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Is chloride a conservative ion in forest ecosystems?

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Abstract Chloride (Cl^-) has often been assumed to be relatively unreactive in forest ecosystems, and is frequently used as a conservative tracer to calculate fluxes of water and other ions. Recently, however, several studies have detailed cycling of Cl^- in vegetation and soils. In this study Cl^- budgets are compiled from 32 catchment studies to determine the extent to which Cl^- is conserved in the passage through forest ecosystems. Chloride budgets from these sites vary from net retention (input > output) to net release (output > input). In the overall data set, including those sites with very high inputs of seasalt Cl^-, there was a strong correspondence between inputs and outputs. However, sites with low Cl^- deposition (<6 kg ha^{-1} year^{-1}) consistently showed net release of Cl^-, suggesting an internal source or a declining internal pool. The results indicate that Cl^- may be a conservative ion in sites with high Cl^- deposition, but in sites with low deposition Cl^- may not be conservative. We discuss the possible causes of the Cl^- imbalance and reasons why Cl^- may not be conservative in ecosystem functions.

Keywords Catchment · Chloride · Chlorine · Mass balance · Soil · Tracer · Watershed

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Introduction

Beginning with the work of Eriksson (1955), chloride (Cl^-) export from catchments in streamflow has been considered to be controlled primarily by Cl^- inputs in precipitation. Chloride is assumed in many studies to be largely unreactive in ecosystems, with little uptake or release by vegetation or soils (Schlesinger 1997). Chloride is often used as a conservative tracer in catchment mass balance studies, in that the increase in concentration in Cl^- as water moves through the ecosystem from precipitation to stream water is taken to be an indicator of water loss by evapotranspiration and is used to calculate water residence times (e.g., Kirchner 2003) and mass balances of other, non-conservative elements (e.g., Hedin et al. 1995). Mass balances of Cl^- in ecosystems have long been used for calculating water and solute transport (Lockwood et al. 1995), but are also used for risk assessments for e.g., nuclear waste (Campbell et al. 2003). The few studies that have focused specifically on Cl^- transport do indicate that there can be imbalances in catchment Cl^- budgets, which are typically attributed to unmeasured dry deposition (Juang and Johnson 1967), mineral weathering (Peters 1991) or interactions with vegetation and soil (Lovett et al. 2005; Öberg et al. 2005; Öberg and Sandén 2005; Svensson et al. 2007).

Several recent studies have indicated that, rather than being unreactive, Cl^- participates in a complex biogeochemical cycle (Öberg et al. 2005; Öberg and Sandén 2005; Bastviken et al. 2007, 2009). Chloride can be immobilized in ecosystems by several different processes, including (1) ion exchange (Larsson and Jarvis 1999), (2) adsorption onto iron and aluminum oxides (Nodvin et al. 1986), (3) uptake by biota, including vegetation and microbes (Ohrui and Mitchell 1996; Lovett et al. 2005; Bastviken et al. 2009), and (5) conversion to organic forms of chlorine (Clutterbuck et al. 1940; Myneni 2002; Bastviken et al. 2007). These processes may result in net retention of Cl^- in ecosystems on varying time scales when internal chlorine pools are increasing in magnitude or net release of Cl^- when internal pools are declining. In addition, Cl^- can be released by rock weathering from some bedrock types, providing an ecosystem input in addition to atmospheric deposition (Peters and Ratcliffe 1998; Lovett et al. 2005).

In this study, Cl^- mass balances for a range of catchments are compared to examine the extent to which Cl^- outputs reflect Cl^- inputs. Included data originate mainly from forested catchments in eastern North America and Europe spanning a wide range of climatic, hydrologic, geologic, and vegetation conditions. Our objective is to provide a framework for understanding relative controls on Cl^- mass balances, including the importance of sources and sinks in vegetation and soils. Additionally, we evaluate the limitations in data collection and analysis techniques used to compute the mass balances across a broad range of environmental conditions.

Materials and methods

Data were obtained from catchments in the North Temperate forest region (Table 1, Fig. 1). We added three nonforested catchments in Wales to increase the number of sites with very high Cl^- deposition. In most cases, the data had previously been published and we cite the reference in the text; if unpublished or supplementary data were included we state that in the text (see Table 1).

The catchments

The catchment studies were chosen based on availability of data, catchment size, land-use, % surface water, and sampling interval. Only small (<5 km^2), catchments that were free of recent large-scale physical disturbance and free of road salt application were considered. These criteria eliminated local differences in Cl^- export related to deforested or developed land. Also, only catchments with stream water chemical sampling intervals of 3 weeks or less were chosen to ensure that seasonal patterns and higher flow events were adequately represented. Thirty-two catchments were identified at 23 sites located in the Czech Republic, Estonia, Finland, France, Germany, Great Britain, Norway, Sweden, and United States. All of the catchments were forested except three catchments in Wales, Llyn Brianne and the two catchments at Plynlimon, which were included to improve the number of sites having high Cl^- deposition. Details about the catchment characteristics are given in Table 1.

Input and output data

In the catchment studies, annual inorganic Cl budgets were compiled using existing flux data or stream and precipitation volume and chemistry data. These data cover in most cases a period of over 10 years (range 1–33 years) (Table 1). For input estimates, some of the data sets included throughfall (13 sites), and others included bulk deposition (18 sites) and one had only wet-only deposition (Panola Mountain). Bulk deposition is collected in a continuously open funnel, and as such it collects wet deposition and the portion of the dry deposition that impacts on the walls of the funnel or falls into the funnel by gravity (Likens and Bormann 1995). None of the catchments had independent estimates of Cl^- dry deposition. We consider the Cl^- balances to be more complete in those catchments that had throughfall data because dry deposition and cloud-water deposition are washed off the canopy in throughfall and therefore included in the throughfall measurement. Inputs are underestimated by wet-only or bulk deposition measurements, which do not include all of the dry and cloud deposition. Cloudwater was collected at the Welsh sites, with the four catchments (Reynolds et al. 1997; Neal et al. 2004, 2010), but the atmospheric input was estimated based on a modeled term for cloud water inputs because the cloudwater collector was not designed to give a correct estimate of the areal average volume of cloudwater. We noted on our

Table 1 Description of the catchment sites in the study

Site and location	Latitude, longitude	Size (km^2)	Forest type	Sampling years	Deposition sampling method	Cl input/output (kg ha^{-1} year^{-1})	Ref.
Aneboda, Sweden	57°07′N, 14°32′E	0.19	Coniferous	9	TF	13.9/19.6	1
Bear Brook, ME, USA	44°52′N, 68°06′W	0.11	Deciduous	3	TF	15.4/19.6	2
Birkenes, Norway	58°23′N, 08°15′E	0,42	Coniferous	19	BD	33.7/52.9	3
Coweeta-14, NC, USA	35°03′N, 83°25′W	0.61	Deciduous	4	BD	7.0/6.4	4
Coweeta-18, NC, USA	35°03′N, 83°25′W	0.13	Deciduous	12	BD	5.7/6.3	4
Coweeta-2, NC, USA	35°03′N, 83°25′W	0.12	Deciduous	12	BD	5.1/6.2	4
Coweeta-27, NC, USA	35°03′N, 83°25′W	0.39	Deciduous	12	BD	9.4/9.2	4
Coweeta-32, NC, USA	35°03′N, 83°25′W	0.41	Deciduous	4	BD	8.4/8.5	4
Coweeta-34, NC, USA	35°03′N, 83°25′W	0.33	Deciduous	4	BD	6.6/7.4	4
Coweeta-36, NC, USA	35°03′N, 83°25′W	0.49	Deciduous	12	BD	6.2/9.9	4
Fernow forest, w-4, WV, USA	39°02′N, 79°41′W	0.39	Deciduous	15	BD	2.1/3.6	5
Forellenbach, Germany	48°56′N, 13°25′E	0.69	Coniferous	16	BD	4.6/8.4	3
Gammtratten, Sweden	63°51′N, 18°07′E	0.45	Coniferous	6	TF	2.0/2.9	1
Gårdsjön, Sweden	58°03′N, 12°01′E	0.37	Coniferous	10	TF	96.0/93.3	6
Hietajärvi, Finland	63°09′N, 30°40′E	4.64 (24% lake)	Coniferous	15	BD	1.0/1.3	3
Hubbard Brook, w-3, USA	43°56′N, 71°45′W	0.42	Deciduous	29	BD	3.1/4.2	7
Hubbard Brook, w-6, USA	43°56′N, 71°45′W	0.13	Deciduous	33	BD	3.5/4.3	7
Kindlahöjden, Sweden	59°45′N, 14°54′E	0.19	Coniferous	9	TF	8.9/9.2	1
Kosetice Observatory, Czech Republic	49°34′N, 15°05′E	0.29	Coniferous	18	TF	5.4/2.9	8
Lehstenbach, Germany	50°08′N, 11°52′E	4.2	Coniferous	6	TF	11.1/10.7	9
Llyn Brianne catchment C16, Great Britain	52°08′N, 03°44′E	0.72	Heath/grass	2	BD	76.1/78.3	10
Lysina, Czech Republic	50°03′N, 12°40′E	0.27	Coniferous	1	TF	10.1/5.6	11
Maryland, HCWS, USA	39°27′N, 79°25′E	2.55	Deciduous	1	TF	4.3/8.7	12
Panola Mountain, GA, USA	33°37′N, 84°10’W	0.41	Deciduous	12	WD	2.8/5.92	13
Pluhuv Bor, Czech Republic	50°04′N, 12°46′E	0.22	Coniferous	1	TF	6.0//5.2	11
Plynlimon catchment Afon Cyff, Great Britain	52°25′N, 03°40′E	3.07	Heath/grass	2	BD	120.4/125.7	10
Plynlimon catchment, Upper Hafren, Great Britain	52°29′N, 03°43′E	1.17	Moorland	18	BD	135.1/140.9	16
Plynlimon catchment, Nant Tanllwyth, Great Britain	52°28′N, 03°43′E	0.51	Coniferous	5	BD	175.5/165.6	17

Table 1 continued

Site and location	Latitude, longitude	Size (km^2)	Forest type	Sampling years	Deposition sampling method	Cl input/output (kg ha^{-1} year^{-1})	Ref.
Saarejärve, Estonia	58°39′N, 26°45′E	3.32	Coniferous	13	TF	5.4/3.6	14
Steinkreuz, Germany	49°52′N, 10°27′E	0.5	Deciduous	6	TF	7.6/7.7	9
Strengbach, France	48°10′N, 07°22′E	0.8	Mixed coniferous/deciduous	3	TF	20.1/20.3	15
Valkea-Kotinen, Finland	61°14′N, 25°03′E	0.3 (12% lake)	Coniferous	15	BD	1.4/3.1	3

Deposition sampling method: *TF* throughfall, *BD* bulk deposition, *WD* wet deposition only

1. Integrated monitoring in Sweden, Swedish Environmental Research Institute, 2007-October
2. Rustad et al. (1994), Colin Neal, Centre for Ecology & Hydrology, UK, personal communication, September-2010
3. ICP Integrated Monitoring Programe Centre, Finnish Environment Institute 2009-September
4. Swank and Crossley (1988)
5. USDA Forest service (Mary Beth Adams, USDA Forest Service, personal communication, October 5, 2006)
6. (Hultberg and Grennfelt 1992)
7. Cary Institute of Ecosystem Science, 2007-October
8. Czech Hydrometeorologicla Institute, 2009-September
9. Matzner (2004)
10. Reynolds et al. (1997)
11. Kram et al. (1997)
12. Castro and Morgan (2000)
13. Peters et al. (2006)
14. The Estonian Environment Information Centre 2009-October
15. Probst et al. (1992)
16. Neal et al. (2010), Colin Neal, Centre for Ecology & Hydrology, UK, personal communication, September-2010
17. Neal et al. (2004), Colin Neal, Centre for Ecology & Hydrology, UK, personal communication, September-2010

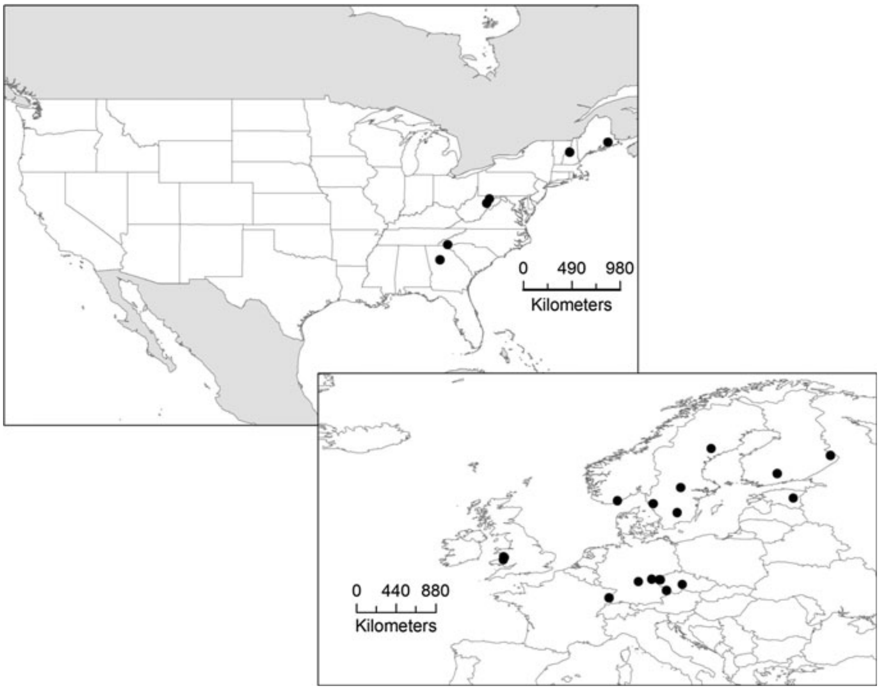

Fig. 1 Map of Europe and North America showing locations of catchment sites

graphs which catchments had throughfall data and which did not.

Output was estimated from streamwater data for the catchments. Details of the data set are given in Table 1.

Results

The annual average precipitation for the catchments ranged from 750 mm at Steinkreuz catchment (Germany) to 2650 mm at Upper Hafren catchments (Wales, UK).

The Cl^- inputs and outputs vary from year to year, and in most cases in this data set we were able to average across several years (Table 1). There was a large variation in Cl^- input in the data set, although most of the sites were below 20 kg ha^{-1} $year^{-1}$ (Fig. 2). The median Cl^- input was 6 kg ha^{-1} $year^{-1}$. The Cl^- input was lowest at Hietajärvi (Finland) with average annual input of 1 kg ha^{-1} $year^{-1}$. The highest input was at Nant Tanllwyth (Wales, UK) at 175 kg ha^{-1} $year^{-1}$.

The Cl^- budgets in this study show that the sites varied from net release to net retention of Cl^-. In general, there were more sites (app. 70%) showing a net release than those showing a net retention of Cl^-. Less than half of the catchments (40%) were in balance to within ±10% (i.e., (input–output)/input < 0.1) (Fig. 3). The imbalance reached as high as −123% for one catchment (Valkea-Kotinen, FI).

The catchment data show strong relationships between Cl^- inputs and outputs (Fig. 2). A simple linear regression of the data show a R^2 of 0.99 ($p < 0.001$) and the 1:1 line is within the 95% confidence interval of the regression line. That means when the entire data set is considered, the Cl^- output in general reflects the Cl^- input. Closer examination of the data with low Cl^- input (i.e., < 25 kg ha $^{-1}$ $year^{-1}$), suggests that the slope diverges more from the 1:1 slope. In order to emphasize the shape of the relationship between the two variables and to more objectively analyse where the Cl budget data are diverging, we fit the data with a LOESS curve (Epanechnikov kernel with 90% smoothing) created in SPSS (SPSS Statistics 17.0). The LOESS curve through the data draws attention to a deviation from the 1:1 line for the catchment data receiving less than approximately 6 kg ha $^{-1}$ $year^{-1}$ (Fig. 2b). For catchments with Cl deposition input more than 6 kg ha $^{-1}$ y^{-1} the curve approximates the 1:1 line.

For the sites that had multiple years of input and output data, in some cases the net balance was consistently positive or negative, but in other sites the

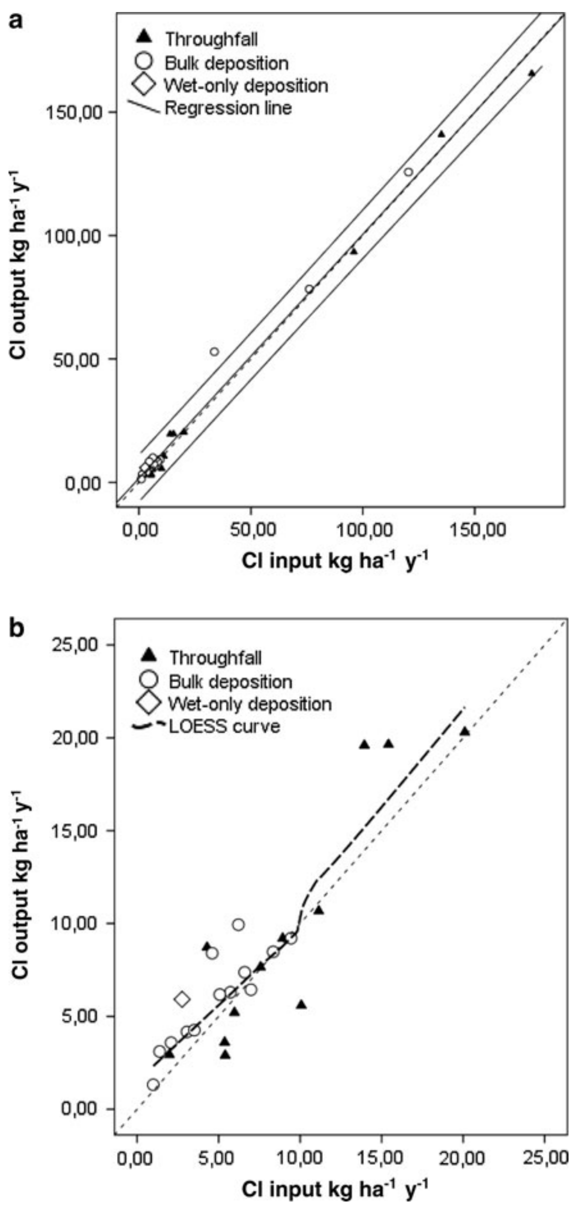

Fig. 2 **a** Relationship between chloride inputs and outputs for all investigated catchments. The *triangles* represent sites that used throughfall, the *circles* represent sites that used only bulk deposition for the estimate of input, and the *diamond* represents a site that used only wet-only deposition. The linear regression line and its 95% confidence limits are shown. **b** Input and output data for catchments with input <25 kg ha year. The LOESS curve is the *dashed line* through the data. The *dotted line* is the 1:1 line

sign of the net balance varied from year-to-year. The Hubbard Brook Experimental Forest (New Hampshire, USA) had the longest record, and it switched from net retention (input > output) of Cl^- for most years prior to 1981 to net release (output > input) for most years after 1981. Lovett et al. (2005) interpreted this pattern to be the result of a reduction of the sink associated with forest growth in the catchment. Other sites in our data set changed back and forth between net retention and net release in different years without any obvious pattern, possibly related to hydrologic conditions in the catchment, although there is no clear relationship between net flux and precipitation amount in the data ($R^2 = 0.0016$).

Discussion

The quality of Cl^- data is critical in calculations of mass balances of solutes and calculations of water transport. Small imbalances could result from measurement errors. In this study, almost half of the sites have imbalances of greater than 25%, and such large deviations could represent sources or sinks of Cl^- in the ecosystems, which would have major implications for solute transport and water balance calculations that assume that Cl^- behaves conservatively.

Overall, the catchment data show a strong 1:1 relationship between Cl^- inputs and outputs, but for catchments with low Cl^- deposition (<6 kg ha^{-1} $year^{-1}$) outputs are almost always greater than inputs. Does this apparently nonconservative behavior result from methodological problems or real sources and sinks of Cl^- in the ecosystems?

Methodological issues in measuring ecosystem inputs and outputs are well known. Atmospheric inputs consist of wet deposition (Cl^- dissolved in precipitation), dry deposition (direct deposition of gaseous and particulate Cl^-) and at some sites, cloud-water deposition (Cl^- dissolved in cloud droplets that deposit directly to vegetation) (Lovett 1994). Measurements of dry and cloud water deposition are particularly vexing. For atmospheric deposition estimates, ecological studies typically use some combination of the following measurements: (1) wet-only precipitation in collectors that are open only during precipitation events, (2) bulk deposition in continuously open collectors, which collect wet deposition and the fraction of the dry deposition that results from particles large enough to settle from the atmosphere, (3) dry deposition of particles estimated from atmospheric concentration measurements and deposition models, and (4) throughfall and stemflow measured using funnels and tree

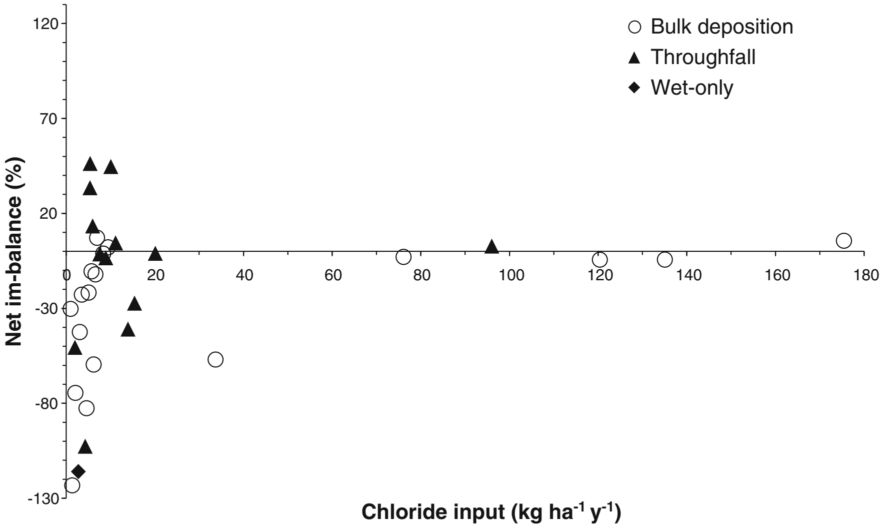

Fig. 3 The % net balance [(input − output)/input × 100] of chloride in each catchment versus input for each catchment. A positive % means a net retention of chloride and a negative % means a net loss of chloride. A higher % means a larger imbalance in the chloride budget

collars below the canopy. Throughfall plus stemflow fluxes provide an integrative measure of total deposition to the canopy, assuming there is minimal leaching or uptake of Cl^- by the canopy (Hultberg and Grennfelt 1992). Canopy leaching of Cl^- is usually negligible (Lovett et al. 2005). In this study we used throughfall, when available (in 13 catchments), as the best estimate of total Cl^- input. Because some of the catchment studies in our study did not have throughfall data, we estimated inputs using bulk deposition or wet-only deposition, whichever was available. Including any unmeasured dry deposition in these input estimates would move those points represented by circles and squares to the right on Fig. 2a and b. For the nine catchments in our data set that have both throughfall data and bulk deposition data, we estimated the contribution of dry deposition (calculated as throughfall–bulk deposition) to the total throughfall deposition and found it to range from 15 to 75% (mean 43%) of the total throughfall deposition. Because of this variation it is difficult to estimate how much the bulk deposition points in the graphs would change if dry deposition were known and included in the deposition estimate.

Output estimates are also problematic. For these catchment sites, export is estimated as the product of the streamflow (measured at a stream gauging site at the outlet of the catchment) and the Cl^- concentration in stream water measured at the same site. Because stream output can be episodic, the frequency of measurement may affect the accuracy of the export estimates. Stream water concentrations of Cl^- vary with streamflow in some watersheds (e.g., Peters et al. 1998) but not in others (e.g., Johnson et al. 1969). Rainfall and throughfall can decrease the soil water and streamwater concentrations of Cl^- through dilution, but may also increase the Cl^- concentration through movement of soil water with high Cl^- concentrations (Peters et al. 1998). However, the relationship is more complicated as it has also been observed that concentrations may vary seasonally, probably because of different soil conditions and water transport processes (Peters et al. 1998; Kirchner 2003; Lovett et al. 2005; Svensson et al. 2007) or vegetation uptake (Lovett et al. 2005). Seasonal and stream flow variability certainly have an effect when estimating short-term (<1 year) output fluxes, but when several years are averaged the errors are small (Alewell et al. 2004).

Few of the catchment studies have attempted to evaluate uncertainty in the measurements. However, at one of the best-studied sites, Hubbard Brook Experimental Forest in New Hampshire, USA, the analytical uncertainty for chloride determination has been estimated to be less than 5% (Buso et al. 2000) and the uncertainty of water flux measurements in precipitation and stream flow is also estimated to be less than 5% (Bailey et al. 2003). Uncertainty for the dry deposition component at this site is unknown but is would be substantially higher (Lovett et al. 2005). The uncertainties in input and output measurements are not unique to chloride, and in fact would be at least as large for budgets of other ions, although the issue is rarely addressed.

Given these uncertainties in the inputs and outputs, we suggest that the most reliable conclusions can be drawn from general patterns of chloride budgets across sites, rather than from the budget for any individual site.

Is chloride conservative?

Considering the data set as a whole, there is a strong 1:1 relationship between Cl^- inputs and outputs, indicating a conservative behaviour of chloride in the forests. However, for sites with low Cl^- inputs (<6 kg ha^{-1} $year^{-1}$), which includes about a third of the catchments in this study, there is a consistent net release of Cl^- in the catchment data sets. This pattern was observed even for the two low-deposition sites that used throughfall as an estimate of deposition. This net release could be due to unmeasured inputs from rock weathering, but the fact that the discrepancy in the Cl^- balance is pervasive at low-deposition sites and that Cl^- in bedrock is rare suggests that another factor may be responsible, likely a net decline in an ecosystem Cl^- pool. Vegetation can contain an appreciable pool of Cl^-, and aggrading vegetation can sequester Cl^- while vegetation disturbance can release that Cl^- (Lovett et al. 2005). In this data set, because the net release is occurring across many catchments with forests of different ages and vegetation types, vegetation is not likely to be the major control. More likely it is a net release of Cl^- from the soil pool. This release could occur through desorption of Cl^- that was previously adsorbed to iron and aluminum oxides (Nodvin et al. 1986), especially if soil solution concentrations were decreasing. Another possibility is net release of Cl^- from soil organic matter (SOM). The Cl^- can be bound into SOM as organochlorine compounds created by microbial action (Myneni 2002; Bastviken et al. 2007; Ortiz-Bermudez et al. 2007) and the Cl^- can be re-mineralized as SOM is decomposed. If the mass of SOM or the Cl:C ratio were declining, there would be a net release of Cl^- over time. The data from low-input sites in this study suggest some leaching of that Cl as the inorganic Cl^- ion, but the Cl could also be leached in an organic form, and in fact organically bound Cl has been found in both soil water and stream water (Asplund and Grimvall 1991; Rodstedth et al. 2003). However, we are aware of only one study that has analysed the output of organically bound Cl on a catchment scale, and the output flux of organically bound Cl was only a few percent of the Cl^- fluxes (Svensson et al. 2007).

In the past decade, studies have revealed that Cl^- participates in a complex biogeochemical cycle (Asplund et al. 1991; Winterton 2000; Lee et al. 2001; Myneni 2002; Öberg 2002), involving for example, formation and degradation of chlorinated organic matter (consumption and release of Cl^-), volatilization, leaching and precipitation (Asplund et al. 1993; Öberg and Grön 1998; Dimmer et al. 2001; Hoekstra et al. 2001; Johansson et al. 2001; Rodstedth et al. 2003; Öberg et al. 2005). Areas receiving rather high Cl^- deposition (30–50 kg ha^{-1} $year^{-1}$) on the west coast in Sweden have a higher amount of chlorinated organic matter in the soil than sites on the east coast receiving Cl^- amounts of less than 5 kg ha^{-1} $year^{-1}$ (Johansson et al. 2003). In addition, a soil-column study showed that long soil water residence time and high Cl^- load gave higher initial retention and subsequent release rates of Cl^- in soils (Bastviken et al. 2006). It is therefore without doubt that Cl^- can be retained and released within the soil, but how such processes affect mass balances at the watershed or plot scale has not been thoroughly investigated.

It is unclear why a net release was observed predominantly in the low-deposition sites in our data set. One possibility is that it is in fact happening at most sites, but is easier to observe in the low-deposition sites because the input and output fluxes are smaller. In areas receiving very large loads of seasalt, the Cl^- output almost equals the input, but this balance does not preclude internal cycling of Cl^- (Kelly et al. 2008). The portion of the Cl^- flux that would participate in ecosystem retention or release processes is negligible in environments with very high Cl^- deposition, compared to environments with low Cl^- deposition where it could have major influence.

Another possibility for the net release being observed mainly in low-deposition sites is that release from the SOM or sorbed Cl pools may be caused by reduction in Cl^- in soil solution associated with reductions in Cl^- deposition. The sites in this study are in eastern North America and Europe, where reduction in Cl^- deposition has occurred in recent decades as a result of efforts to reduce sulfur emission from power plants, because the processes that remove sulfur also remove HCl (Lovett et al. 2005). It is likely that our high-deposition sites receive most of their Cl^- deposition from marine sources, whereas the lower-deposition sites may receive a substantial fraction of their inputs from pollution sources. Because the pollution sources have declined but the marine sources have remained relatively constant, the release of Cl^- would be most evident in low-deposition systems.

Chloride is a generally highly abundant in soil and retention and mineralization of the anion in soil organic matter appears to be common (Bastviken et al. 2007). Therefore, we are not surprised to see effects of such processes at the catchment scale. On the other hand the major driving variables for those processes are unknown, but likely include Cl^- input among other variables. Further research is needed to understand the processes behind Cl^- retention and mineralization and its consequences on catchment Cl^- budgets.

In conclusion, this synthesis of data indicates that Cl^- may act as a conservative ion under conditions of high Cl^- deposition, but not under condition of low deposition (less than about 6 kg ha^{-1} $year^{-1}$), and that processes controlling net retention and release of Cl^- from plant and soil pools may be relatively more important in ecosystems with low or moderate Cl^- deposition. These results highlight the need for better understanding of the processes of Cl^- cycling in soils and vegetation.

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