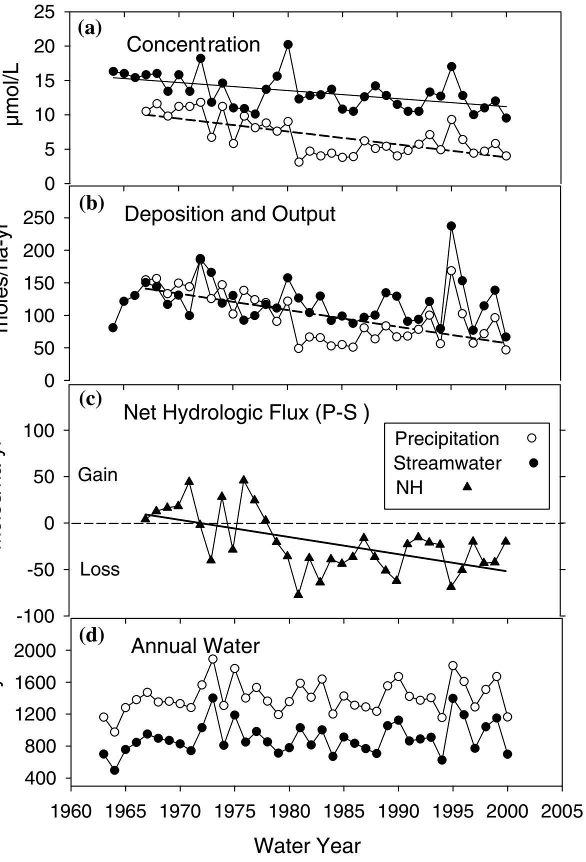

Figure 13. Long-term record of annual mean concentration (a) and flux (b) of Cl^- in bulk deposition and stream water, net hydrologic flux of Cl^- (c), and precipitation and stream flow water amounts (d) for W6.

NHF of -39 mol ha^{-1} $year^{-1}$ with a range from -15 to -77 mol ha^{-1} $year^{-1}$. We discuss possible reasons for this shift in Discussion.

Responses to disturbance

Chloride additions

In a fertilization study designed to investigate the effects of changes in the Ca and Al concentrations in soil, $CaCl_2$ and $AlCl_3$ were added to sugar maple stands on the south-facing slopes of the HBEF (Berger et al. 2001). The $CaCl_2$ application resulted in Cl^- additions of 250 mmol m^{-2} in 1996 and the same amount in 1997, while the $AlCl_3$ application resulted in 200 mmol m^{-2} in 1996 and 300 mmol m^{-2} in 1997. Thus, in both treatments 500 mmol m^{-2} of Cl^- were added over the 2-year period. For comparison, bulk deposition of Cl^- was about 10 mmol m^{-2} (100 mol ha^{-1}) during the same 2-year period.

Berger et al. (2001) reported measurable increases in foliar Cl concentrations as a result of these Cl^- additions. Foliar Cl^- levels were higher in both $AlCl_3$- and $CaCl_2$-treated plots than in control plots in both 1996 and 1997, although the responses were statistically significant only for the $CaCl_2$ plots in 1997 (Table 1). In both years, the response to $CaCl_2$ addition was greater than the response to $AlCl_3$ addition. This difference may result from the fact that Ca is an essential nutrient for plants whereas Al is not, and Cl^- uptake would provide an effective counter-ion for Ca^{2+} uptake by the trees. Foliar Ca levels were also increased in the $CaCl_2$ treatments in both years, and foliar Al was increased in the Al treatments in 1997 (Table 1). In the $CaCl_2$ treatments, the increased Cl^- uptake (treatment – control) balanced on average only about 22% of the increase in Ca^{2+} uptake (on a charge equivalent basis), indicating that Cl^- was not the main counter-ion for Ca uptake. In addition to the increases in tissue concentrations, Berger et al. (2001) found significant increases in Cl^- in throughfall in both treatments relative to the controls in both 1997 and in 1998 Table 1). Throughfall fluxes of Ca^{2+} did not increase significantly, and Al was not measured in throughfall. This experiment indicated that increases in Cl^- deposition to this forest increased both concentrations and cycling of Cl^- in the vegetation. The magnitude of the effect on foliage varied with the form of the Cl^- added.

In another experiment, Cl^- was added to forest plots at the HBEF to determine the effect of a mobile anion on the leaching of cations from the soil (Christ et al. 1999). Addition of Cl^- solutions at 100 μmol l^{-1} (as either HCl or $CaCl_2$) increased the Cl^- concentration in soil water by 62, 56, and 52 μmol l^{-1} in Oa, Bhs and Bs2 horizons, respectively. This result suggests some uptake or adsorption of Cl^- throughout the soil profile. In the Oa horizon solution, the Cl^- additions caused a weakly significant ($p = 0.06$) increase in base cation concentrations averaging 46 μmol l^{-1}, but there was no significant effect in the Bhs or Bs2 horizons (Christ et al. 1999).

Vegetation manipulations

Several watershed-scale vegetation manipulations have been done at the HBEF since 1965. Watershed 2 (W2) was experimentally deforested in the winter of 1965–1966, without removal of forest products. Regrowth of vegetation was inhibited with herbicides until the summer of 1969 (Likens et al. 1970). Watershed 4 (W4) was progressively strip-cut in 25-m wide strips along the elevational contours, with a buffer strip of living trees left along the stream corridor. One third of the watershed was cut in each of the years 1970, 1972, and 1974, with removal of timber products. Watershed 5 (W5) was logged by a commercial whole-tree harvest in 1983–1984, with removal of timber products.

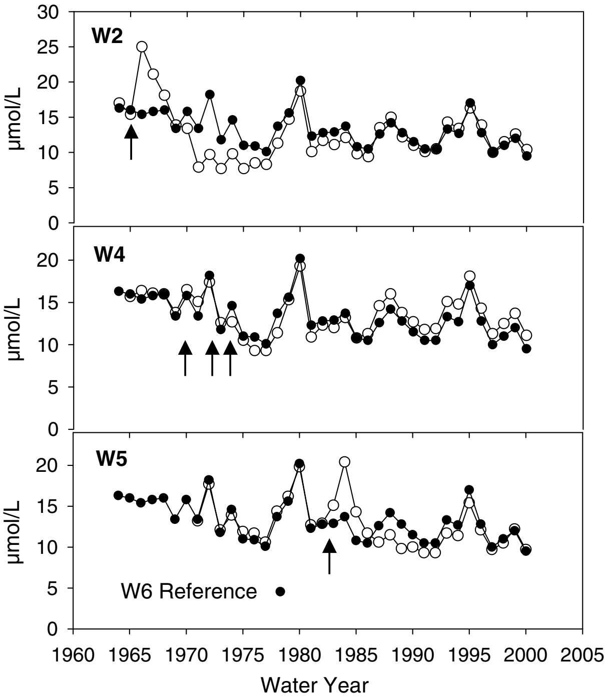

Figure 14. Annual mean concentration of Cl^- in stream water in the disturbed watersheds W2, W4, and W5. Concentrations in W6 are plotted in each panel as a reference. Dates of harvest of the disturbed watersheds are indicated with arrows.

After the devegetation of W2, Cl^- concentration and export flux increased dramatically (relative to W6, the biogeochemical reference watershed) the following year and remained elevated for 4 years (Figures 14 and 15). After that, Cl^- export was generally less than that of W6 for the next 16 years, until 1986. A similar response was seen for the whole-tree harvest in W5, where the Cl^- export was elevated relative to W6 for 4 years after the harvest, then fell below that of W6 and has remained lower through 2000 (Figure 15). The strip cut of W4 was more moderate in that only a third of the watershed was cut each year and a buffer zone was left along the stream. Nonetheless, export of Cl^- was elevated the year after each of the successive cuts, and the export was reduced relative to W6 from 1976–1984. Interestingly, and in contrast to W2 and W5, concentration and export from W4 appear to be slightly greater than from W6 since 1985 (Figures 14 and 15).

The measurement of Cl^- export from W2 could have been influenced by the herbicides added in 1966, 1967, and 1968. In 1966, the herbicide Bromacil was added, and the Br^- in that compound may have positively interfered with the streamwater Cl^- analysis used at that time (Likens et al. 1970; Buso et al. 2000). The maximum potential interference was equivalent to an input of

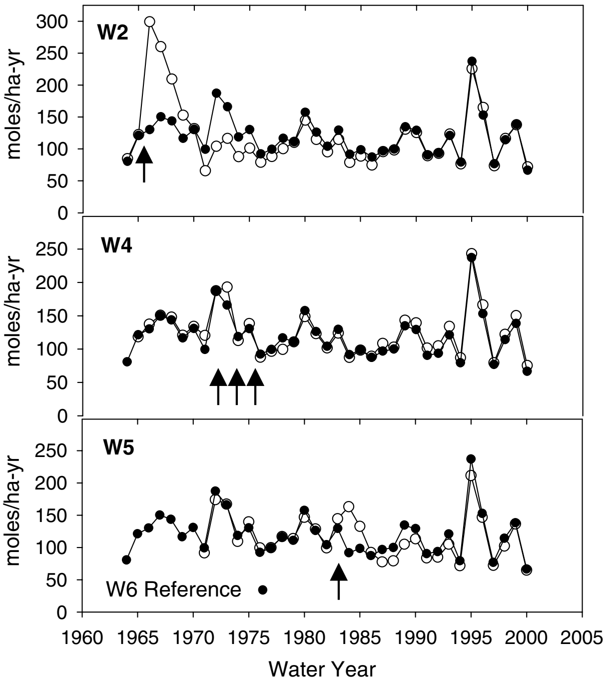

Figure 15. Annual export of Cl⁻ in stream water in the disturbed watersheds W2, W4, and W5. Export in W6 is plotted in each panel as a reference. Dates of harvest of the disturbed watersheds are indicated with arrows.

85 mol Cl^- ha^{-1}. Based on samples taken by the manufacturer (Dupont), only 20% of the Bromacil in W2 was exported within 18 months after the application, suggesting that the Br^- was largely retained in the watershed (Pierce 1969). Thus, the Cl^- export might be overestimated by as much as 17 mol ha^{-1} for 1966 in W2. This represents only 6% of the measured Cl^- output for that year (Figure 15), and thus no correction has been made to the long-term data.

In 1967 and 1968, the herbicide 2,4,5-T was added to the watershed. The Cl contained in this herbicide technically represents 19.7 mol ha^{-1} of Cl^- deposition each year (Likens et al. 1970). Only trace amounts (<1 ppb) of this herbicide were detected in streamwater in 1967 and 1968 (Pierce 1969), but it is not clear whether the herbicide was retained as an organochlorine compound in the soil or whether it was degraded, releasing its Cl. If the herbicide is considered as a Cl^- input, the net effect would be to make the NHF of Cl^- less negative (Figure 16) by about 20 mol Cl^- ha^{-1} $year^{-1}$ for 1967 and 1968. While the herbicide inputs add some uncertainty to the quantitative budget of Cl^- after the disturbance of Cl, they do not change the conclusion that Cl^- was quickly released from the watersheds after the harvest. We note that

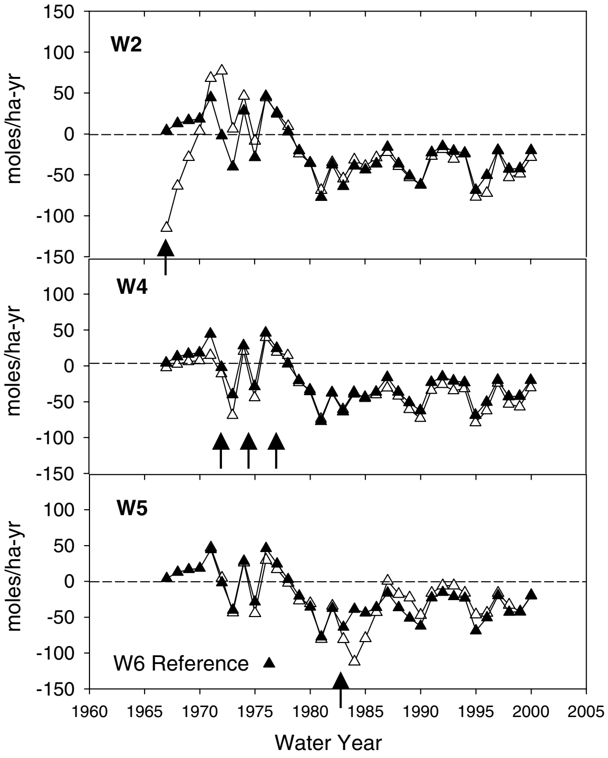

Figure 16. Annual net hydrologic flux (precipitation inputs − stream water outputs) of Cl^- in the disturbed watersheds W2, W4, and W5. NHF in W6 is plotted in each panel as a reference. Dates of harvest of the disturbed watersheds are indicated with arrows.

watersheds 4 and 5 also showed an increased loss of Cl^- after cutting, despite that fact that no herbicide was used.

Thus, each of the treated watersheds showed the same qualitative pattern of Cl^- export. In each watershed, concentration and export of Cl^- increased (relative to W6) in the years immediately following the manipulation. After some time interval (which was different for each manipulation), the concentration and export decreased to a level less than W6 and remained there for several years. As a result of these patterns, the NHF of Cl^- became more negative than W6 (greater net export) immediately after each manipulation, and then more positive than W6 some years later (Figure 16). Watershed 2 lost 382 mol ha^{-1} of Cl^- more than W6 during the period 1965–1970, during and immediately after the treatment. From 1971 to 1986, W2 lost 350 mol ha^{-1} less than W6, indicating that the watershed had recovered 92% of the Cl^- it lost from the devegetation. Likewise, W5 lost 125 mol Cl ha^{-1} more than W6 during the period 1983–1986. During 1987–2000 it lost 177 mol ha^{-1} less than W6, indicating a recovery of 142% of the lost Cl^-.

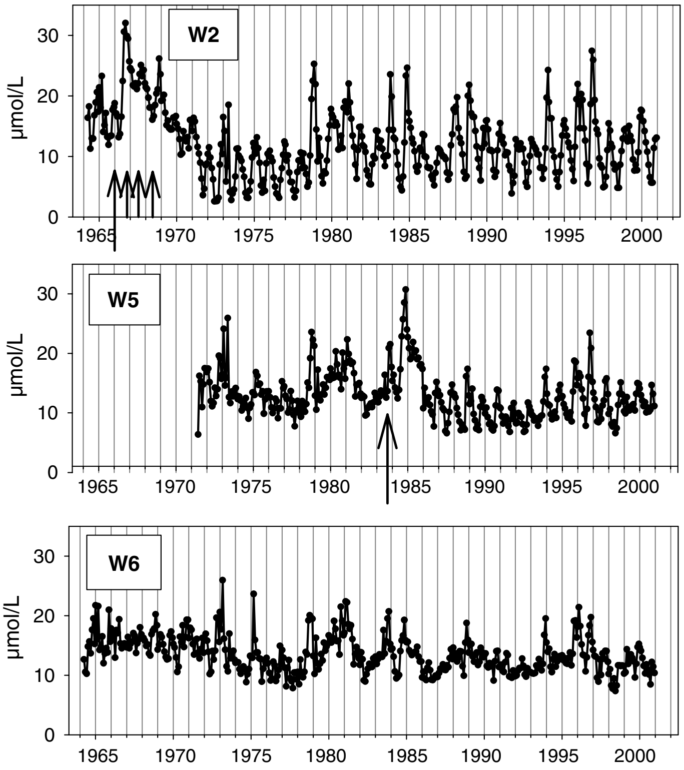

Figure 17. Monthly mean concentrations of Cl^- in the streams of the two clearcut watersheds (W2 and W5) and the reference watershed (W8). Arrows in W2 and W5 panels denote the years of the vegetation disturbance. Vertical lines are plotted in the beginning of January of each year.

In both of the clearcut watersheds (W2 and W5), Cl^- concentrations in stream water displayed a seasonal cycle after the harvests, with highest concentrations in late fall and lowest concentrations in mid-summer (Figure 17). Neither of these watersheds showed a seasonal cycle before the harvests, and the reference watershed (W6) has never shown a seasonal cycle (Figure 17).

Kaufmann et al. (2003) reported on the behavior of Cl^- in another type of vegetation manipulation experiment that was performed in an 'artificial forest' at the HBEF. They grew experimental monocultures of red pine (*Pinus resinosa*) in small plots containing a very sandy soil, in what is known as the 'Sandbox Experiment.' When the aboveground tree biomass was harvested after 15 years of growth, leaching losses from the sandboxes greatly exceeded precipitation inputs. Subsequent investigation indicated that the excess Cl^- leaching from the boxes came primarily from decomposition of roots, litter, and SOM (Kaufmann et al. 2003).

Discussion

Our long-term study of Cl at the HBEF has revealed some interesting patterns that invite further discussion. We will focus on four interrelated topics: the source of Cl^- in atmospheric deposition, the behavior of Cl^- after vegetation manipulation, the source of the current net export of Cl^-, and the change in the NHF during the course of the study.

Source of Cl^- in atmospheric deposition

Globally, the greatest source of Cl^- to the atmosphere is from the oceans, via the generation of aerosols from salt spray (Graedel and Keene 1996). If the source of the Cl^- in bulk deposition at HBEF were sea salt, we would expect that Cl^- and Na^+ would be highly correlated and would occur in roughly the sea salt molar ratio of 1.2. This has been the case since the early 1980s, but was not the case in the 1960s and 1970s, when there was substantially more Cl^- than Na^+ deposited, and the two were uncorrelated (Figure 3) (Likens nd Bormann 1995). This observation implies that there was another source of the Cl^- in bulk deposition during the 1960s and 1970s. That source was probably fossil fuel combustion in the eastern US, primarily combustion of coal, which emits HCl (Graedel and Keene 1996). The elevated S deposition at HBEF attests to the presence of coal combustion products in the atmosphere (Likens et al. 2001). Sulfur deposition also declined sharply during the 1970s, and the flue gas desulfurization processes which have been implemented to reduce S emissions from power plants also remove $>90\%$ of the HCl that is emitted during coal combustion (McCulloch et al. 1999). Although emissions data for HCl from the eastern US are not available, we know that SO_4^{2-} concentrations in bulk deposition at this site are strongly correlated to S emissions upwind (Likens et al. 2001, 2002), and we observe that concentrations of Cl^- and SO_4^{2-} in bulk deposition decreased in a similar manner through the 1970s (Figure 18). While other processes (e.g. waste incineration) could contribute to Cl emissions that reach Hubbard Brook, the parallel trends of Cl and S deposition suggest to us that the decline in Cl^- deposition at the HBEF is probably a result of reduced Cl emissions from coal combustion.

We hypothesize that there has been a shift during the course of this study in the relative dominance of the two major sources of Cl^- in bulk deposition, coal combustion and sea salt. Prior to 1981, coal combustion was the dominant source, and it yielded Cl^- concentrations in bulk deposition that were higher than, and uncorrelated with, concentrations of Na^+. As coal combustion emissions of Cl^- declined during the 1970s, sea salt became the dominant source, resulting in the current situation in which Cl^- and Na^+ concentrations are highly correlated and close to the sea salt ratio. Concentrations of Cl^- have not continued to decline like those of S in the past 15 years because the sea salt deposition of Cl^- masks what we expect is a continued decline in coal-derived Cl^-.

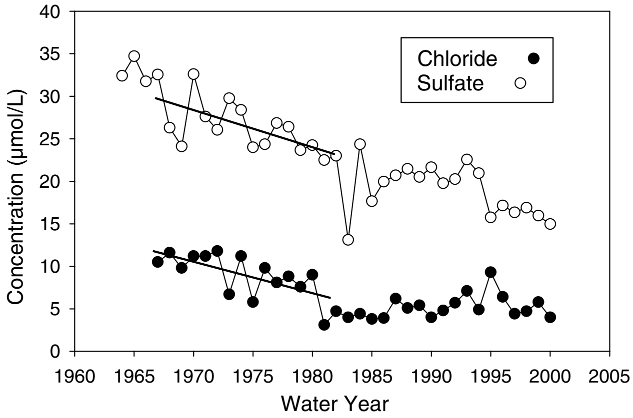

Figure 18. Trends in concentration of Cl^- and SO_4^{2-} in bulk deposition. Lines are least-squares regressions for the period 1967–1981.

Our Cl^- addition experiments suggest that changes in Cl^- availability affect Cl^- cycling in throughfall and soil solution and Cl^- concentrations in plant tissue. Thus the overall decline in Cl^- deposition prior to 1980 probably affected the cycling and accumulation of Cl^- in the ecosystem, although we do not have direct measurements of that effect.

Behavior of Cl^- *after vegetation manipulations*

The behavior of Cl^- after the devegetation of W2, the strip cut of W4, and the whole-tree harvest of W5 was consistent with loss and recovery of Cl^- from a vegetation biomass pool. We interpret these results to indicate that Cl^- in vegetation was released by leaching or mineralization from detritus in the years immediately after the cutting events. This release was followed by a period of recovery, in which the aggrading vegetation sequestered Cl^- at a rate faster than the reference watershed, thus reducing the export relative to the reference stream. Unfortunately, we do not have direct measurements of Cl^- accumulation in aggrading forest biomass. The period of net export lasted 4–5 years in the case of the devegetation and the whole-tree harvest, and only one year for each portion of the harvest for the 'gentler' strip-cut. The period of recovery was more protracted than the period of Cl^- losses, lasting 16 years for W2 and 12 years for W5.

The observed seasonal cycling of Cl^- concentrations in stream water after the clearcuts of W2 and W5 further supports this interpretation. We suggest that during the vigorous regrowth period after the clearcuts, vegetation uptake reduces stream water Cl^- concentration in the growing season, while in the late fall the Cl^- concentration is increased due to reduced plant uptake and leaching of Cl^- from fresh litter. No seasonal cycling is observed in these watersheds prior to the clearcuts, and no seasonal cycling is observed at all in the reference watershed (W6). This seasonality corresponds to similar cycling of NO_3^- concentration in streamwater (Likens and Bormann 1995), although NO_3^- tends to reach peak concentrations during the spring snowmelt while Cl^- peaks during the late fall. The difference in timing of peak concentration may reflect the fact that most of the Cl in fresh litter is in ionic form and is easily leached, unlike N which is mainly bound in organic compounds. In any event, the seasonality of Cl^- concentrations after the disturbances represents additional evidence for an important influence of plant uptake on Cl^- losses from the ecosystem.

The behavior of Cl^- after the devegetation and harvesting experiments is similar to the behavior of N after the same experiments, although the quantities of Cl^- lost and regained were much smaller (Figure 19). For each experiment, N was lost in large quantities from the watersheds after the experiments, and regained slowly in the following years (Bormann and Likens 1979; Likens et al. 1970, 1978). An important difference between the elements is that during the recovery phase, N accumulation in the ecosystem was more than sufficient to offset unmeasured sources like dry deposition, so that the net hydrologic flux of N was positive. In contrast, Cl^- accumulation during the recovery phase was not sufficient to offset unmeasured sources, and NHF remained negative in the 1980s and 1990s (Figure 16).

One could ask if the losses of N and Cl^- reflected their relative proportions in vegetative biomass. If we assume that the foliar concentration of N in the mature trees of Hubbard Brook is about 2.1% (Melillo et al. 1982) and the foliar concentration of Cl is about 0.04% (Berger et al. 2001), then the N:Cl ratio in foliage would be about 53 on a mass basis or 133 on a molar basis. As noted above, there were 0.382 kmol Cl^- ha^{-1} excess loss from W2 during the 6 years during and after the devegetation. If decomposition of foliage supplied most of the nutrients for these initial losses from the ecosystem, then we would expect $0.382 \times 133 = 50.8$ kmol ha^{-1} of excess N loss from W2. In fact, the N loss from W2 exceeded the loss from W6 by 33.9 kmol N ha^{-1} during the 6 years after the W2 devegetation (Likens et al. 1978). The fact that the N loss was less than would be expected from the N:Cl ratios in foliage suggests either that (1) other rapidly decomposing tissues (e.g., twigs, bark, roots) had lower N:Cl ratios, (2) there was a gaseous loss of N from the system or (3) there was N retention in soil organic matter, microbial biomass, or in the stream channel that was not matched by Cl^- retention.

We can also compare the retention of Cl^- during the recovery phase of the W2 experiment with the biomass aggradation during the same period to estimate the Cl^- concentration of the aggrading ecosystem. We calculated the concentration (C) of Cl in biomass for the measurement interval as:

$$C = \frac{(P_t - S_t) - (P_r - S_r)}{\Delta B_t} \tag{1}$$

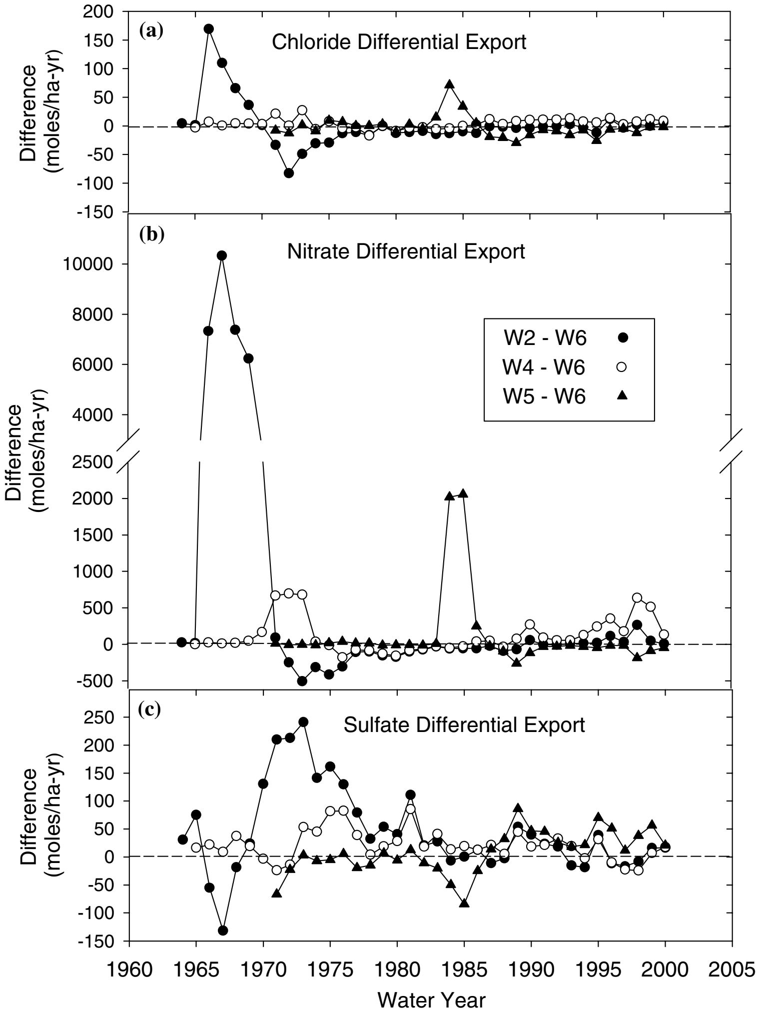

Figure 19. Ion export in disturbed watersheds minus export in watershed 6 plotted versus time for each of the disturbed watersheds. (a) Cl^-, (b) NO_3^{2-}, (c) SO_4^{2-}. Note break in vertical scale in (b).

where *P* and *S* are cumulative precipitation inputs and streamwater outputs, respectively, from the year revegetation began (1969) until the measurement year, ΔB is the accumulation of biomass over that period, and the subscripts *t* and *r* represent treated and reference watersheds, respectively. The calculations reveal estimated Cl^- concentrations in aggrading biomass that decline with time over the 20 years of recovery documented by Reiners (1992) (Table 2). This decline in calculated concentrations probably represents the increasing biomass accumulation of woody tissue as the succession continues, because

Table 2. Aboveground biomass accumulation at several times during the recovery of W2 (from Reiners 1992) and cumulative Cl^- retention in W2 for the same time periods, calculated from the difference in export between W2 and W6

Year	AG biomass (kg ha^{-1})	Cl^- retention (mol ha^{-1})	Calc Cl concentration (μmol g^{-1})
1971	2924	N/A	N/A
1973	7526	116	15.4
1979	24,439	265	10.8
1989	52,000	350	6.7

Estimated biomass concentration in W2 calculated using Eq. (1) in text. This calculation assumes we have completely measured Cl^- retention, and that all of the retention results from vegetation uptake.

woody tissues tend to have lower nutrient concentrations than foliage or fine roots. Concentrations of other nutrients in biomass also declined with time during the recovery (Reiners 1992). We should note that only aboveground biomass aggradation was reported by Reiners (1992), so actual concentrations of Cl^- in plant tissue would be expected to be lower than the values shown in Table 2 by the ratio of aboveground/total biomass accumulation. On the other hand, if a significant amount of Cl^- were desorbed from the soil after the disturbance, this would represent an additional Cl^- source in the watershed (increase in numerator of Eq. (1)) and would mean that our Cl^- concentrations in biomass are underestimated.

Note that the behavior of Cl^- after the experiments in watersheds 2 and 5 does not parallel the behavior of SO_4^{2-}, which is often considered a similar mobile anion in the soil (Figure 19). Sulfate showed a decline, rather than an increase, in export after these experiments. The decline in SO_4^{2-} export after disturbance has been attributed to nitrification-induced soil acidification, which increases the soil SO_4^{2-} adsorption capacity in the mineral soil (Nodvin et al. 1986). Chloride export, in contrast, does not appear to be strongly affected by the increased soil anion adsorption capacity. Similarly, Webb et al. (1995) found that after a severe insect defoliation of forested watersheds in Virginia, Cl^- concentration in stream water increased (as did NO_3, K^+, Ca^{2+}, and Mg^{2+}), while SO_4^{2-} concentration decreased. These data and ours from the HBEF suggest that Cl^- cycling and net export from these systems is controlled primarily by biological, rather than geochemical processes.

It is important to note an alternative possible explanation for the increased loss of Cl^- and the decreased loss of SO_4^{2-} after the harvesting experiments. The protonation of anion adsorption sites associated with the large inputs of nitric acid immediately after vegetation disturbance results in increased adsorption of SO_4^{2-} (Nodvin et al. 1988). Because SO_4^{2-} has a greater affinity than Cl^- for HBEF soils, it is possible that the increased adsorption of SO_4^{2-} following forest disturbance displaced Cl^- from soil anion adsorption sites resulting in a temporary release of Cl^- from the ecosystem for the period immediately following the disturbance. However, this process does not explain the seasonal cycling of Cl^- concentrations observed in stream water after the clearcuts.

Another important point is that during the recovery phase following deforestation, W5 and, at times, W2, were still net exporters of Cl^- (i.e., NHF < 0) (Figure 16). At first glance it may be difficult to reconcile this with our calculations above, which indicate net Cl^- accumulation in biomass during these recovery periods. However, we must also consider that the reference watershed (W6) exported even more Cl^- than either W2 or W5 during their recovery periods (Figure 16). The consistent net export of Cl^- from W6 that occurred after 1979 must arise from unmeasured net sources of Cl^- to the watershed. The nature of these sources is discussed below in 'Source of current net export of Cl^{-1}. If we consider the net export from W6 after 1979 to be an estimate of these unmeasured sources, and add that source to the inputs, then it becomes clear that both W2 and W5 accumulated Cl^- during their recovery periods.

Source of current net export of Cl^-

As discussed above, the NHF (bulk deposition inputs – stream water outputs) of Cl^- from W6 has been consistently negative since 1980. Considering only the years since 1982, when biomass accumulation in W6 has been negligible (Likens et al. 2002), the ecosystem has exported an average of 38 mol ha^{-1} $year^{-1}$ more Cl^- that it has received in bulk deposition. What is the source of this excess Cl^- ?

There are four potential sources: (1) Dry deposition not measured by the bulk deposition collector. Bulk deposition collectors trap some portion of the particulate dry deposition, but are not efficient at collecting fine particles or gases that could be deposited on the canopy (Lovett 1994). (2) Weathering of Cl^- from rocks. Some minerals contain Cl^-, and decomposition of those minerals by natural weathering processes could release Cl^- to the soil. (3) Desorption of Cl^- from the soil in response to lowered inputs of Cl^- and lowered concentrations in soil solution, and (4) Net release of Cl^- from SOM through mineralization. We can make estimates of some of these sources, but not others.

Dry deposition. For elements that are do not have significant uptake or release in the canopy, dry deposition can be estimated as the flux of the element in throughfall plus stemflow minus its flux in incident precipitation (e.g., Lindberg and Lovett 1992). We measured this 'net throughfall flux' of Cl^- near W6 for the growing seasons of 1989–1992, and found it to average 12.5 mol Cl ha^{-1} for the 4-month period. This value is an underestimate of the dry deposition of Cl^- because the estimate did not include stemflow, which can add 5–10% to below-canopy fluxes of Cl^- (Johnson and Lindberg 1992), and because it ignores dry deposition in the winter. Nonetheless, it would appear that dry deposition could account for a portion, but not all, of the measured NHF in the period 1982–2000 (38 mol ha^{-1} $year^{-1}$).

Weathering. Our best estimate of Cl^- weathering is 1.7–3.4 mol ha^{-1} $year^{-1}$ (see mineral weathering section above), which accounts for only about 4–8% of the NHF. This estimate is highly uncertain because there are few measurements of Cl in local rocks. Nonetheless, we think mineral weathering is probably a minor contributor to the NHF.

Desorption from the soil. If Cl^- is adsorbed onto soils during periods of high concentration in soil solution, and then is desorbed slowly as concentrations in soil solution decline, this process would constitute a net source of Cl^- during the desorption period. Our model estimates of the responses of soil Cl^- to changes in deposition indicate a moderate Cl^- desorption (about 7 mol ha^{-1} $year^{-1}$) between the mid-1960s and 1982, and little net adsorption or desorption after 1982 when deposition rates stabilized. Chloride is usually considered to be bound only electrostatically to soils (Mott 1981), suggesting a quick equilibration with soil solution and little time lag in net retention or release from soils. Also, the behavior of Cl^- after disturbance is nothing like the behavior of SO_4^{2-}, which is known to be more strongly adsorbed by iron and aluminum oxides (Nodvin et al. 1986). Furthermore, if Cl^- were being desorbed from minerals, we would expect its concentration in soil solution to increase as the water passes through the mineral soil horizons. In fact, Cl^- concentrations are lower in mineral horizons than in organic horizons (Figure 10). Given these considerations, we do not believe that desorption of Cl^- in these soils is a significant contributor to the current NHF.

Mineralization of Cl^- from SOM. Net release of Cl^- from decomposing SOM could occur if the SOM pool were declining or if the Cl content of SOM currently being formed were lower than the Cl content of SOM being mineralized. We have no data on Cl content or dynamics in SOM, and as such cannot evaluate this possibility quantitatively. Mineralization of S from SOM is thought to be an important process maintaining the current net export of S from W6 and other watersheds in the northeastern US (Likens et al. 2002; Gbondo-Tugbawa et al. 2001). However, S is different from Cl in that S in plants is primarily bound in organic compounds, whereas Cl is primarily in inorganic forms (Marschner 1995; Oberg 1998). Thus one might expect Cl to be leached out quickly in the initial stages of litter decomposition rather than released slowly through mineralization. However, we know that formation and mineralization of organic chlorine compounds occur during the decomposition process in soils (Myneni 2002; Rodsteth et al. 2003), and that the slow turnover of organic matter may cause enough of a time lag that the current release of Cl could be due to mineralization of Cl stored in organic matter formed during the high-deposition period of the 1960s.

In summary, our data are insufficient to attribute the NHF of Cl^- to any one source or combination of sources. Our best estimate is that dry deposition contributes one third to one half of the post-1982 NHF (38 mol Cl ha^{-1} $year^{-1}$), and the remaining 50% or more results from some unknown combination of sources, but probably largely from the mineralization of Cl from SOM. Given our general lack of information on Cl dynamics in SOM, this represents an important area of future research.

Change in net hydrologic flux over time

We noted above that there has been a distinct change in the NHF from W6 (the reference watershed) over time during this study. Early in the record (prior to 1979), the watershed showed years of net Cl^- export (NHF < 0) and years of net retention (NHF > 0). The mean NHF for the 1965–1979 period was $+11$ mol ha^{-1} year^{-1}. After 1979, the NHF was consistently negative, with a mean for the period 1979–1996 of -40 mol ha^{-1} year^{-1} (Figure 13c).

What could cause such a shift in the NHF? One possible explanation is an increase in unmeasured inputs. The negative NHF in recent years is partially due to inputs of Cl^- from dry deposition. If dry deposition were lower in the early years of the record, the NHF might have been more nearly in balance. However, this explanation does not seem likely. We have no reason to expect dry deposition inputs to have been lower during the early period; in fact, we expect that dry deposition rates were higher then because bulk deposition inputs were higher. Bulk deposition of Cl^- dropped from a mean of 140 mol ha^{-1} year^{-1} in 1967–1978 to a mean of 70 mol ha^{-1} year^{-1} in 1979–1996.

The other possible explanation for the change in NHF over time is a change in retention of Cl^- within the watershed. If we assume that dry deposition inputs were at least as high prior to 1979 as they have been since 1979, then the NHF indicates that there was a process causing watershed retention of Cl^- during the pre-1979 period that, on average, was slightly greater than the unmeasured dry deposition inputs, causing the slightly positive NHF. There are three principal candidates for this retention process: (1) Cl^- adsorption on Fe and Al sesquioxides in the mineral soil, (2) Cl^- incorporation into detritus and SOM, and (3) Cl^- sequestration into vegetation biomass. As discussed above, our model estimates indicate that Cl^- was probably desorbing from soils, rather than adsorbing to them, throughout the period of record. Similarly, although we know very little about the behavior of Cl during the formation and decomposition of SOM, it seems unlikely that the Cl concentration in SOM would be increasing during a period when the Cl^- deposition was decreasing. A caveat to this reasoning is that both Cl^- adsorption and incorporation into SOM are also affected by factors other than the supply of Cl^- itself. For instance, Cl^- adsorption may increase with decreasing SO_4^{2-} adsorption if the two anions compete for adsorption sites. In addition, formation of organic Cl compounds in SOM is influenced by pH and nitrogen availability (Oberg et al. 1996). The unknown influence of these secondary factors means that we cannot rule out changes in soil retention of Cl^- during this period.

We know, however, that accumulation of Cl^- in vegetation biomass can be a significant sink for Cl^-, as indicated in the discussion above concerning the recovery of the deforested watersheds. The total plant biomass (aboveground + belowground) on the reference watershed (W6) was estimated from tree surveys in 1965, 1977, 1982, and every 5 years thereafter. From 1965 to 1982 plant biomass was accumulating on the watershed, but since 1982 the biomass accumulation has been essentially zero (Likens et al. 1998, 2002). This biomass accumulation would represent a sink early in the record that has declined or disappeared at about the same time the Cl^- retention declined.

If we assume that the unmeasured sources of Cl^- to W6 prior to 1979 were equal to the mean net export of Cl^- (38 mol ha^{-1}) since 1982 (when the biomass aggradation ceased), then the retention process must account for, on average, at least 49 mol Cl ha^{-1} $year^{-1}$ (38 unmeasured sources + 11 measured net retention prior to 1979). Prior to 1977, forest biomass was accumulating at a rate of 4.85 Mg ha^{-1} $year^{-1}$ (Likens et al. 1994, 1998). If we assume that the concentration of Cl in accumulating tissue is similar to our calculated concentration after 20 years of recovery of W2 (6.7 μmol g^{-1}), then the accumulation of Cl in vegetation prior to 1977 would be 32 mol ha^{-1} $year^{-1}$. This value is lower than the expected retention process, but of the same order, and we must remember that the calculations of Cl content in vegetation in Table 2 are very crude estimates. Other studies of aggrading forests have reported higher rates of Cl accumulation in biomass. For instance, in a Japanese temperate forest that was accumulating aboveground biomass at a rate of 11.4 mg ha^{-1} $year^{-1}$, Ohrui and Mitchell (1996) calculated aboveground Cl accumulation of 141 mol ha^{-1} $year^{-1}$. These data indicate 12.4 mol Cl accumulation per mg of biomass accumulation (i.e., a weighted average Cl concentration in biomass of 12.4 μmol g^{-1}); if we use that ratio with our observed biomass accumulation rate (4.85 Mg ha^{-1} $year^{-1}$), we calculate a Cl accumulation rate of 60 mol ha^{-1} $year^{-1}$. This value is slightly higher than watershed retention of 49 mol ha^{-1} $year^{-1}$ calculated from the input–output budgets.

Because both the temporal pattern and the quantitative amount of Cl^- retention by the watershed approximately match our estimates of the accumulation of Cl^- in biomass, we suggest that biomass accumulation is the most likely process to explain the observed net retention early in the record. The rate of retention would have declined later in the record primarily because vegetative biomass accumulation has ceased, and secondarily because the atmospheric deposition of Cl^- has decreased, reducing Cl^- availability to plants.

Plotting the major terms in the Cl^- budget over time illustrates these trends Figure 20). The decline in the estimated biomass accumulation (‘B’ in the figure) of Cl^- from 1970 to 1982 coincides with the decrease in the residual term (‘R’) to consistent negative values. This residual term has been interpreted in other element budgets as a loss from a soil pool (e.g., for Ca, Likens et al. 1998; for S, Likens et al. 2002). In the case of Cl^-, although we do not know what accounts for the residual term, we believe that underestimates of dry deposition and mineralization of Cl from soil organic matter are the largest contributors to this residual term.

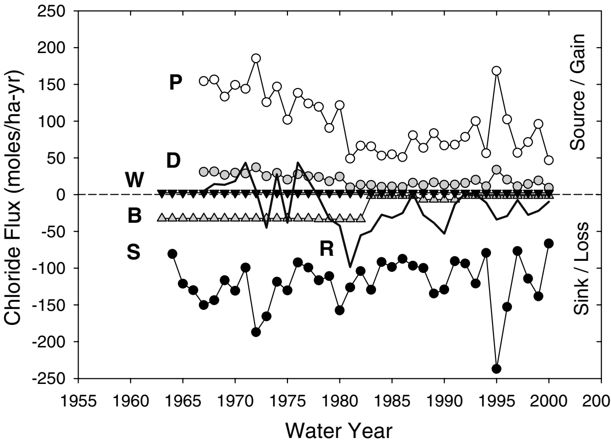

Figure 20. Trends in budget terms for Cl$^-$ from 1964–2000. P, bulk deposition inputs (measured); D, dry deposition inputs (estimated as 20% of bulk deposition, based on throughfall estimates that dry deposition is 50% of bulk deposition for the 40% of the year that the canopy is foliated (see text). Dry deposition in winter assumed negligible); W, weathering input (estimated at 1.7 mol ha^{-1} year^{-1}, see text); B, biomass increment (estimated at 32 mol ha^{-1} year^{-1} early in the record, declining as biomass increment declines, see text); S, stream flow export (measured); R, residual term (see text for discussion).

Summary and conclusions

Bulk deposition of chloride at the HBEF declined substantially during the 1970s, but has not shown a sustained trend since about 1981. Evidence presented in this paper suggests that in the 1960s and 1970s the dominant source of atmospheric Cl$^-$ deposition was from pollutant sources, probably coal burning. In the last two decades, however, the lower Cl$^-$ inputs are dominated by marine sources. Over the 34 years of this study there was no significant trend in chloride export in streamwater, but the net hydrologic flux (NHF = bulk deposition inputs – streamwater outputs) changed substantially. Early in the record the NHF was on average positive, indicating net retention of Cl$^-$ within the system, but since about 1981 the NHF has been consistently negative, indicating net export or an unmeasured source. We believe that accumulation of Cl$^-$ in vegetation during the 1960s and 1970s offset the unmeasured source and resulted in net ecosystem retention. Although we have no direct measurements of Cl$^-$ accumulation in vegetation, our estimates suggest that an aggrading forest could sequester at least 32 mol Cl ha^{-1} year^{-1}, or about a third of the annual average bulk deposition flux to this ecosystem. Accumulation of vegetative biomass on the reference watershed has ceased since about 1982, leading to the apparent net export (negative NHF) since that time. Dry deposition can account for at least part of the apparent net export, and we suggest that mineralization of Cl from SOM may also contribute.

Experimental Cl^- additions to the forest floor cause increases in Cl^- concentration in foliage, throughfall, and soil solution. Manipulations of vegetation also affect the Cl^- cycle. Harvesting or devegetation of watersheds causes an increase in the Cl^- concentration and flux in streamwater for several years after the disturbance. This period of release is followed by a period of reaccumulation of Cl^- that may last more than 15 years. During the reaccumulation period the Cl^- concentration in streamwater shows a seasonal cycle corresponding to vegetation uptake in the growing season and release from detritus in the dormant season. Uncut watersheds show no seasonal cycle. The behavior of Cl^- after disturbance parallels that of NO_3^-, for which export increases after disturbance due to reduced plant uptake and mineralization from detritus, rather than SO_4^{2-}, for which export decreases after disturbance due to pH-dependent adsorption into mineral soils. The seasonal cycling of Cl- after the disturbance represents an additional parallel between the behaviors of Cl^- and NO_3^-.

Thus, the interannual variation on Cl^- export from the system primarily reflects the atmospheric inputs, but the net retention and cycling of Cl^- within the system appears to be largely under biological, rather than geochemical, control.

This analysis has exposed many areas of inadequate knowledge of the Cl^- cycle in forests. Chief among those are the rates of dry deposition and mineral weathering, processes of Cl^- sorption and incorporation into organic matter in soils, and Cl^- concentrations in biomass, detritus, and soils. All of these subjects deserve more research. Meanwhile, the apparent importance of biological accumulation and release of Cl^- should dictate skepticism of studies that use Cl^- as a conservative 'tracer' in ecosystem studies.

Acknowledgments

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