Export of chloride after clear-cutting in the Hubbard Brook sandbox experiment

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Abstract. The objective of this study was to discern the source of higher than usual concentrations of chloride in drainage water collected from experimental forest plots after clear-cutting. When the sandbox experiments were initiated at the Hubbard Brook Experimental Forest Station three vegetation types were established: red pine, grass, and minimally vegetated (scattered lichens and bryophytes) as the "bare" control plot. After 15 years of growth the trees were cut down and above-ground biomass removed from the red pine sandbox. For several years prior to the cut, high concentrations ($\sim$ 75 μM) of dissolved Cl^- in drainage waters occurred in November/December. This is attributed to the buildup of rainfall-derived Cl^- due to evapotranspiration that depletes soil moisture to low levels resulting in a lack of drainage during this period. The excess Cl^- is quickly flushed out by subsequent drainage over a few weeks and Cl^- concentrations return to values characteristic of rainfall and throughfall. After the trees were removed in May, 1998, Cl^- continued to be leached from the system. The concentration of Cl^- peaked (175 μM) in Sept. 1998 and did not return back to base level concentration until Dec. 1999. The Cl^- release pattern is distinctly different from that of dissolved NO_3^-, which peaked about one year later than Cl^-. An excess (over that of the control sandbox) of 78 g Cl^- was released in the 1.5 year period after clear-cut, showing that a large amount of leachable chloride is stored in the bulk soil/root/ organic matter fraction. Lack of uptake by trees may be part of the reason for this chloride pulse. But an analysis of chloride content in roots and litter indicates that as much as 50% of the chloride leached from the sandbox may have come from the decaying roots and litter. Additional chloride may have been released from the soil organic matter by decomposition. The biochemical behavior of Cl^- in systems such as this should be evaluated before assuming Cl^- to be conservative for purposes of hydrological transport or soil weathering studies.

Introduction

Understanding the effects of experimental cutting on basic ecosystem processes is important to managers and scientists interested in sustainable forestry. Completely contained ecosystems such as the monolith or 'sandbox' type provide an opportunity to include a control and quantify ionic fluxes. F.H. Bormann and colleagues initiated the Sandbox Experiment at the Hubbard Brook Experimental Forest in 1983 to quantify levels of nitrogen fixation in pine ecosystems. Subsequent studies

allowed the use of these sandboxes to estimate primary mineral weathering rates (Bormann et al. 1998).

Chloride is an often-ignored element in biogeochemical studies of forested ecosystems. If chloride is even measured in forested systems, it is often for the purpose of using it as a hydrological tracer (c.f. Neal (1997)). Indeed, in most natural systems where Cl^- has been considered, it is found to behave conservatively (Velbel 1995). Chloride is a much-studied component of agricultural systems, where the concern is typically centered on plant response to high salinity resulting from irrigation (Staples and Toenniessen 1984). It has long been known that chloride is utilized by plants in photosynthesis, and is considered to be a micronutrient (c.f. Flowers (1984)).

Because mass balance dictates that output equals input plus any change in storage, and because input of chloride typically equals output of chloride, it is often assumed that storage in forested systems is negligible and that Cl^- acts as a conservative tracer of water movement. However, studies on decomposing spruce needles suggest that a net formation of organic chlorine takes place in the organic fraction of soil and this net change may be as large as 0.5 kg/ha/yr (Öberg and Grøn 1998). Recently, the halogenation of organic molecules in plant material has been shown to begin with dehydration of Cl^- and formation of H-bonds with organic functional groups as plant material ages (Myneni 2002). Consequently, because chloride is indeed utilized by plants, the steady state behavior of Cl^- in watersheds may not continue if a major perturbation occurs. In fact, in the early research at Hubbard Brook Likens et al. (1970) found a 65% increase in Cl^- concentrations in stream water about six months after clear-cutting of Watershed 2. They acknowledged the existence of a small chloride reservoir within the system. Some of this chloride was attributed to the herbicides that were used to prevent re-vegetation of the watershed, but the added chemicals did not account for all of the chloride that was released. The question as to the origin of this chloride remains unanswered. Dahlgren and Driscoll (1994) also noted a small increase in stream water chloride following clear-cutting of Watershed 5 at Hubbard Brook; however, they noted a small decrease or no change in soil water chloride. An increase of chloride output in stream water in connection with clear-cutting has been found also in many other investigations (Rosen 1990). There is obviously some question as to the conservative nature of chloride in systems undergoing perturbation. Might the removal of trees result not only in decreased uptake, but also decomposition of organic matter that results in a large export of chloride? The objective of the present study is to determine a potential source of higher-than-average chloride concentrations in water draining the sandboxes after clear cutting and removal of above-ground biomass.

Methods

Data presented here were collected from the sandbox experiments established at the Hubbard Brook Experimental Forest in central New Hampshire that have been previously described (Bormann et al. (1987, 1993)). Soil in the sandboxes (7.5 × 7.5 m) was comprised of a 15 cm layer of local water-washed stones, 1.9–3.8 cm in diameter covered by 1.3 m of 0.95 cm screened and homogenized glacial out-wash of granitic and metamorphic origin. Mixed topsoil (5 cm) from the original surface was tilled into the upper 20 cm of the sand to help the seedlings survive. Two vegetated sandboxes (one planted with red pine, the other with grass) and a control sandbox (containing only patchy bryophytes but here referred to as being bare) were lined with Hypalon (a DuPont polymer) that had been leached with rainwater to remove possible contaminants. The sandboxes were instrumented with a network of bottom drains leading to an underground chamber to measure water discharge and chemistry (Bormann et al. 1993). Water samples were collected on a weekly basis; the water analysis for each week represents a composite of the water collected over the seven days prior to sampling. Red pine seedlings were planted June 6, 1983. A buffer of six rows of seedlings was planted outside of the sandbox. All seedlings in the main part of the sandbox had 0.25 m^2 growing space. Height of border trees was not statistically different (p > 0.05, t-test) from non-border trees (Bormann et al. 1993).

In May 1998 all red pine above-ground biomass was carefully removed for analysis of cations and nutrients. Samples of soil, litter, and roots were all collected immediately after the clear-cut. Root matter was collected from trees cut from the buffer zone. No root matter was collected from inside the sandbox so that this me-socosm could be left in an undisturbed state for further study of the effluent. The soil was washed off the roots with tap water. After collection roots were separated by system and collar and oven dried (65 °C) samples were finely ground in a large blender or Wiley mill. A simple 24-hour deionized water rinse was completed to account for any background contamination that might have been present due to the tap water rinse. Chloride was extracted from the ground roots and litter by adding 40 ml 0.1 M NaNO3 to 1.0 g of root/litter and 1.5 g Garco G-60 activated carbon (Gaines et al. 1984). Extractions were placed on a shaker table for 48 hours, filtered, and analyzed on a Perstorp Analytical Enviroflow 3500 auto-analyzer. Chloride was extracted from the soil similarly to the roots, except that no activated carbon was necessary as there was no color interference.

Soil organic matter content was determined by combustion at 550 °C. Routine analyses on the water draining the sandbox were performed weekly on a composite sample. Anions were determined by ion chromatography.

Two throughfall collectors made up of a funnel and collection reservoir were placed 1.5 m off the ground in random locations within the pine sandbox. Samples were retrieved weekly during the growing seasons of 1994–1996. Throughfall volume data was acquired from the Hubbard Brook data archives for Watershed 6, site D. Site D was chosen to estimate water input from throughfall due to the evergreen vegetation (red spruce and balsam fir). Weekly rainfall data were obtained from the
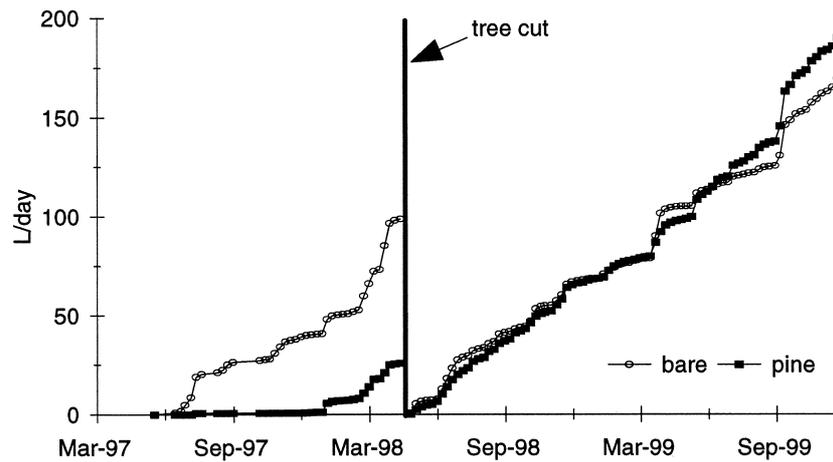
Figure 1. Cumulative discharge in pine sandbox before and after tree cut.

National Atmospheric Deposition and Precipitation site NH02, located at the base of the Hubbard Brook Experimental Forest.

Results

Because of the close spacing of the red pine trees, and the size of the trees after 15 years of growth, transpiration overwhelmed the hydrological inputs and resulted in a lack of discharge during the summer and early fall months. Immediately after the trees were cut and removed, the amount of water draining the pine sandbox became equal to that draining the bare sandbox (Figure 1). The long-term trend indicates that previous to the clear cut, the trees were transpiring to such a degree that no water was able to drain out of the pine sandbox during the growing season and an annual peak in chloride was associated with the end of the growing season (Figure 2).

Throughfall concentration data (three-year average) collected from the pine sandbox show a chloride concentration enrichment of 42.5% over rainfall. Measured throughfall chloride concentrations averaged 16.7 μmol/l (S.D. 12.1), whereas rainfall concentrations averaged 7.1 μmol/l (S.D. 8.7). Because only concentrations and not total volume of water were measured in the sandbox throughfall collectors, the annual volume of throughfall was estimated based on a four-year average for Hubbard Brook Watershed 6, site D. Based on the volume measurements of throughfall vs. rainfall, we assume that approximately 46% of the water volume entering the system is throughfall and 54% is incident rainfall. Applying these values to the pine sandbox, the amount of chloride entering the pine system was corrected to account for the contribution of throughfall (Table 1).

During three years prior to the cut various amounts of chloride were leached out of the pine system (Table 1). In 1995 more chloride was lost than was contributed
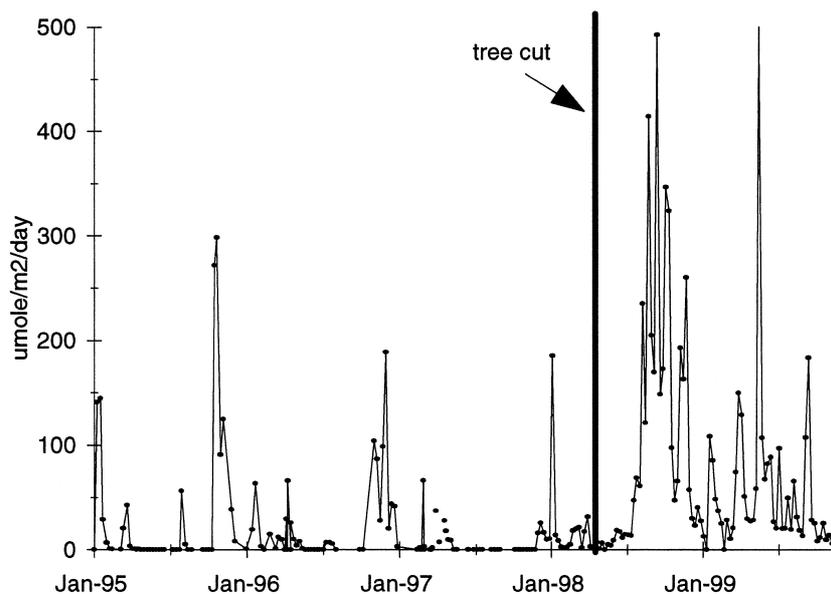
Figure 2. Long term trend of chloride flux from pine sandbox.

by rainfall and throughfall, but during 1996 and 1997 only 38% and 50% of the chloride entering the system was lost in drainage water. After clear-cutting the annual amount of chloride lost from the pine system was 917% of the input.

Both chloride and nitrate experienced peaks after clear-cutting. The nitrate peak showed a longer lag than that of the chloride (Figure 3, no water collected during the winter of 2000 due to freezing). Dissolved organic carbon (DOC) data are plotted for comparison (G. Hawley, written comm.). The amount of chloride leaching from the pine sandbox after clear-cutting was obtained by the difference between the fluxes in the pine and bare sandboxes (Figure 4). Integrating under this curve provides us with a total mass of 77.5 g excess chloride being released from the pine sandbox over the 1.5 years between clear-cut and return to baseline conditions.

Mean chloride content in the roots was 308 and 293 mg/kg for the system and collar roots, respectively, corrected for minor (10 mg/kg) Cl obtained during the DIW wash (Table 2). More than likely some of the chloride found in that rinse was not due to the tap water because whole roots (less surface area) were washed with tap water whereas ground roots were used for extractions. The total mass of roots in the sandbox was estimated based on the density of the trees and mass of roots per tree retrieved from the buffer zone. The litter layer provides another 5.9 g Cl^-. As compared to the amount of chloride in the roots and litter, the mass of chloride in the bulk soil is immense. Given its large mass, bulk soil could account for about an additional 1000 g of chloride based on the chloride extraction results. In contrast, the amount of chloride available in the bare sandbox bulk soil is only 283 g.

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Table 1. Mass of chloride in rain water, throughfall and in sandbox effluent during three years before cut and the first year post cut (mass reported on a per sandbox area (56.25 m^2) per year basis; standard deviation reported for original data in parentheses).

	BARE SANDBOX			PINE SANDBOX				
	Rainfall Cl, un-corrected (g)	Cl in effluent (g)	percent of input lost to output	Rainfall Cl, cor-rected (g)	Throughfall Cl (g)	Total input (g)	Cl in effluent (g)	percent of input lost to output
1995	11(0.4)	9(0.4)	82%	6	9	15	18(0.4)	120%
1996	23(1.0)	15(0.7)	65%	12	20	32	12(0.5)	38%
1997	6(0.1)	12(0.9)	200%	3	5	8	4(0.2)	50%
avg.	13	12	92%	7	11	18	11	61%
post-cut	6	9	150%	6	—	6	55	917%
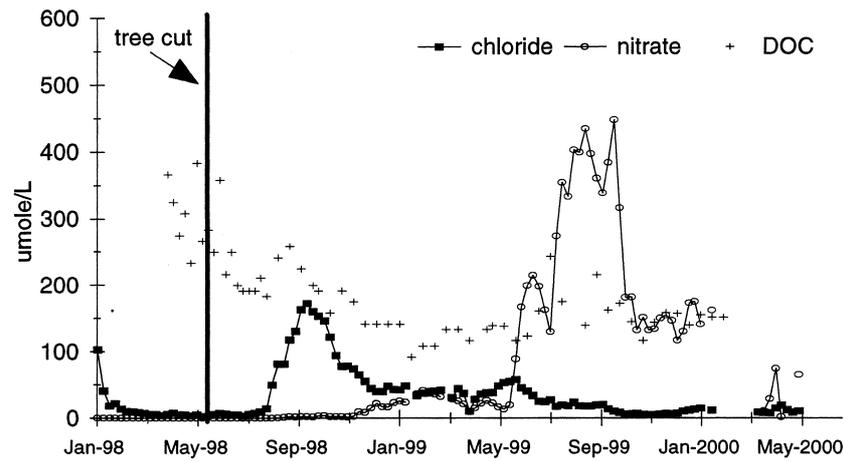
Figure 3. Chloride, nitrate and DOC concentrations in pine sandbox effluent.
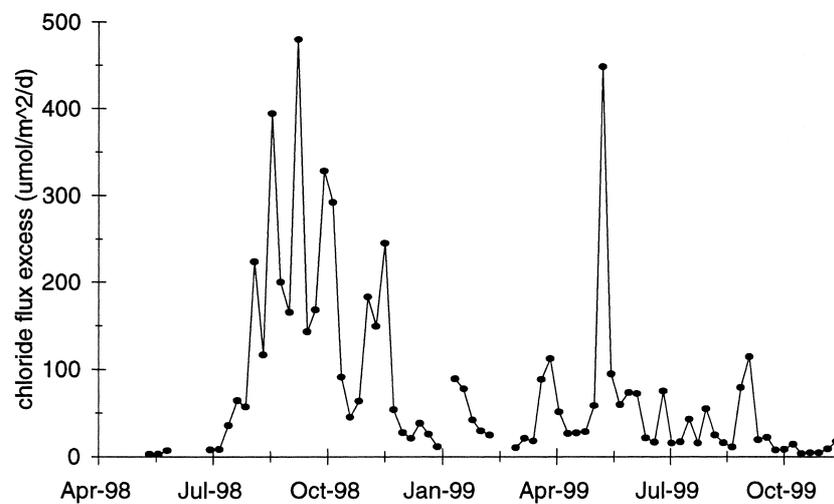
Figure 4. Post-cut difference in chloride flux between pine and bare sandboxes.

Discussion

In the last few years before the trees were cut down, intense evapotranspiration in the pine sandbox resulted in no drainage of water during the growing season. A lack of drainage led to a build up of chloride in the soils that was partly flushed at the end of the growing season when drainage commenced (Figures 1 and 2). Surprisingly, the average chloride mass leached from the bare and pine sandbox was similar prior to clear-cutting even with a 32% higher amount of input (due to throughfall) in the pine sandbox (Table 1). This strongly suggests a storage reser-

Table 2. Chloride mass in roots, litter, and bulk soil for the pine sandbox (chloride in bare soil presented for comparison). Unless otherwise stated, values are per sandbox area (56.25 m^2) and are calculated from May 5, 1998 to Nov 30,1999. Root chloride is corrected for DIW wash. Standard deviation shown in parentheses.

		Cl (mg/kg)	total mass (kg)	mass Cl (g)	% of total excess
Total excess chloride in outflow				77.5	—
Chloride from available sources:					
Roots	system	308(155)	40.8	12.3	16
	collar	293(230)	61.2	17.9	23
Litter		457(347)	1.3	5.9	8
Pine soil		13(9)	94,292	1226	1581
(Bare soil)		3(3)	94,292	283	

voir in the pine sandbox that was available for leaching after the entire above-ground biomass was removed.

The removal of trees results in drastically reduced uptake of chloride, and the lack of uptake may partially explain the pulse of chloride. A greater amount of chloride is seen exiting than can be accounted for in incoming precipitation and throughfall after the trees are removed suggests that not all the chloride is tied up in the above-ground tree biomass. Therefore, there must be some storage occurring in the soil/root/organic matter pool while the trees are still alive. For the period 1995–1997 the total amount of chloride entering the sandbox in rainfall and throughfall minus that lost in the effluent was 55 − 34 = 21 grams (Table 1), representing about 31% storage of Cl$^-$ input. If this represents typical storage for three years, then over the 12 year period, 1986–1998, the storage of Cl$^-$ could have been as much as four times higher or about 84 g. In the 1.5 years after the trees were removed, excess flux of chloride from the pine system was equal to 77.5 g, which is equivalent to about 12 years of storage. We discuss three potential sources of this excess chloride 1) root material, 2) soil microzones near roots, and 3) litter/soil organic material decomposition that leads to subsequent leaching of chloride.

Plant physiologists have long known that chloride is a micronutrient for plants. Chloride was first shown to be essential to photosynthesis by Warburg and Luttgens (1944). Biochemical functions require no more than 100 mg/kg chloride when tested in the lab, but concentrations in plant tissues are often found to be higher than this, probably due to field requirements of osmoregulation, interactions with other nutrients, and reaction to stress (Fixen 1993). At chloride levels as low as a few micro-molar the danger of chloride toxicity is not an issue. Instead, at lower concentrations such as are observed at Hubbard Brook, the plant may actually store chloride in the vacuoles for reasons of osmotic potential. When Cl$^-$ is in short supply the plant is forced to use energy-costly organic salts for turgor control (Fixen 1993). Because these trees were probably stressed for water every growing season there is good reason to believe that osmotic adjustment may have been achieved by accumulating solutes to lower the free energy of water in order to maintain the nec-

essary gradients for water retention in the cell. If chloride is stored for osmotic control, it may have been sequestered in the fine root material that was most likely lost during the process of removing the roots from the soil (power washing). This suggests our estimate of chloride available from the roots is conservative. In first examining the chloride available in the below-ground biomass, we found the amount of chloride extracted from the roots alone could account for about 40% of the excess chloride flux after tree-cutting (Table 2). It is doubtful, however, that all of the extractable chloride in the roots was available for leaching just a few months after the trees were cut. But considering that much of the finest, most easily degradable root material may have been lost, this may not be such a gross overestimate.

Because there was such an overwhelming amount of extractable chloride available from the pine soil, it would seem likely that this soil reservoir serves as the major pool of excess chloride. High transpiration rates create high soil-water demand at the root surface and concurrently attract a large flux of ions to the root. Although it is possible that micro-zones of high chloride existed, it is likely that they were available to water transport due to the fact that pore-scale transport gradients quickly reverse to release chloride to bulk solution as is seen in the annual flushing events (Figure 3). In fact, Parfitt et al. (1997) have shown that salts sequestered by *Pinus radiata* accumulate in soil micropores during the dry summer period and are slowly released to macropore flow during the rainy season. Although water in the soil most likely became concentrated with chloride during the growing season, the annual flushing event, in combination with hydraulic data indicating the moisture in the pine and bare sandboxes were similar every winter (K. Keller, written comm.), suggests that any water concentrated with chloride most likely exited the system on an annual basis.

Because organic matter was not removed from the soil prior to chloride extraction, the amount of extractable chloride soil represents not only the soil mineral fraction, but also the soil organic fraction, therefore the soil chloride may have an organic origin. Chlorine is found in organic compounds and Myneni (2002) has recently shown that organo-Cl compounds constitute the major Cl fraction in weathering plant material of soils. As the plant material is weathered, chlorine is transformed from the inorganic-Cl to organic compounds. How labile this chlorine may be is still unknown.

When considering the possibility of organic matter decay as a release mechanism for chloride, it is also interesting to note the relationship with DOC (Figure 3). In general, DOC declines after the clear-cut, but there is a small peak that occurs about a week prior to the chloride peak. The delay in the chloride peak is suggestive of a retardation mechanism typical in chemical transport through porous media. There may have been a pulse of DOC due to decomposition. The lag in chloride may represent the time it took for the labile chloride to be leached from the organic compound. Öberg et al. (1996) observed formation of organically bound chlorine during spruce needle decomposition. The net changes varied seasonally, with net formation during the fall and net mineralization during summer. Additionally, the lag in the nitrate peak is not inconsistent with an organic matter decom-

position origin of the chloride. The lag in the nitrate peak occurs as the nitrate pool builds up in the soil after the main source of uptake (trees) is removed. Nitrate is highly mobile and the only significant mechanism for immobilization is uptake and incorporation into vegetation. Bormann and Likens (1979) suggested the delayed response of nitrate release after clear-cutting arises from high C:N ratios of the material being decomposed early on when the dissolved nutrients in the soil water are assimilated by increasing populations of microorganisms. As the C:N ratio of the decomposing material decreases, the excess nitrogen-containing ions released by decomposition are leached from the soil profile.

There is ample evidence that this system was sequestering chloride and that this chloride was available for release after the trees were removed. Given the long tailing nature of the chloride release and evidence that annual flushing results in removal of any microzones of high chloride content, the most likely explanation of the source of the chloride lies in the decomposition of organic matter, including soil organic matter, roots, and leaf litter.

Conclusions

In many undisturbed forested systems chloride does seem to behave conservatively (Velbel 1995). Nevertheless, it cannot be denied that a perturbation, especially one as severe as complete clear-cutting, does effect chloride cycling. The fact that this system is an exaggeration of a natural system is acknowledged. And it is well known that ionic signals are attenuated as the size of the reservoir grows. However, quite a few larger scale studies have found chloride to behave less conservatively than expected (Likens et al. 1970; Rosen 1990). We conclude that careful consideration should be given by those attempting to use chloride in any conservative manner in a soil system subject to perturbation.

Acknowledgements

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