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The role of organic-matter-bound chlorine in the chlorine cycle: a case study of the Stubbetorp catchment, Sweden

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Abstract. The objective of this study is to construct a balanced chlorine budget for a small forested catchment, focusing on the interaction between chloride (Cl_{inorg}) and organic-matter-bound chlorine (Cl_{org}). Data from the actual catchment are combined with secondary data from other sites to elucidate more clearly which parts of the cycle are fairly well known and which are more or less unknown. The budget calculations show that the principal input and output fluxes of Cl in the catchment are inorganic but that the main pool is Cl_{org} in the soil. In addition, the budget calculations suggest that a considerable portion of Cl_{inorg} in soil is transformed to Cl_{org} and subsequently leached to deeper soil layers, that net mineralization of Cl_{org} takes place in soil, preferably in deeper soil layers, and that degrading organic matter is a major source of Cl_{inorg} in runoff. The loss of Cl_{org} through runoff is small to negligible in relation to other fluxes. It appears as if dry deposition of Cl_{inorg} is at risk of being underestimated if Cl_{inorg} is assumed to be conservative in soil. The pool of organic-matter-bound chlorine in soil is considerably larger than the annual flux of chloride through the system. The estimates suggest that the amount of Cl_{org} in the upper 40 cm of the soil at the investigated site is approximately twice as large as the Cl_{inorg}. Furthermore, the amount of Cl_{org} biomass is small in relation to the occurrence of Cl_{org} in soil. Finally, the estimates indicate that the transport of volatile Cl_{org} from the soil to the atmosphere may influence the chlorine cycle.

Introduction

It is well documented that chloride participates in a complex biogeochemical cycle (Neidleman and Geigert 1986; Asplund and Grimvall 1991; Grimvall and de Leer 1995; Gribble 1996; Winterton 2000; van Pee 2001; Laturnus et al. 2002; Öberg 2003). Still, it is widely believed that all chlorinated organic compounds are xenobiotic, that chlorine does not participate in biological processes, and that it is present in the environment mainly as chloride ions (Cl_{inorg}) (e.g. Schlesinger 1997). In the late 1980s, it was revealed that large amounts of naturally formed chlorinated organic compounds are present in the environment (Müller and Schmitz 1985; Asplund et al. 1989; Enell et al. 1989). Continued studies have made clear that a vast array of organisms (e.g. fungi, bacteria, lichen, algae, higher plants, insects, vertebrates) are able to convert chloride to organic chlorine, that thousands of chlorinated compounds are produced naturally, and that organic-matter-bound chlorine is as abundant as the chloride ion, at least in organic soil (Gribble 1996; Hjelm 1996). Notwithstanding these findings, the biogeochemical cycling of chlorine must still be considered a virgin area of research, as very little is understood of the major sources, sinks, and transport routes as well as of the underlying processes.

Chlorine is one of the most abundant elements on the surface of the earth. In soil, it is present both as chloride ions (Cl_{inorg}) and as an integrated part of the organic matter, i.e. organically bound (Cl_{org}) (Hjelm 1996; Johansson 1996; Myneni 2002). The major source of Cl_{inorg} is the oceans, whereas organic-matter-bound chlorine originates from a variety of sources. The geochemical cycling of Cl_{inorg} – i.e. the cycling of Cl_{inorg} which is driven by a combination of physical forces (such as wind, water, and fire) and chemical forces (such as weathering, precipitation, and ion exchange) – has been studied for decades. Research into the more complex *bio*geochemical cycling that involves the formation, degradation, and cycling of inorganic as well as organic chlorine compounds is newer. Consequently, there is extensive information on the geochemical cycling of Cl_{inorg}, but far less is known of the biogeochemical cycle of chlorine as a whole, involving both Cl_{inorg} and Cl_{org}.

Aim

The objective of the present study is to construct a balanced chlorine budget based on best possible estimates of the various components in the cycle for a forested catchment in SE Sweden to elucidate, on a general level, which parts of the terrestrial chlorine cycle are fairly well known and which are more or less unknown. The starting point for constructing the budget is the conceptual model outlined in Figure 1. The main fluxes (Cl_{inorg} in precipitation and stream flow) and pools (Cl_{inorg} and Cl_{org} in soils) are measured at the specific catchment whereas the other pools and fluxes are based on data from other sites. Each component of the budget is estimated and the reliability of each estimate is subsequently discussed and evaluated in relation to current knowledge and in relation to its relative importance in relation to other components in the budget.

Site description

The Stubbetorp catchment (58°44′ N; 16°21′ E) is situated in the southeast of Sweden in the county of Östergötland, near the coast of the Baltic Sea (Figure 2). The catchment is 0.87 km^2 and is situated in a forested, mountain area. The bedrock is granite and thus poor in chloride. The approximate altitude is 100 m a.s.l. The long-term annual mean precipitation of the region is approximately 600 mm and the annual mean temperature is about 6 °C (Raab and Vedin 1995). The hydrology and hydrochemistry of the catchment has been described in detail by Maxe (1995).

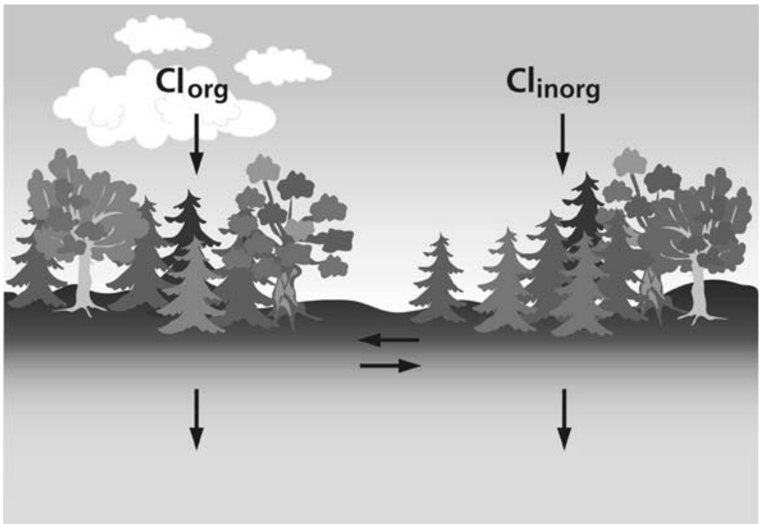

Figure 1. A conceptual model of the chlorine cycle in the terrestrial environment. From the right to the left the arrows in the figure illustrate input of Cl_{inorg} by e.g. wet-deposition; output of Cl_{inorg} by leaching; input of Cl_{org} by e.g. wet-deposition; output of Cl_{org} by the formation of volatile Cl_{org} and output of Cl_{org} by leaching (after Öberg and Grøn 1998).

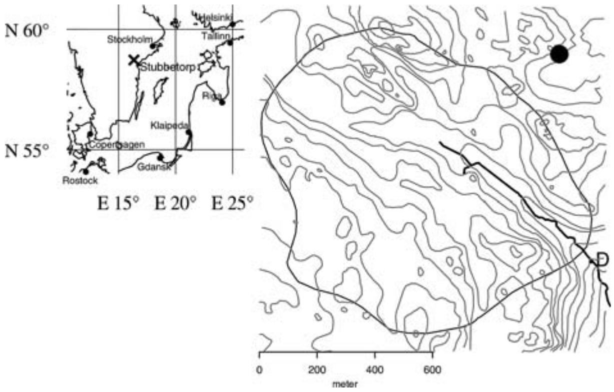

Figure 2. The position of Stubbetorp catchment in south east Sweden (58°44′ N; 16°21′ E) and a topographic map with watershed limits of the catchment. The creek is marked with a dark line and the location of the weir is marked with a D.

Areal estimates and calculations of standing volume for the 22 stands in the catchment were carried out in 2002. The age of the stands ranged from 21 to 126 years, with an average age of 72 years. *Pinus sylvestris* is the dominant tree species (81%) followed by *Picea abies* (13%), while the proportion of deciduous tree species, mainly *Betula* spp., is low (3%). The area of the stands ranges from 0.1 to 5.6 ha, and in December 2001 the standing volume ranged from 9

Table 1. Standing volume, estimated in field for each stand by the local forestry authorities and woody biomass for each stand in the Stubbetorp catchment estimated by the use of the Biosims model.

Stand	Area (ha)	Standing Volume (m^3sk)				Woody biomass (Odt total)		
		Pine	Spruce	Decid.	Total	Stem	Branches	Total
2092	3.6	88	59	0	147	41	29	70
2087	5.6	200	0	50	250	70	49	119
2094	0.6	27	0	0	27	8	5	13
2277	2	118	0	0	118	33	23	56
2264	1.1	76	0	0	76	33	19	52
2101	0.1	9	0	0	9	4	2	6
2259	1.8	155	18	0	173	76	43	119
2271	15	1620	0	0	1620	712	399	1111
2095	1.1	120	0	0	120	53	30	82
2254	2.3	271	0	0	271	119	67	186
2278	3.8	466	0	0	466	205	115	320
2273	4.7	121	485	0	606	266	149	416
2099	3.8	451	51	0	502	221	123	344
2265	5.3	715	0	0	715	314	176	490
2262	2.7	365	0	0	365	160	90	250
2275	4.1	553	62	0	615	270	151	422
2256	1.1	86	86	44	216	90	39	129
2255	2.3	180	273	0	453	189	82	271
2257	1.1	66	153	0	219	91	40	131
2076	5.1	1106	123	0	1229	512	223	735
2274	1.6	375	41	0	416	173	76	249
2091	15	3501	2334	0	5835	2429	1060	3489
Total	**83.8**	**10669**	**3685**	**94**	**14448**	**6070**	**2989**	**9059**

to 5835 m^3 sk (m^3 sk = forest cubic meter, the standard Swedish forestry measurement unit for standing trees, including volume of stem, bark and tree top excluding branches).

According to the estimates made by the local forestry authorities, the standing volume of the catchment in 2002 was 10,699 m^3 sk of Scots pine (*Pinus sylvestris*), 3685 m^3 sk of spruce (*Picea abies*), and 94 m^3 sk of broad-leaved species (e.g. birch, *Betula sp.* and aspen, *Populus tremula*; Table 1.

Input estimates

Wet deposition of Cl_{inorg}

Wet deposition of $\mathrm{Cl_{inorg}}$ in the Stubbetorp catchment has been estimated by Maxe (1995) at 0.41 g $\mathrm{Cl^-\ m^{-2}\ yr^{-1}}$ during the 1986–1990 period, indicated in Figure 3 by arrow (a). This estimate was achieved by combining average rainwater chemistry data for the 1983–1987 period obtained from Swedish Precipitation Chemistry Network from the Meteorological Department at the

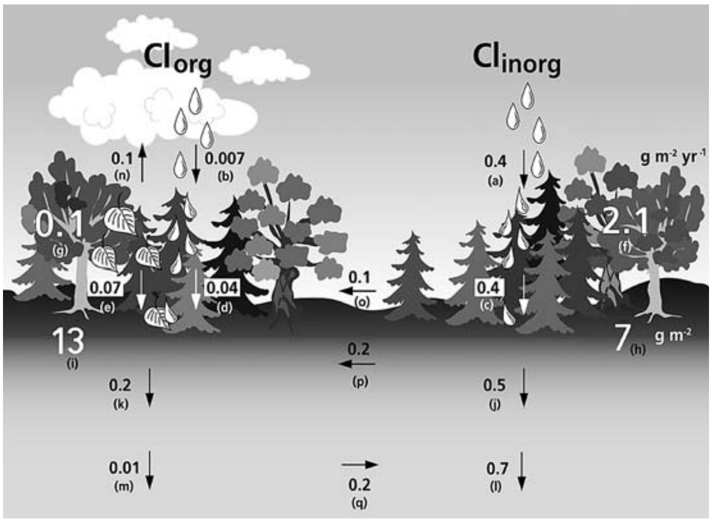

Figure 3. A roughly estimated balanced chlorine budget of the Stubbetorp catchment, south east Sweden (58°44′ N; 16°21′ E). The wet deposition of Cl_{inorg} (a), loss of Cl_{inorg} and Cl_{org} by run-off (l) and the pool of Cl_{inorg} (h) and Cl_{org} (i) in soil are based on measurements carried out in the catchment. The other estimates are based on data from other sites and are to be considered as 'informed guesstimates' rather than estimates. Transports are given on an annual basis and all estimates are in g m^{-2}. The fluxes and pools are (a) wet-deposition of Cl_{inorg}, (b) wet and dry deposition of Cl_{org}, (c) dry deposition of Cl_{inorg}, (d) Cl_{org} in throughfall, (e) Cl_{org} in litterfall (f) Cl_{inorg} in biomass, (g) Cl_{org} in biomass, (h) pool of Cl_{inorg} in soil, (i) pool of Cl_{org} in soil, (j) leaching of Cl_{inorg} from top-soil, (k) leaching of Cl_{org} from top-soil, (l) loss of Cl_{inorg} by run-off, (m) loss of Cl_{org} by run-off, (n) transport of volatile Cl_{org} to the atmosphere, (o) transformation of Cl_{inorg} to Cl_{org} in/on vegetation, (p) transformation of Cl_{inorg} to Cl_{org} in top-soil, (q) transformation Cl_{inorg} of Cl_{org} to in deeper soil.

University of Stockholm (MISU) (today operated by IVL, http://www.ivl.se/en/miljo/projects/prec_net/) with data on the amount of precipitation as measured at the Simonstorp meteorological station, situated 5 km west of the catchment and run by the Swedish Meteorological and Hydrological Institute (SMHI), for the same period (Maxe 1995). According to Maxe, monthly precipitation samples were collected in two open collectors of MISU design from November 1986 to December 1990. The mean amount of precipitation over this period was 592 mm yr^{-1}. This agrees well with the long term mean (586 mm yr^{-1}; 1961–1990) measured at the regular meteorological station at Simonstorp (Alexandersson et al. 1991). The actual precipitation in Stubbetorp was estimated to be 688 mm yr^{-1} for the 1986–1990 period using the same correction factors as SMHI (Eriksson 1983). The correction factor used by SMHI includes the correction of measured annual precipitation amounts. The systematic errors in precipitation measurement are the losses due to the wind field deformation around the gauge, the adhesion and the evaporation.

Reliability of the estimate

The wet-deposition of $\mathrm{Cl_{inorg}}$ is without doubt one of the most solid estimates of the Stubbetorp budget as well as for chlorine budgets in general. The deposition estimate is here based on data collected in the actual catchment over a period of 5 years. The amount of precipitation in the region is well described and the annual deposition has a coefficient of variation of 0.15 (http://www.IVL.se). The mean annual concentration of chloride in precipitation has a coefficient of variation of 0.35 (http://www.IVL.se). Since the estimated chloride deposition in the budget is based on a 5 year period, the uncertainty of the estimated deposition is consequently less.

Wet deposition of Cl_{org}

$\mathrm{Cl_{org}}$ was not measured in wet deposition at the actual site. However, it is well documented that precipitation in general contains $\mathrm{Cl_{org}}$ (Enell et al. 1989; Häsänen and Manninen 1989; Keller 1989; Grimvall et al. 1991; Schleyer et al. 1991). According to these measurements, the concentration of $\mathrm{Cl_{org}}$ in precipitation ranges from a few nanograms to around 0.030 mg $\mathrm{l^{-1}}$. According to Laniewski et al. (1995), the concentration of $\mathrm{Cl_{org}}$ in wet deposition in the region is approximately 0.010 mg $\mathrm{Cl_{org}\ l^{-1}}$. The wet deposition of $\mathrm{Cl_{org}}$ in Stubbetorp catchment is here estimated by assuming an average concentration of 0.010 mg $\mathrm{Cl_{org}\ l^{-1}}$ in combination with the corrected wet deposition data given above (688 mm $\mathrm{yr^{-1}}$); this gives a wet deposition of 0.007 g $\mathrm{Cl_{org}\ m^{-2}\ yr^{-1}}$, indicated in Figure 3 by arrow (b).

Reliability of estimate

$\mathrm{Cl_{org}}$ has by no means been monitored to the same extent as $\mathrm{Cl_{inorg}}$ since $\mathrm{Cl_{org}}$ is not included in the atmospheric chemistry network measurements and there are to our knowledge no long-term measurements available from any site in the world. Nevertheless, it can be concluded that precipitation does without doubt contain $\mathrm{Cl_{org}}$ and even though concentrations up to 0.030 mg $\mathrm{l^{-1}}$ have been detected, the previously conducted studies suggest that the concentrations usually are lower. Hence, even if the concentration in precipitation was 0.030 mg $\mathrm{l^{-1}}$, the contribution of $\mathrm{Cl_{org}}$ in wet deposition would still be minor in relation to other fluxes in the budget.

Dry deposition of Cl_{inorg}

Maxe (1995) estimated the dry deposition of $\mathrm{Cl_{inorg}}$ to be 0.31 g $\mathrm{Cl^{-}\ m^{-2}\ yr^{-1}}$ using the assumption that wet and dry deposition of $\mathrm{Cl_{inorg}}$ together equal the stream outflow (Figure 3; arrow (c)).

Reliability of estimate
The estimate is based on wet deposition data, which are quite solid, in combination with stream flow data, which also are solid. However, the point of departure for the estimate is the assumption that Cl_{inorg} is inert in soil and hence conservative with respect to water. The fact that Cl_{inorg} participates in a complex biogeochemical cycle makes conclusions based on the assumption that Cl_{inorg} is conservative questionable. In section 'Transformation of Cl_{inorg} to Cl_{org}', we evaluate the estimate made by Maxe (1995) in light of the organic chlorine components of the cycle.

Input of Cl_{org} by throughfall

Throughfall has not been measured at the actual site and this term is instead based on data collected at Klosterhede spruce forest in northwest Denmark, which, to our knowledge is the only site at which deposition of Cl_{org} by throughfall hitherto has been studied (Öberg et al. 1998). The study at Klosterhede gave concentrations of Cl_{org} from 0.005 to 0.43 mg Cl_{org} l^{-1} with a median value of 0.071 mg Cl_{org} l^{-1} which is considerably higher than is normally found in precipitation. The concentration values were combined with throughfall data from the study period, and the deposition was estimated to be 0.006–0.09 g Cl_{org} m^{-2} yr^{-1} with a median deposition of 0.037 g Cl_{org} m^{-2} yr^{-1}. We are aware of one additional study in which concentrations (but not deposition) of Cl_{org} in throughfall have been measured; a study of throughfall in three German coniferous forests (Schleyer et al. 1991). The concentrations of Cl_{org} detected at Klosterhede spruce forest in Denmark are in line with measurements made in Germany. The studies by Öberg et al. (1998) and Schleyer et al. (1991) are to our understanding the only ones that have so far focussed on the concentration of Cl_{org} in throughfall, and both studies suggest that considerable amounts of organic chlorine are transported by this route. We assume here that the contribution by throughfall in the Stubbetorp catchment is similar to that detected at Klosterhede: 0.04 g Cl_{org} m^{-2} yr^{-1} indicated by arrow (d) in Figure 3.

Reliability of estimate
The similarities between the studies in Denmark and Germany suggest that the detected concentrations of Cl_{org} can be used to make rough extrapolations to throughfall in general. However, the data is too scattered and the data base is too small to allow conclusions whether or not e.g. stand age and species distribution will have a considerable influence on the amount of Cl_{org} or not. Hence, even though it can be concluded that throughfall most likely contains Cl_{org}, the estimate made in the present paper ought rather to be considered an 'informed guesstimate' than an estimate. In order to obtain a better estimate, it would be necessary to collect throughfall bi-weekly or monthly at a sufficient number of places in each of the stands in the catchment over a time-period of at least a year.

As elaborated upon by Öberg et al. (1998), the importance and influence of dominating wind-directions and distance to the forest edge on the distribution of pollution and major ions has pointed out by several authors (Potts 1978; Hasselrot and Grennfelt 1987; Draaijers et al. 1988; Beier et al. 1993). In the study by Öberg et al (1998), the whole area was dominated by strong westerly winds. Therefore, dry deposition should be greatest at the western edge of the forest. However, no pattern whatsoever could be distinguished that pointed to a relationship between the concentrations of organic carbon or Cl_{org} and the position of the collectors within the forest. The study by Öberg et al. (1998) suggests that Cl_{org} in throughfall at the investigated site originate mainly from internal sources, i.e. from sources within the forest. First, dry deposition of particles and gases from external sources usually renders a deposition gradient from the forest edge and inwards, whereas compounds that originate from internal sources (e.g. K^+) do not exhibit such a pattern (Beier et al. 1993). Apparently, if the forest edge influenced the results of the study by Öberg et al. (1998), it was hidden by the variation within the forest, which strongly indicates that dry deposition was negligible or at least very small in relation to sources within the forest. Second, the concentrations of Cl_{org} closely followed that of organic carbon in the study (Öberg et al. 1998). This trend indicates a common source, and there is evidence that organic carbon in throughfall mainly originates from internal sources within the forest (Collier et al. 1989; Qualls and Haines 1991; Guggenberger and Zech 1994). Third, the concentration of compounds that originate from internal sources (e.g. K^+) is generally higher during the growing season than during the dormant season, which was the case with organic carbon and Cl_{org} in the present study. Substances that mainly originate from external sources, such as the sea or fossil fuel combustion (e.g. Cl^-, SO_4^{2-}, Na^+ and Mg^{2+}) tend to show the opposite pattern (Beier et al. 1993).

This suggests that the dry deposition at Stubbetorp and elsewhere is small in relation to the amount deposited by throughfall, and that internally formed compounds as well as dry deposition are included in the throughfall estimates given above.

Input of Cl_{org} by plant litter

Plant litter has not been studied in Stubbetorp catchment and data from the Klosterhede study is used to get a best estimate of this flux (Öberg and Grön 1998). The net primary production (NPP) of an ecosystem is the total amount of biomass formed by plants, including stem wood, branches, leaves, plants, and roots. A large fraction of the NPP is delivered to the soil as dead organic matter. Even though few studies have focused on the concentration of Cl_{org} in plant litter (Nkusi and Müller 1995; Öberg et al. 1996b; Engvild 1986; Myneni 2002) and even fewer have focused on quantitative estimates (Öberg and Grøn 1998), it is clear that plant litter contains Cl_{org}. Litter fall at Klosterhede spruce forest in northwest Denmark was collected every third month for a year (Öberg and Grøn 1998). The total input of Cl_{org} during the investigated year was 0.035 g m^{-2} yr^{-1}, not including the contribution from roots and ground vegetation. The total deposition of litter during the investigated year was estimated to 280 g m^{-2} yr^{-1} (d.w.).

So far, information is only available on the organochlorine content of the aboveground parts of higher plants, and no information is available on roots or lower plants such as ferns and mosses. It is clear that the annual growth and death of fine roots contributes considerably to the soil organic matter content (Vogt et al. 1986; Nadelhoffer and Reich 1992). The transport of Cl_{org} from plants to soil will consequently be underestimated if only the aboveground litter fall is taken into account. The amount of biomass that reaches the ground annually through decomposing roots and aboveground litter varies strongly among ecosystems, and the deposition rate decreases with increasing latitude from tropical to boreal forests (Houghton 1995). The Stubbetorp catchment is situated in the temperate region and the average input of decomposing biomass into temperate forest soils has been determined to be 650 g m^{-2} yr^{-1} (Houghton and Skole 1990). A best estimate of the contribution from biomass litter is thus achieved by using the estimated average biomass input for temperate forests in combination with concentration data from Klosterhede, i.e. we assume that the input of biomass litter at Stubbetorp is 650 g m^{-2} yr^{-1} with a Cl_{org} content corresponding to the median value detected in Klosterhede (i.e. 0.1 mg g^{-1} d.w.), the annual contribution from biomass litter can be estimated to be 0.065 g Cl_{org} m^{-2} yr^{-1}, here rounded to 0.07 g Cl_{org} m^{-2} yr^{-1} and indicated by arrow (e) in Figure 3.

Reliability of estimate

The concentration data originates from the hitherto only study of Cl_{org} in plant litter and it is combined with average input of decomposing biomass in temperate forests in general. Hence, the estimated contribution from plant litter is more to be considered an ‘informed guesstimate’ than an estimate. To obtain a better estimate of the contribution by plant litter, it would be necessary to collect litter over at least 1 year, preferably longer, to determine the amount of litter and the Cl_{org} content in the litter. A reliable estimate of the plant litter contribution would in addition require estimates of belowground plant litter, which is a rather time-consuming and complicated task (Nadelhoffer and Reich 1992).

Pool estimates

Pool of Cl_{inorg} and organic Cl_{org} in biomass

The estimated pool of Cl_{inorg} and Cl_{org} in biomass is here based on the estimated biomass in the catchment for 2002 in combination with data on the Cl_{inorg} and Cl_{org} content of fresh plant material from previous studies.

Biomass estimation

The Biosims method (Parikka 1998, 2000) is here used to estimate the woody biomass in the Stubbetorp catchment. This method has been used in several other studies dealing with woody biomass mapping, wood fuel supply, forest resource mapping, and biomass nitrogen and carbon content calculations (e.g. Parikka and Vikinge 1994, 2001; Hektor et al. 1996; Vinterbäck et al. 1998; Lönner et al. 1998; Parikka 2000, 2003).

The ratio method (Alemdag 1982a; Crow and Slaegel 1988) is here used to estimate the standing woody biomass of the catchment; i.e. the woody biomass inventory is based on a traditional forest inventory, and on ratios between woody biomass and stand variables such as stem volume and height. Sample plot data from the Swedish National Forest Survey (NFS) (e.g. Kempe 1988) are used to determine ratios between stem volume and woody biomass. The NFS data used for this study pertain to the same geographical region where the Stubbetorp catchment is located.

The following were determined: (1) stem volume and weight, including bark, (2) stem volume and the weight of the whole tree (from the cutting edge to the tree top), and (3) stem volume and the weight of the branches, including needle biomass. These ratios were determined for the following cutting classes defined by the NFS: B1–B3 (young forest), C1–C3 (thinning), and D1–D2 (clear-cutting). Woody biomass is expressed in dry weight in relation to stem volume – m^3 sk. These ratios or functions have been used by researchers such as (Alemdag 1982a, b; Brown and Lugo 1984; Singh 1984; Parikka 1998, 2000). Stumps are not included in the calculations. It is assumed that the biomass carbon content is 50% of the oven dry mass of woody biomass (Hakkila 1989; Parikka 2003).

Using the Biosims method, the woody biomass was estimated to be 6070 Oven dried tons (Odt) as stems and 2989 Odt in branches including needles. This renders a total of approximately 9059 Odt biomass (Table 1) which corresponds to 104.1 Odt ha^{-1} or 10.4 kg m^{-2}.

Cl_{inorg} in biomass

All organisms contain Cl_{inorg}, which is mainly used to adjust the turgor and ionic strength of the cells. In addition, it is well documented that Cl_{inorg} also participates in certain essential processes such as photosynthesis (Hind et al. 1969). From a biogeochemical point of view, the amount of Cl_{inorg} in organisms is considered as a temporary storage that varies with the amount of living organisms in the system. The variation is largest in areas with pronounced seasons, as for example during summer and autumn in the temporal regions since this is the time life proliferates in these areas.

The pool of Cl_{inorg} in biomass is here estimated by combining the estimates of biomass given above with data on Cl_{inorg} concentrations in plant tissue. The concentration of Cl_{inorg} in fresh plant tissue can range from as little as 0.03 mg g^{-1} (w.w.) in severely deficient plant tissues to as much as several percent in plants growing in salt marshes (Page 1982). According to a compilation by Lobert et al. (1999), woody and leafy tissues contain on an average 0.109 mg $\mathrm{Cl_{inorg}}$ $\mathrm{g^{-1}}$ (d.w.) and 0.389 mg $\mathrm{Cl_{inorg}}$ $\mathrm{g^{-1}}$ (d.w.) in temperate areas, respectively.

If we assume that the former concentration is valid for "stems" in the above biomass estimate (i.e. 6070 tons) and that the latter concentration is valid for "branches including needles" (i.e. 2989 tons), the pool of $\mathrm{Cl_{inorg}}$ in biomass in the catchment can be estimated to 662 and 1163 kg $\mathrm{Cl_{inorg}}$, respectively, which corresponds to 21.0 kg $\mathrm{Cl_{inorg}}$ $\mathrm{ha^{-1}}$ or 2.1 g $\mathrm{Cl_{inorg}}$ $\mathrm{m^{-2}}$, indicated by (f) in Figure 3.

Cl_{org} in biomass

Although more than 80 plant species are known to produce chlorometabolites (Engvild 1986), few studies have dealt with the quantification of such compounds in plants. In one study, eight plant species representing different plant families were analyzed for the total amount of $\mathrm{Cl_{org}}$ (Nkusi and Müller 1995), and concentrations were found to range from 0.07 to 0.1 mg $\mathrm{Cl_{org}}$ $\mathrm{g^{-1}}$ (d.w.). In another study, common beech leaves, spruce needles, sphagnum moss, and bulk samples of grass were found to contain 0.01–0.1 mg $\mathrm{Cl_{org}}$ $\mathrm{g^{-1}}$ (d.w.) (Asplund 1995). These studies indicate that the concentration of $\mathrm{Cl_{org}}$ varies among plants and it is likely that the concentration also varies among different types of plant tissues within the same plant (e.g. stem, leaves, and bark). However, the data that have so far been collected are too scattered to permit differentiated estimates for various types of plants or plant tissues. In addition, a recent study by Myneni (2002) suggests that the concentration of $\mathrm{Cl_{org}}$ in biomass might be lower than the studies by Asplund (1995) and Nkusi and Miller (1995) suggest. We therefore base our estimates on the assumption that the $\mathrm{Cl_{org}}$ content of vegetation is in the lower range of previous determinations, i.e. 0.01 mg $\mathrm{Cl_{org}}$ $\mathrm{g^{-1}}$. A total biomass of 9059 Odt biomass or 10.4 kg $\mathrm{m^{-2}}$ thus gives a total pool of $\mathrm{Cl_{org}}$ in biomass in the catchment of 90.59 kg $\mathrm{Cl_{org}}$, which corresponds to 1.04 kg $\mathrm{Cl_{org}}$ $\mathrm{ha^{-1}}$ or 0.104 g $\mathrm{Cl_{org}}$ $\mathrm{m^{-2}}$, here rounded to 0.1 g $\mathrm{Cl_{org}}$ $\mathrm{m^{-2}}$, indicated by (g) in Figure 3.

Reliability of estimates

The biomass estimate is based on actual measurements in the catchment but the concentration data on $\mathrm{Cl_{inorg}}$ as well as $\mathrm{Cl_{org}}$ originates from other sources. The concentration of $\mathrm{Cl_{inorg}}$ is based on average concentrations of woody and leafy tissues in the temperate region whereas the concentration of $\mathrm{Cl_{org}}$ is based on a few unreplicated samples of fresh plant litter. Hence, the estimated pools in biomass are more to be considered an 'informed guesstimate' than an estimate. To obtain a better estimate of these pools, one would need to collect fresh plant material of various types (wood, branches, leaves) and analyse for $\mathrm{Cl_{org}}$ and $\mathrm{Cl_{inorg}}$.

A few previous studies have measured $\mathrm{Cl_{org}}$ in various plant species (Engvild 1986; Nkusi and Müller 1995; Myneni 2002), but the pool of $\mathrm{Cl_{org}}$ in biomass has never been calculated. Our estimates suggest that the pool of $\mathrm{Cl_{org}}$ in biomass is considerably smaller than the pool in soil. A recently conducted study by Myneni et al. (2002) confirms that Cl_{inorg} is transformed to Cl_{org} in plant leaves. Hence, during incremental growth, biomass increases and the stand acts as a sink of Cl_{inorg} due to the transformation Cl_{org}. The pool of Cl_{org} in biomass in the Stubbetorp catchment is smaller than the pool in soil but still of the same order of magnitude as the annual wet deposition of chloride. Even if the incremental growth is 10% or even larger, the transformation of Cl_{inorg} to Cl_{org}, due to the increment (0.01 g m^{-2} yr^{-1}) would be small or negligible in relation to other fluxes.

It should be noted that the pool only is estimated for above ground biomass and that the total biomass probably is larger. However, since there are no data available for the concentration of Cl_{org} in below ground biomass and the belowground biomass is unknown in the catchment, it is hard to make even an informed guesstimate for this component of the budget. Hence, it has been left out, but it should be kept in mind that the pool of both Cl_{inorg} and Cl_{org} in biomass most likely is underestimated.

Pool of Cl_{inorg} and organic Cl_{org} in topsoil

Soil samples were collected in the catchment in May 2003. The catchment was divided into a grid with eight lines running in a north–south direction and eight lines in a west–east direction, the lines being located approximately 105 m apart. Samples were collected either to the bedrock or to a depth of 40 cm with a soil corer (diameter 38.5 cm^2) at 49 of the nodes on the grid. In 19 cases, the soil was too shallow to permit collection to a depth of 40 cm.

Area-based estimates of Cl_{inorg} and Cl_{org} in the upper 40 cm of soil gave 7 g Cl_{inorg} m^{-2} (h) and 13 g Cl_{org} m^{-2} (i), respectively.

Reliability of estimate

The pool estimates of Cl_{inorg} and Cl_{org} are among the most solid estimates of the Stubbetorp budget since the estimate is based on concentration measurements of 49 bulk samples collected along a grid at the site. The variability depends largely on two factors: the heterogeneity in the soil and the method. A larger number of samples will give a more reliable estimate of the average but the variation is unlikely to decrease since previous studies suggest that the concentration of chlorine in soil within a site normally varies with two orders of magnitude (e.g. Johansson et al. 2003a, b). The concentration of Cl_{inorg} and Cl_{org} in the soil samples was 0.001–0.357 mg Cl_{inorg} g^{-1} (d.w.) and 0.005–0.364 mg Cl_{org} g^{-1} (d.w.), respectively. The variation shows a visual spatial pattern, which suggests that the uncertainty in the pool estimate is much less than the variation among the concentrations. A reliable estimate of the uncertainty can consequently not be given at present since simple statistical calculations based on the variation in concentrations would overestimate the uncertainty of the pool estimate. A more precise determination of the uncertainty would demand an in depth analysis of the spatial variability.

Topsoil samples have been collected from around the world, and the concentration of organic chlorine has been found to vary from a few micrograms per gram to milligram levels (Asplund and Grimvall 1991; Hjelm 1996; Johansson 1996; Johansson 2000; Öberg 2003). No samples have so far been reported as having levels below the detection limit (0.4 μg Cl_{org} g^{-1}, d.w.). Even though the *concentration* of Cl_{org} has been determined in soil samples collected at various sites worldwide, the amount of Cl_{org} that is *stored* in soil has to our knowledge only been determined at five sites, including the Stubbetorp catchment (Öberg and Grøn 1998; Johansson et al. 2003a; Rodstedth et al. 2003; Johansson et al. 2004). Three of these sites are situated in Scandinavia and two are situated in the Anhui Province in southeast China. In a study conducted in Sweden, 200 samples collected as part of the Swedish National Survey of Forest Soils and Vegetation in the 1985–1987 period were analyzed for Cl_{org} (Johansson et al. 2003b). The concentrations ranged from 0.2 to 0.5 mg Cl_{org} g soil (d.w., 1st and 3rd quartiles), which gave a median pool of 8.3 g m^{-2} of Cl_{org} in the upper 15 cm. In another study, soil samples were collected in Klosterhede spruce forest in northwest Denmark in 1993 (Öberg and Grøn 1998). The pool was estimated to be 14 g Cl_{org} m^{-2} in the top 20 cm and 60 g Cl_{org} m^{-2} to a depth of 60 cm. The pool of Cl_{org} has also been determined in a forest soil and a paddy field situated in the Anhui Province in southeast China. Approximately 30 samples were collected to a depth of 15 cm at each site, and the amount stored in the soils was found to be around 4.2 g Cl_{org} m^{-2} in the forest soil and 2.5 g Cl_{org} m^{-2} in the paddy soil (Johansson et al. 2004). The present study suggests that the pool of Cl_{org} in the Stubbetorp catchment is 13 g m^2 which thus slightly less than the pool observed at the Klosterhede forest in NW Denmark, similar to the pool level found in southern Sweden, and larger than the pool level found by the Chinese study.

The pool of Cl_{org} is considerably larger than any of the annual fluxes, suggesting that any actions that will cause a change in the pool will inevitably have a strong influence on the fluxes. Without doubt, changes that influence the transformation from Cl_{inorg} to Cl_{org} in soil and vice versa will be of considerable importance. Most of the forest stands in Stubbetorp are mature, and the area was not subject to any considerable changes, such as clear-cutting, during the observation periods.

Still, a few words are in order regarding the assumption that the pool of Cl_{org} in soil is in steady state. Little is known of the dynamics of the chlorine cycle in the field, so the following must be considered rather speculative. A number of studies indicate that the net transformation rate of Cl_{inorg} to Cl_{org} in soil and vice versa is influenced by environmental variables such as pH, chloride, and nitrogen (Öberg et al., 1996a; Johansson et al. 2001; Johansson et al. 2003b). Abrupt changes that have a profound influence on such variables are doubtless also likely to influence the chlorine cycle. For example, clear-cutting, which is known, among other effects, to cause the increased mineralization of organic matter in soil and increased soil humidity, will most likely also influence the chlorine cycle. Reports of the increasing transport of Cl_{inorg} in the run off after clear-cutting could consequently be the result of an increased transformation of Cl_{org} to Cl_{inorg} (e.g. Kauffman et al. 2003).

Furthermore, it is possible that the pool of Cl_{org} in soil continuously increases from the very first moment that organic matter starts to accumulate in an ecosystem, and that the soil acts as a continuous sink of Cl_{inorg}. If this is so, then the dry deposition of Cl_{inorg}, for one, is being underestimated to the same extent that Cl_{inorg} is withdrawn in the formation processes, provided that dry deposition is determined as runoff minus wet deposition.

Output estimates

Leaching from topsoil

It is well documented that organic matter is transported from topsoil in groundwater recharge areas, and that the organic matter which subsequently precipitates at lower levels is eventually mineralized even though the turnover rate for the various fractions varies from months to perhaps thousands of years (Schlesinger 1997). The fact that all soil samples so far analyzed have contained Cl_{org}, and that Cl_{org} apparently is a natural constituent of organic matter, infers that Cl_{org} is transported with the organic matter in regions with recharge formation. The transport of Cl_{org} from topsoil has not been detected *in situ* in the catchment under study. However, the concentration of Cl_{org} has been determined in soil leachates from a series of soil cores that were collected in the catchment, stored in climate chambers over a period of 4 months, and irrigated with artificial rain (Öberg and Sandén 2004). It was found that 30–50% of the chlorine that left the soil cores was organically bound. On average, the transport of Cl_{org} by the leachate corresponded to 0.17 g m^{-2} yr^{-1}, while the transport of Cl_{inorg} corresponded to 0.49 g m^{-2} yr^{-1}. We assume that these figures can be extrapolated to the field situation. Since the estimates are rather uncertain, they are rounded to 0.2 g Cl_{org} m^{-2} yr^{-1} and 0.5 g Cl_{inorg} m^{-2} yr^{-1}, and indicated in Figure 3 by (k) and (j), respectively.

Reliability of estimate

The data originates from soil cores stored in climate chambers. Extrapolation from laboratory data to field situations is always doubtful. However, it is well documented that the concentration of organic matter in soil leachate in top-soil in the temperate region in general is considerably higher than the concentration in run off (e.g. McDowell and Likens 1988) and the concentration of organic matter in the leachate from the soil cores was within the span reported from top soil at other sites (e.g. Michalzik et al. 2001). Hence, even though the estimates based on the soil cores are rather uncertain, the major conclusion, i.e.

that considerable amounts of Cl_{org} are lost from top-soil through this route remains solid. To get a more reliable estimate of the output from top soil one would need to collect a sufficient number of field samples over a sufficient period of time and determine the amount of water and the concentration of Cl_{inorg} and Cl_{org} in these samples. The design of a future study aiming at more reliable estimates of the loss by leaching would need careful planning since different sampling techniques have different draw backs with respect to e.g. organic components vs. the inorganic components, water flux determinations vs. determination of chemical composition, etc. (Rowell 1994).

Transport by runoff

The transport of Cl_{inorg} by surface-water runoff from the Stubbetorp catchment, indicated by (l) in Figure 3, has previously been determined by Maxe (1995) as amounting to 0.71 g Cl^- m^{-2} yr^{-1} by combining runoff data from 1986 to 1990 from the catchment with Cl_{inorg} concentration values. The runoff measurements were made by SMHI using a weir. Stream-water chemistry was usually monitored through weekly sampling.

In an ongoing study, the concentration of Cl_{org} has been determined biweekly since October 2002 in a tributary that drains approximately one-third of the catchment (Svensson et al. forthcoming). The water flux has been measured biweekly at the same site since January 2003. At one occasion during 2003, the concentration of Cl_{org} was determined in six replicates at the outlet from the whole catchment (Svensson et al. in preparation). The concentration in the six replicates ranged from 74 to 81 μg Cl_{org} l^{-1}, which is within the range of the observations made in the tributary during 2003 (23–99 μg Cl_{org} l^{-1}). If we assume that the concentrations determined in the tributary can be extrapolated to the whole catchment (indicated by (m) in Figure 3) and use the mean runoff of 230 mm in combination with the concentration determinations of the tributary, the average transport of Cl_{org} is estimated to be 0.009 (0.007–0.010, 1st and 3rd quartiles) g Cl_{org} m^{-2} yr^{-1}, which in the figure is rounded to 0.01 g Cl_{org} m^{-2} yr^{-1}.

Reliability of the estimate

The estimated transport of Cl_{org} is a rather reliable component of the budget. The uncertainty of the estimate lies in the fact that it is based on a mean concentration value from 1 year's measurements in the outlet from a sub-catchment rather than from actual flow-specific measurements in the outlet from the whole catchment. There are some indications that the concentration of Cl_{org} varies seasonally, is flux-dependent and varies inter-annually (Svensson et al. in preparation). In addition, even though the concentrations determined in the outlet from the whole catchment are within the span of the concentrations determined in the outlet from the sub-catchment (23–99 μg l^{-1}), the concentrations in the outlet from the whole catchment (74–81 μg l^{-1}) are actually in the upper region of the concentrations measurements conducted in the outlet from the sub-catchment in 2003 (3rd quartile: 44 μg l^{-1}). This could be due to natural variation, but it could also be due to that the concentration in the outlet from the whole catchment actually is higher than in the tributary, which would render an underestimation of the transport of Cl_{org} by run-off from the catchment. In order to get a more reliable estimate of the transport of Cl_{org} from the catchment it is necessary to conduct flow-specific measurements in the outlet from the whole catchment, preferably over longer time-periods to catch inter-annual variations.

Volatilization

Over the past few years, a number of studies have revealed that chlorinated volatiles are emitted from terrestrial sources (Khalil and Rasmussen, 1999; Redeker et al. 2000; Rhew et al. 2000; Dimmer et al. 2001; Hoekstra et al. 2001; Haselmann 2002; Laturnus et al. 2002). Even though the information is still very scattered, it is clear that chloromethane, chloroform, and perhaps also other chlorinated volatiles are formed in various ecosystems such as coniferous forest soils, peatlands, (coastal) wetlands, and paddy fields. Various emission rates have been reported. For example, one report recorded emissions of chloromethane from coastal salt marches in the US in the 0.0004–3.2 g Cl_{org} m^{-2} yr^{-1} range (Rhew et al. 2000), while a study of chloromethane and chloroform from Irish salt marshes reported fluxes of 0.001–0.029 g Cl_{org} m^{-2} yr^{-1} (Dimmer et al. 2001). The latter study also reports fluxes of chloromethane and chloroform from a coniferous forest floor of around 0.1 g Cl_{org} m^{-2} yr^{-1}. The study by Dimmer et al. was carried out in a coniferous forest in the temperate region whereas the other studies have been carried out in quite different ecosystems (salt marshes). Hence, even though chloride deposition at the Irish west coast is about one order of magnitude higher than at Stubbetorp (Jordan 1997), an extrapolation based on the study by Dimmer on coniferous forest soil in Ireland appears to be the best available estimate for transport of volatile organic chlorine from the Stubbetorp catchment. Thus, we have here assumed that the volatilization of Cl_{org} from the Stubbetorp catchment is of the same extent as that of the Irish forest studied by Dimmer et al. (2001), i.e. 0.1 g m^{-2} yr^{-1}, indicated by arrow (n) in Figure 3.

Reliability of the estimate

The estimate of volatilization is without doubt the most uncertain in the budget. No measurements have been done in the actual catchment and very few studies have been carried out around the world, hence the comparative data is scarce. In order to get a better estimate, one would need to carry out a field study based on a sufficient number of field kuvettes over a sufficiently long time period, i.e. at least a year. Since calibration of field kuvettes with regard to concentration vs flux measurements is a tedious task, this is probably the most time-consuming and elaborate part of the additional studies that would be needed to make the chlorine budget of the catchment more reliable.

As mentioned, few studies have focused on the formation of chlorinated volatiles in soil, but, as also mentioned, it is clear that both chloromethane and chloroform are formed in forest soil by soil microorganisms (Watling and Harper 1998; Dimmer et al. 2001; Haselmann et al. 2000a, b, 2002; Hoekstra et al. 1998, 1999, 2001; Laturnus et al. 2000, 2002). The fluxes not only appear to vary strongly among ecosystems, but also diurnally and seasonally (Dimmer et al. 2001; Haselmann et al. 2000a). The studies conducted so far have not been designed to handle such variations, so the estimates made are consequently rather rough: as indicated by several authors, it is still impossible to reliably quantify the relative contribution of terrestrial processes to the atmospheric burden (e.g. Khalil and Rasmussen 1999). Reliable rate determinations for forested systems have so far not been made, and it is rather unclear how much chlorine may actually be lost from the system through this route.

Due to so little being known of the loss of Cl_{org} through volatilization in terrestrial environments, the volatilization estimate is among the figures with least substantial support in the budget. The highest annual rate (1.2 g Cl_{org} m^{-2}) reported so far is from a salt marsh (Rhew et al. 2000), while the rate in a coniferous forest soil in Ireland was found to be 0.1 g Cl_{org} m^{-2} yr^{-1}. Nevertheless, even if the formation of chlorinated volatiles in a forest soil is ten times lower than in a salt marsh, volatilization will doubtless cause the soil to act as a considerable chloride sink, taking into account that the wet deposition of Cl_{inorg} at Stubbetorp is 0.4 g m^{-2} and the transport out of the system by runoff is 0.7 g m^{-2}.

Transformation of Cl_{inorg} to Cl_{org}

Net formation of Cl_{org} in biomass

It appears as if plant litter as well as throughfall contains Cl_{org}, which suggests that Cl_{inorg} at one time or another is converted to Cl_{org} by plants or by organisms living in or on plants. Recently conducted studies by Myneni et al. (2002 and pers comm.) verify that Cl_{inorg} is converted to Cl_{org} in plant leaves. Unfortunately, no information is available on *in situ* transformation rates of Cl_{inorg} by plants or other organisms. The transformation rate of the Cl_{inorg} in plants as a result of Cl_{org} formation can be roughly determined on the basis of the amount of Cl_{org} lost from the biomass as litter and by throughfall, assuming that steady state is at hand in biomass with regard to the Cl_{org} pool.

According to the above calculations, the annual amount of Cl_{org} lost from the biomass pool through litter fall and throughfall was estimated to be 0.065 and 0.04 g Cl_{org} m^{-2} yr^{-1}, respectively. Assuming steady state infers that the same amount of Cl_{inorg} is annually transformed to Cl_{org} in or on the biomass (i.e. a net formation of Cl_{org} or a net consumption of Cl_{inorg}), as given in Eq. (1), roughly estimated to be 0.105 g m^{-2} yr^{-1}, here rounded to 0.1 g m^{-2} yr^{-1} and indicated in Figure 3 by (o).

$$\mathrm{Bf} = \mathrm{Bl} + \mathrm{Tf} = 0.105\,\mathrm{g\,m^{-2}\,yr^{-1}} \tag{1}$$

Bf (biomass formation) = annual transformation from Cl_{inorg} to Cl_{org} in biomass; Bl (biomass litter) = annual transport of Cl_{org} from biomass to soil by biomass litter; Tf (throughfall) = annual transport of Cl_{org} from biomass to soil by throughfall.

Reliability of estimate

The estimate takes its point of departure in deductive reasoning based on two assumptions (1) that the net-transformation from Cl_{inorg} to Cl_{org} in biomass equals the loss by litterfall and throughfall and (2) that the amount of Cl_{org} stored in biomass is in steady state. The first assumption is logically indisputable but the estimates of the amounts lost by litterfall and throughfall are rather uncertain, hence the estimated transformation of Cl_{inorg} to Cl_{org} in biomass is also quite uncertain and should consequently be viewed more as a 'guesstimate' than an estimate. The assumption that the amount of Cl_{org} stored in biomass is in steady state is not based on any empirical evidence. We cannot rule out whether or not the amount of Cl_{org} stored in biomass increases with incremental growth, neither is it possible to rule out whether or not the concentration in biomass varies with age, etc. What can be deduced is that if the pool in biomass is constantly increasing, then this factor must be added to the transformation of Cl_{inorg} to Cl_{org} in biomass. However, the total pool of Cl_{org} in biomass in the Stubbetorp catchment is of the same order of magnitude as the annual wet deposition of Cl_{org}. Hence, since small changes in this pool will have a small influence on the other components of the cycle, and nothing is known about changes over time in the biomass pool of Cl_{org}, we have chosen to exclude this component of the cycle.

In order to achieve a better estimate of the transformation rates in biomass one would need to carry out studies using some sort of markers such as ^{36}Cl in combination with estimates of loss by throughfall and litterfall as well as changes in the biomass pool over time.

Net formation of Cl_{org} in topsoil

A number of studies strongly suggest that degradation of organic matter in general involves the conversion of Cl_{inorg} to Cl_{org} (Öberg et al. 1996b; Hjelm et al. 1999; Myneni 2002). Though the underlying process has not been conclusively discovered, it has long been known that a vast array of soil microorganisms are able to convert Cl_{inorg} to Cl_{org} (Clutterbuck et al. 1940; Hunter et al. 1987), and that there are a number of cell-free soil enzymes that catalyze chlorination (e.g. Shaw and Hager 1959; Hager 1966; Sae 1969; Morrison and Schonbaum 1976; Hewson and Hager 1979; Neidleman and Geigert 1986). There are also indications that a transformation from Cl_{inorg} to Cl_{org} may be abiotically induced (Keppler et al. 2000). A recent study showed that as much as 20–50% of the chlorine leached from soil cores kept in climate chambers was organically bound (Öberg and Sandén 2004). The amounts of Cl_{org} lost from the soil in the leachate did not decrease with time, strongly suggesting that a considerable amount of Cl_{org} was forming in the soil causing a considerable withdrawal of Cl_{inorg} from the soil water. These observations are in line with a large number of studies reporting unexplained Cl_{inorg} retention or 'sorption' in topsoil (Grim 1968; Hanes 1971; Gebhart and Coleman 1974; Likens et al. 1977; Baes III et al. 1984; Chen et al. 2002; Cook et al. 1994; Lee 1997).

In spite of the research mentioned above, the processes governing the chlorine cycle in soil are as yet poorly understood. Most likely, release of Cl_{inorg} (mineralization of Cl_{org}) takes place simultaneously with a consumption of Cl_{inorg} (formation of Cl_{org}). The sum of the two rates thus forms the basis of net changes of the pool. The spatial variation in Cl_{org} in soil is far too large to allow *in situ* identification of annual changes in an area (Johansson et al. 2003b; Rodstedth et al. 2003).

An alternative to *in situ* measurements is to estimate the net consumption of Cl_{inorg} by totaling the input and output of Cl_{org} and Cl_{inorg} in a catchment as presented in Eq. (2), under the assumption that the pool of Cl_{org} in soil is in steady state. The output of Cl_{org} from topsoil comprises volatilization and leaching, which were above estimated to be 0.1 and 0.2 g m^{-2} yr^{-1}, respectively. Since the input of Cl_{org}, which is comprised of the transformation of Cl_{inorg} to Cl_{org} in biomass and soil, indicated by arrows (o) and (p) in Figure 3, must equal the output, the sum of (o) and (p) can be estimated to be 0.3 g m^{-2} yr^{-1}. The transformation of Cl_{inorg} to Cl_{org} in biomass (o) was previously estimated to 0.1 g m^{-2} yr^{-1} and the net-formation in soil can thus be estimated to 0.2 g m^{-2} yr^{-1} (Eq. (3)).

$$\mathrm{Sf} + \mathrm{Bf} = \mathrm{V} + \mathrm{L} \tag{2}$$

$$\mathrm{Sf} = \mathrm{V} + \mathrm{L} - \mathrm{Bf} = 0.1 + 0.2 - 0.1 = 0.2\,\mathrm{g\,m^{-2}\,yr^{-1}} \tag{3}$$

Sf (soil formation) = transformation of Cl_{inorg} to Cl_{org} in soil; V (volatilization) = transport of volatile Cl_{org} from soil to atmosphere; L (leaching) = transport of Cl_{org} by soil leachate from topsoil to deeper soil levels; Bf (biomass formation) = annual transformation from Cl_{inorg} to Cl_{org} in biomass.

Reliability of estimate

Since all of the components underlying the estimate are uncertain, the estimate is apparently also quite uncertain and among those that are to be considered as 'guesstimates' rather than estimates. However, even though the estimated magnitude of the transformation of Cl_{inorg} to Cl_{org} is most uncertain, it remains clear that this route takes place and is of such magnitude that it is likely to influence the geochemical cycling of Cl_{inorg}. More reliable estimates of the transformation rates in soil one would demand studies using some sort of markers such as ^{36}Cl in combination with better estimates of the other components in Eq. (3).

Precipitation and subsequent mineralization of Cl_{org}

The concentration of both organic matter and Cl_{org} in runoff water is lower than in soil water. This suggests the transport from soil to surface water is considerably lower than the transport from the topsoil to lower layers in soil. The fact that organic matter is leached from topsoil and then precipitates at lower levels as water moves through the soil is well documented; it has, for example, been shown that organic carbon pool is underestimated if deeper soil layers are not taken into account (Eriksson 1991). It is well documented that organic matter is degraded at all depths in soil, although the degradation rate for various fractions varies strongly from weeks to hundreds or even thousands of years (Schlesinger 1997). As elaborated upon in a recent paper (Öberg and Sandén 2004), the fact that chlorine is a natural constituent of soil organic matter suggests that Cl_{org} would follow the same pattern as the organic matter, i.e. considerable amounts being leached from topsoil and subsequently precipitated at lower levels.

Summing up the input–output balance according to Eq. (4), the net mineralization rate is estimated to be 0.2 g m^{-2} yr^{-1}, indicated by arrow (q) in Figure 3.

$$M = Bf + Sf - V = 0.1 + 0.2 - 0.1 = 0.2\,g\,m^{-2}yr^{-1} \tag{4}$$

M (net mineralization) = transformation of Cl_{org} to Cl_{inorg}; Bf (biomass formation) = annual transformation from Cl_{inorg} to Cl_{org} in biomass; Sf (soil formation) = transformation of Cl_{inorg} to Cl_{org} in soil; V (volatilization) = transport of volatile Cl_{org} from soil to atmosphere.

Reliability of estimate

As in the case with the estimated transformation of Cl_{inorg} to Cl_{org} in top soil, the estimated transformation of Cl_{org} to Cl_{inorg} in deeper soil, all of the components underlying the estimate are uncertain. The estimate is thus also quite uncertain and among those that are to be considered as 'guesstimates' rather than estimates. However, as elaborated upon by Öberg and Sandén (2004), it remains clear that this route takes place and is of such magnitude that it is likely to influence the geochemical cycling of Cl_{inorg}. In order to achieve more reliable estimates of the transformation rates in deeper soil one would need to carry out studies using some sort of markers such as ^{36}Cl in combination with better estimates of the other components in Eq. (4).

Re-evaluating the dry deposition of Cl_{inorg}

The previous estimate of the dry deposition in the Stubbetorp catchment by Maxe (1995) was based on the assumption that chloride is inert in soil and that dry deposition equals run-off minus wet deposition, which is common practice in hydrochemical and hydrological studies (Schlesinger 1997). The present study suggests that estimates based on the assumption that chloride is inert in soil will underestimate the dry deposition since two sinks are overlooked.

(1) Transformation of Cl_{inorg} to Cl_{org} in soil (followed by leaching, volatilisation and perhaps an increment in soil Cl_{org}). First, our budget calculations suggest that the principal input and output fluxes of chlorine are Cl_{inorg} (a, c and l) and that the major pool is Cl_{org} (i), and these components were measured in the catchment, which makes this conclusion robust. The fact that the main input is inorganic and the main pool in the system is organic infers that conversion from inorganic to organic forms is occurring in soil as discussed in the section on transformation of Cl_{inorg} to Cl_{org} in soil. As outlined in the section on 'Transformation of Cl_{inorg} to Cl_{org}' in soil, the conclusion that such a conversion is taking place in soil is strengthened by a number of laboratory and field studies.

(2) Transformation of Cl_{inorg} to Cl_{org} in biomass (followed by leaching, litterfall and perhaps an increment in biomass Cl_{org}). As outlined in the Section on 'Transformation in biomass', it appears indisputable that Cl_{inorg} is transformed to Cl_{org} in biomass, although the rate remains uncertain.

Hence, it appears indisputable that the dry deposition in Stubbetorp must be larger than the previously estimated 0.3 g m^{-2} yr^{-1}. Using the fairly robust estimates of wet deposition of Cl_{inorg} (a), loss of Cl_{inorg} and Cl_{org} by run-off (l) and the pool of Cl_{inorg} (h) and Cl_{org} (i) in soil in combination with the 'informed guesstimates' of the other components, a balanced budget renders a dry deposition of 0.4 g m^{-2} yr^{-1}, which of course is to be considered an 'informed guesstimate' rather than an estimate.

Conclusions

The chlorine budget of the Stubbetorp catchment outlined in this paper is based on a number of assumptions and data collected at other locations and it is clear that a large number of long-term studies are needed in order to construct a more reliable budget. Nevertheless, a number of solid conclusions can be drawn based on the reasoning presented in the present paper.

(1) The study suggest that the principal input and output fluxes of chlorine in Stubbetorp are Cl_{inorg} (a, c and l) and that the major pool is Cl_{org} (i), and these components were measured in the catchment. The fact that the main input is inorganic and the main pool in the system is organic infers that conversion from inorganic to organic forms is likely occurring, as elaborated upon in the section on 'Transformation of Cl_{inorg} to Cl_{org}' in soil.

(2) The present study strongly suggests that transformation of Cl_{inorg} to Cl_{org} in biomass and soil (o, p), followed by volatilization (n) and leaching (k), must be taken into account when constructing chlorine budgets on a catchment scale. It is clear that in situations where considerable amounts of Cl_{org} are withdrawn though volatilization or leaching, soil will act as a permanent sink of Cl_{inorg}. Hence, the assumption that chloride is inert in soil and that dry deposition equals the run-off minus wet-deposition is thus likely to render an underestimation of the dry deposition.

(3) The transformation of Cl_{inorg} to Cl_{org} in soil and biomass will most likely have a considerable influence the geochemical cycling of Cl_{inorg} in areas with low or moderate deposition of Cl_{inorg} and in areas with moderate to large pools of organic matter. The influence is probably of less importance or negligible in areas with larger wet and dry deposition of Cl_{inorg} and/or a smaller pool of organic matter (and hence Cl_{org}) in soil

(4) The fact that after disturbance Cl_{inorg} is released from soils (based on other catchment studies and the soil core experiments reported here) indicates that mineralization of Cl_{org} is likely. Thus, there is probably a two-way exchange between inorganic and organic forms in the system.

(5) Transport of volatile Cl_{org} from soil to the atmosphere may influence the chlorine cycle, but too little is known to be able to estimate the influence conclusively.

(6) The pool of Cl_{org} in biomass appears to be small in relation to the pool of Cl_{org} in soil and the pool of Cl_{inorg} in biomass and soil.

(7) A considerable portion of the Cl_{inorg} in soil is transformed to Cl_{org} and subsequently leached to deeper soil layers.

(8) Net mineralization of Cl_{org} takes place in soil, preferably in deeper soil layers, and degrading organic matter is a major source of Cl_{inorg} in runoff.

(9) Loss of Cl_{org} by runoff is small to negligible in relation to other fluxes.

A comment on the input from persistent organic pollutants (POPs)

It seems clear that the Cl_{org} in the catchment mainly originates from the transformation of Cl_{inorg} in decomposing litter and topsoil, and to a rather small extent from formation in living plants. The contribution from external sources appears negligible or at least very small. A few words are warranted in relation to the dispersal of chlorinated pollutants. It has been shown that several specific organohalogens are often present in precipitation. For example, DDT, PCBs (polychlorinated biphenyls), PCDDs (polychlorinated dibenzodioxins), chlorobenzenes, chlorophenols, and chloroacetic acids may be found in rain (Atlas and Giam 1981; Paasivirta et al. 1985; Strachan 1988; Frank 1991; Schleyer et al. 1991; Koester and Hites 1992). Anthropogenic compounds can only explain a minor fraction of the total amount of organically bound chlorine in rain, since the former are detected in ppt levels and the latter in ppb levels. Chlorinated organic pollutants are of considerable interest from an ecotoxicological point of view. However, from a chlorine *budget* perspective, the relative contribution of such compounds is negligible. Several attempts have been made to determine the chemical character of the bulk of organically bound chlorine in precipitation (de Lijser et al. 1991; Laniewski et al. 1995), but the major fraction has still not been identified.

Chemical analytical procedures

Samples were transported to the laboratory immediately after sampling and then either dried at 65 °C or stored in deep-freezer at −20 °C until further treatment and analyses.

Cl_{inorg} in aqueous samples

The concentration of Cl_{inorg} in aqueous samples was determined by potentiometric titration using an automatic titrator (Radiometer, Copenhagen). An aliquot of the leachate (15 ml) was mixed with a carrying electrolyte (15 ml; 1 M KNO_3, 0.2 M HNO_3) and titrated with $AgNO_3$ (5 mM) to the endpoint. The endpoint was calculated from two curves, where a solution of 14 ml Milli-Q water, 15 ml carrying electrolyte, and a Cl_{inorg} solution (1 ml 0.01 M) were titrated with $AgNO_3$ (5 mM). Duplicate analyses were conducted when possible and blanks were analyzed twice or more for each round.

Organic carbon in aqueous samples (TOC)

The total amount of organic carbon (TOC) in aqueous samples was determined using a Shimadzu 5000 TOC Analyzer. An aliquot of the sample (10 ml) was diluted with Milli-Q water (40 ml). Duplicate analyses were conducted on each sample. Reference solutions were analyzed as follows: first a Milli-Q water sample, followed by two reference samples with 10 mg TC l^{-1} and 10 mg IC l^{-1}, respectively, followed by a Milli-Q water sample. In addition, Milli-Q water was analyzed approximately each tenth analysis.

Cl_{org} in aqueous samples (AOX)

Cl_{org} in aqueous samples was determined according to the standard procedure for the determination of adsorbable organic halogens (AOX; EU 1485, 1996). In short, the sample was diluted with Milli-Q water to a final volume of 100 ml (3:100 or 1:50; V:V) in an Erlenmeyer flask (300 ml). Activated carbon (50 mg), an acidified nitrate solution (5.0 mL, 0.2 M KNO_3, 0.02 M HNO_3), and approximately 7 drops of concentrated HNO_3 were added to the flasks and the suspension was placed on a rotary shaker (1 h, 200 rpm). The suspension was filtered through a polycarbonate filter (0.45 μm) and rinsed with an acidic nitrate solution (ca. 20 ml 0.01 M KNO_3, 0.001 M HNO_3), followed by acidified Milli-Q water (ca. 20 ml, pH 2, HNO_3). The filter and the filter cake were then combusted under a stream of oxygen at 1000 °C in a Euroglas AOX Analyzer (model 84/85), in which the formed hydrogen halides are determined by microcoulometric titration with silver ions. Each sample was analyzed in duplicates. The difference between the duplicates in the present studies was generally smaller than 0.2 μg Cl_{org}. Blanks were analyzed by the use of Milli-Q water. All samples were clearly above the detection limit, which was ca. 5 μg Cl_{org} l^{-1}.

Cl_{org} in solid samples (TOX)

The concentration of Cl_{org} (TOX) in solid samples was analyzed according to Asplund et al. (1994). In short, a 20-mg milled sample was added to an acidic nitrate solution (20 ml, 0.2 M KNO_3, 0.02 M HNO_3) and shaken on a rotary shaker (200 rpm) for at least 1 h. The suspension was filtered through a 0.45-μm polycarbonate filter and the analyses then followed the procedure for AOX analyses described above. The soil samples used for the pool estimates were only analyzed in unreplicated samples. In all other cases, five to eight replicates of each soil sample were analyzed and the median was used for calculations. The coefficient of variation among the replicates was around 5% or less. Blanks were analyzed according to the same procedure but without addition of soil. All samples were clearly above the detection limit, which was ca. 0.2 μg Cl_{org} g^{-1} (d.w.).

Total amount of chlorine in solid samples (TX)

The total amount of chlorine (TX) was determined by adding 20 mg milled and sieved soil (0.12 mm) to a small crucible followed by direct combustion in the AOX analyzer. For the pool estimates, only one unreplicated sample was analyzed of each soil sample. In all other cases, five replicates of each soil sample were analyzed and the median was used for calculations. The coefficient of variation among the replicates was less than 4%. Blanks were analyzed by combustion of the crucibles without addition of soil. All samples were clearly above the detection limit, which was approximately 0.2 μg Cl_{org} g^{-1}. Cl_{inorg} was calculated as TX − TOX.

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