

Chlorine transport in a small catchment in southeast Sweden during two years

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Abstract Previous studies have revealed that chlorine participates in a complex biogeochemical cycle in soil, which suggests that the transport of chloride through catchments may also be influenced. The present study is based on field observations of organic carbon, chloride (Cl_{in}), and chlorinated organic carbon (Cl_{org}) in precipitation, soil, and runoff over a 2-year period from a small, forested catchment in southeast Sweden. The study reveals that (1) the soil pool is dominated by Cl_{org} , (2) the input via wet deposition and output of Cl_{in} via runoff is 30 times smaller than the total storage of chlorine ($\text{Cl}_{\text{in}} + \text{Cl}_{\text{org}}$) in soil, and (3) the transport is dominated by Cl_{in} . The organic matter that entered the outlet of the catchment was more chlorinated in the autumn than during the rest of the year, and rain events taking place in low-flow

periods had a greater influence on TOC, Cl_{org} , and Cl_{in} than did rain events taking place in high-flow periods. The seasonal pattern in combination with the low-flow versus high-flow pattern and previous findings of increasing chlorine-to-carbon ratios with soil depth suggests that the chlorine-to-carbon ratio variation in the leached organic matter is due that water preferentially comes from deeper layers in low-flow conditions. This study provides well-founded estimates of Cl_{org} and Cl_{in} storage and fluxes for the studied catchment; however, the processes underlying the observed seasonal Cl_{org} variations and transportation processes need further study.

Keywords Catchment · Chloride · Chlorine · Organic chlorine · Soil · Water · Watershed

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Introduction

Chlorine is ubiquitous in the environment, and both chloride (Cl_{in}) and organic chlorine (Cl_{org}) are found in water, soil, and air compartments such as surface water, ground water, precipitation, aerosols, atmosphere, soil air, vegetation, organisms, soil, and sediments (Asplund and Grimvall 1991; Grön 1995; Graedel and Keene 1996; Gribble 1996; Laniewski 1998; Öberg 2003; Laturnus et al. 2005). Cl_{in} is often used as a conservative tracer in hydrological studies as it is

considered to be hydrologically and chemically inert (Christophersen and Neal 1990). It has been suggested that some type of ‘sorption’ process is present in soil (Chen et al. 2002), since retention of Cl_{in} in soil has been reported by several authors (e.g. Grim 1968; Baes et al. 1984; Mulder et al. 1990; Sheppard et al. 1993; Cook et al. 1994; Lee 1997; Nyberg et al. 1999). The previous understanding of Cl_{in} as conservative in soil has been challenged by the past decade of research which has revealed that Cl_{in} participates in a complex biogeochemical cycle, and that the soil system sometimes acts as a source and sometimes as a sink of Cl_{in} (Öberg 2002; Lovett et al. 2005; Öberg et al. 2005). For example, it has been shown that the chlorine cycle in soil (Asplund and Grimvall 1991; Winterton 2000; Lee et al. 2001; Myneni 2002; Öberg 2002) involves formation and degradation of Cl_{org} (consumption and release of Cl_{in}), volatilization, leaching and precipitation of Cl_{org} (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 and Sandén 2005).

There is indisputable evidence that Cl_{in} can be transformed into Cl_{org} in nature, although the underlying processes are not fully understood (Öberg 2002). At present very little is known of the characteristics, such as chemical composition and potential toxicity, of naturally produced Cl_{org} compounds in soil. The environmental impact of chlorinated *anthropogenic* compounds as a group has been of concern since the 1960s (Stringer and Johnston 2001). However, our understanding of *natural* chlorine biogeochemistry remains rudimentary and unsystematic, and improved knowledge of the natural biogeochemical cycle is needed for the effective management of environmental issues concerning chlorine.

It is well known that the chemical composition of soil and soil water varies greatly over time and in space. It is thus necessary to know the particular on-site variation of various chlorine species to be able to reliably estimate, for example, the occurrence of various chlorine species in soil, soil-surface water transport, and how and why the concentration in various environmental compartments varies.

Previous studies of chlorine have primarily dealt with Cl_{in} and Cl_{org} separately. Environmental concerns connected with Cl_{in} have mainly centred on the influence of road salt on vegetation, groundwater, and soil structure (Blomqvist 2001; Löfgren 2001; Thunqvist 2004). The major source of Cl_{in} in areas not directly influenced by road salt is sea spray carried inland via winds and precipitation. As it has been presumed that Cl_{in} is non-reactive in soil, it has been widely used to assess sources and transformations of other ions and to calculate water residence time (Christophersen and Neal 1990; Hedin et al. 1995; Lockwood et al. 1995; Neal and Kirchner 2000).

Cl_{org} in soil and water has mainly been studied from an environmental point of view, and the occurrence of Cl_{org} in environmental compartments is generally regarded as a sign of contamination (Kaczmarczyk and Niemirycz 2005). Numerous studies over the years have dealt with the occurrence and distribution of anthropogenic Cl_{org} compounds of ecotoxicological interest, such as DDT, PCBs, and dioxins (Stringer and Johnston 2001). Over past decades, a small but growing literature has focussed on the natural biogeochemical cycling of chlorine (Keppler et al. 2000; Winterton 2000; Ortiz-Bermúdez et al. 2003; Öberg 2003; Reina et al. 2004; Lovett et al. 2005). Among other matters it has been shown that Cl_{org} is ubiquitous in soil and surface water, most Cl_{org} comprises naturally formed chlorinated organic matter, Cl_{in} is transformed into Cl_{org} and vice versa, the amount of Cl_{org} in organic soils often exceeds the amount of Cl_{in} , and Cl_{org} is lost from topsoil via leaching and volatilization (Asplund et al. 1993; Hjelm et al. 1995; Öberg and Grön 1998; Dimmer et al. 2001; Johansson et al. 2001; Keppler and Biester 2003; Rodstedth et al. 2003; Johansson et al. 2003a; Cox et al. 2004; Öberg et al. 2005; Öberg and Sandén 2005). Transport estimates have so far been based on rather few measurements; replicates over time or in space are rare and simultaneous studies of Cl_{org} and Cl_{in} on catchment scale have not been conducted.

The aim of the present study is (i) to describe the on-site variation in the concentration of Cl_{in} and Cl_{org} in runoff from a small catchment over a period of 2 years, (ii) to estimate the output of

Cl_{in} and Cl_{org} in runoff in relation to the input via deposition, and (iii) to discuss potential sources in light of observed patterns.

Materials and methods

Catchment description

The studied catchment is situated in southeast Sweden ($58^{\circ}44' N$, $16^{\circ}21' E$; Fig. 1) within a larger catchment area previously described as the ‘Stubbetorp catchment’ in Maxe (1995). The distance from the Baltic Sea is approximately 50 km, and larger roads to which road salt is applied are 5 km downstream; this implies that there are no direct road salt effects, as such effects extend for a maximum of approximately 0.5 km (Blomqvist 2001). The topography is broken; the bedrock is dominated by gneissic granite and the soil minerals contain little Cl_{in}

(Maxe 1995). Coniferous forest with pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* L.) is dominant and the age of the forest stand was at the sampling occasion on an average 72 years. Since the 1950s, precipitation has been measured continuously by the Swedish Meteorological and Hydrological Institute (SMHI) at the Simonstorp meteorological station, 5 km west of the sub-catchment. The long-term corrected mean precipitation for the 1951–1980 period is 696 mm yr^{-1} , compensating for measurement losses according to an SMHI correction model (Alexandersson 2003). The catchment area is approximately 0.22 km^2 , as previously estimated by Maxe (1995). The catchment is situated 110–130 m above sea level.

Water discharge measurements

In 1987, a stainless steel V-notch weir was installed at the outlet of the sub-catchment

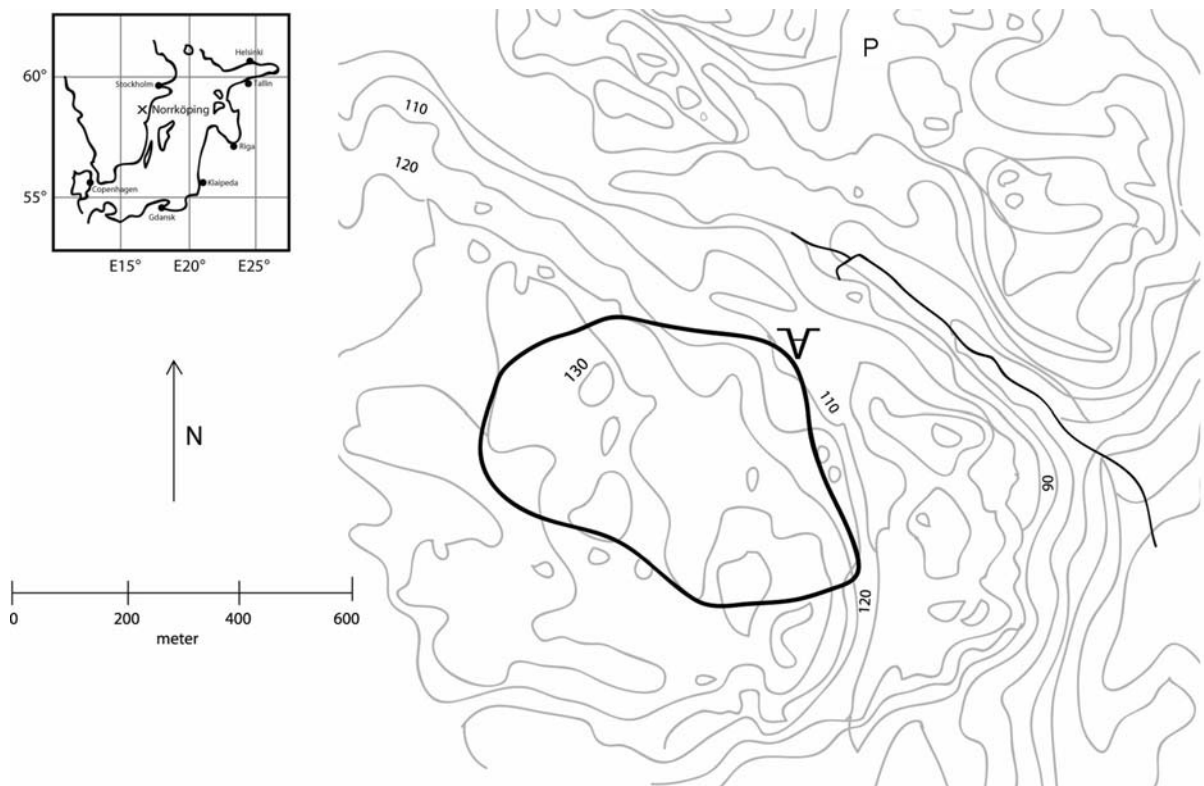


Fig. 1 The catchment area in southeast Sweden ($58^{\circ}44' N$; $16^{\circ}21' E$) is approximately 0.22 km^2 . The location of the weir (located at the “spring”) is marked at the map with a

V and the location of precipitation collectors are 300 m north of the catchment

(hereafter denoted ‘spring’, Fig. 1) to measure water discharge from the catchment. The weir was installed 1 m directly downstream from the spring, so the runoff water had little contact with the air. The water level was continuously registered (except in June 2004 due to technical problems) using a water level gauge (A. Ott, Kempten, Germany); the water discharge was calculated using a discharge rating curve, and average daily records were calculated for the 2003–2004 period (see Fig. 2). Periods with no change in water level are considered to be ‘normal’, as no obvious technical problems were observed and because the same pattern was observed in previous water discharge measurements from 1987 to 1996 (Maxe 1995).

Sampling procedures

Soil samples

Soil samples ($n = 16$) were collected in May 2003 across the catchment. The catchment was divided into a grid with 16 nodes by lines running north–south and west–east, located approximately 130 m apart. The samples were collected with a metal soil corer, 7 cm in diameter, to a depth of 40 cm (ca. 50% of the nodes) or, when the shallowness of the soil did not permit such deep sampling, to the bedrock. Whole soil cores were homogenized, and further sample treatments of the soil core are described in the section, ‘Chemical analysis’.

Precipitation sampling

Precipitation samples were collected approximately 300 m north of the catchment on three occasions between October 2004 and January 2005 (with sampling periods of 14, 19, and 9 days starting on Oct. 7, Oct. 21, and Jan. 2). Precipitation collectors ($n = 9$) were installed at a height of 160 cm in an open field and spaced at least 3.5 m from each other, in line with environmental monitoring standards (Standardization 1995). To avoid any possible influence from surrounding trees, the collectors were installed with an angle of at least 30° between the rain samplers and the tops of any trees. Precipitation was collected in glass funnels, each collecting rain from an effective surface of 0.31 m^2 , and glass flasks of approximately 250 ml, pre-washed with Milli-Q water and then rinsed 5 times with a hexane/acetone (1:1) mixture. Samples from all nine collectors were analysed on the two sampling occasions in October 2004 and from three of the collectors on the sampling occasion in January 2006. The precipitation samples were transported to the lab and stored in a deep freeze (-20°C) until further analysis.

Runoff sampling

Water samples were collected at the outlet of the catchment, at the spring, and directly upstream from the weir for analysis of Cl_{org}

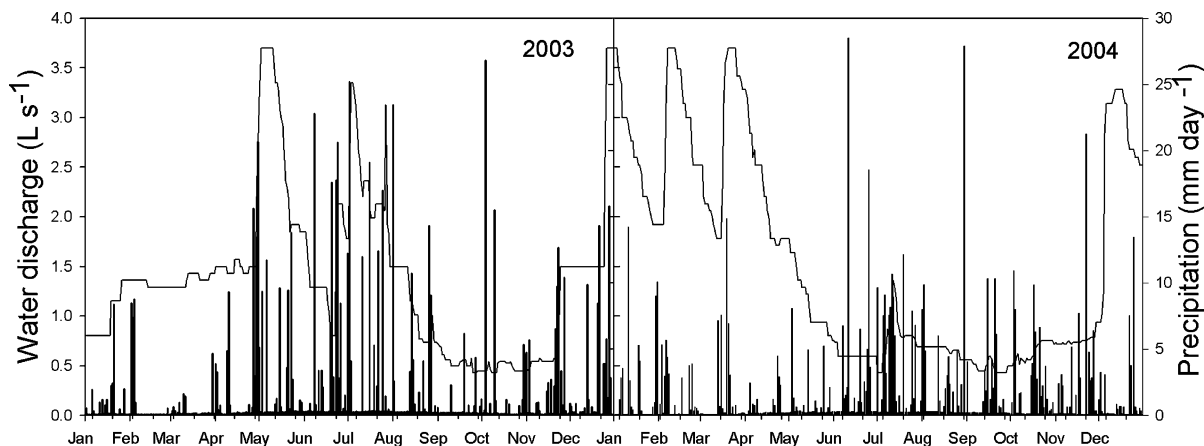


Fig. 2 Precipitation and water discharge in 2003 and 2004 in the catchment. Both precipitation and water discharge are based on daily measurements

(adsorbable organic halogens: AOX), Cl_{in} , and total organic carbon (TOC). The samples were collected in 500-ml high-density polyethylene (PE) bottles (WWR International). Before sampling, the PE bottles were rinsed carefully with reverse osmosis (RO) water and then rinsed three times with the runoff water. The sampling interval was every second week from January 2003 to January 2005. Six replicates were collected on each sampling occasion. The maximum time between the first and last sample collected during a sampling round was 5 min. The samples collected for analysis of AOX, Cl_{in} , and TOC were stored and treated in the same manner as the precipitation samples were. In addition to the bi-weekly sampling rounds, runoff samples were collected around the time of a rain event in August 2003, when approximately 23 mm of rain fell within 2 days. Water samples were collected on three occasions: on the first occasion, 1 week before the water level had started to rise because of the rain, one sample was collected; on the second occasion, approximately 14 h after the rain had started and the water level had risen 3 mm (corresponding to an increase of 0.05 l s^{-1}), samples were collected every 10 min for a total of 17 samples; on the third occasion, 1 day after the rain had stopped, when the water level had returned to the pre-rain level, one sample was collected.

Chemical analysis

Water content and loss-on-ignition in soil

The water content of the soil was determined by drying the soil to a constant weight at 105°C . The soil was sieved using a 2-mm mesh and then milled to 0.5 mm. The milled soil was stored in glass bottles at room temperature until loss-on-ignition (l.o.i.), total chlorine (TX), and total organic halogen (TOX) were analysed (see below). The samples were thoroughly mixed before the analyses were carried out; l.o.i. was determined by combusting the milled soil for 2 h at 620°C , the amount of organic carbon being estimated as 50% of the weight loss. One replicate was analysed per soil core.

Total nitrogen in soil

The total amount of nitrogen was determined by analysing 50–80 mg (<50 mg for soil samples with high carbon contents) of sieved and milled soil (0.12 mm) using a 2400 CHN Elemental Analyzer (PerkinElmer, Wellesley, MA). The detection limits were, as a percentage of dried milled soil, 0.05% for total nitrogen and 0.25% for total carbon.

Cl_{org} concentration in runoff and precipitation

The water samples were analysed for Cl_{org} concentration as adsorbable organic halogens (AOX), (EU 1996). The AOX method measures the sum of chlorine, bromide, and iodine and does not distinguish between the different halogens. Since chlorine is by far the most abundant of these halogens in the soil environment (Brady and Weil 2002), the mass estimates are based on the assumption that chlorine dominates in the samples. If other halides are present in considerable amounts, the method will overestimate the Cl_{org} in the samples.

Briefly described, 20 ml of the water sample was diluted with RO water to a final volume of 100 ml in a 300-ml Erlenmeyer flask. Activated carbon (50 mg; Euroglas), acidified nitrate solution (20 ml; 0.22 M KNO_3 , 0.02 M HNO_3), and approximately 5 drops of concentrated HNO_3 (yielding a $\text{pH} < 2$) were added to the flasks and the suspension was placed on a rotary shaker (180 rpm) for 1 h. The suspension was filtered through a 0.45- μm polycarbonate filter (Euroglas), and then rinsed with an acidic nitrate solution (approximately 20 ml; 0.01 M KNO_3 , 0.001 M HNO_3) followed by acidified RO water (approximately 20 ml, adjusted to $\text{pH} 2$ with HNO_3). The filter was combusted in a stream of oxygen at $1,000^{\circ}\text{C}$ in an AOX analyser (ECS3000; Euroglas) in which the formed hydrogen halides were determined by means of microcoulometric titration with silver ions. One replicate of each sample replicate was analysed. Blanks of 100 ml of Milli-Q water were analysed. The blanks contained $<3 \mu\text{g l}^{-1} \text{Cl}_{\text{org}}$, and the samples were clearly above the Cl_{org} detection limit of $1 \mu\text{g l}^{-1}$. The coefficient of variation (CV; calculated by

dividing the standard deviation by its mean) of the replicates was <15%.

Cl_{org} and Cl_{in} concentrations in soil

The principle for analysing Cl_{org} and Cl_{in} in soil is based on the AOX analysis described above but without addition of activated carbon. The amount of organic halogens (TOX) in a solid sample is analysed after washing the sample with a nitrate solution to remove inorganic halides. The washing procedure is excluded when analysing the total amount of halogens (TX) and the amount of Cl_{in} is achieved by subtracting the amount of organic halogens from the total amount of halogens since this procedure has been shown to be more reliable than extracting the soil and analysing the extract by potentiometric titration (Johansson et al. 2001). Normally, chlorine is by far the most abundant halogen in environmental samples; hence, the total mass of halogens is, by tradition, calculated as the amount of chlorine, as was done in the present study. Below follows a more detailed description of the methods.

The concentration of Cl_{org} (measured as total organic halogens: TOX) in solid samples was analysed according to Asplund et al. (1994). Briefly described, 20 mg of the milled sample was added to an acidic nitrate solution (20 ml; 0.2 M KNO₃, 0.02 M HNO₃) and shaken on a rotary shaker (180 rpm) for at least 1 h. The suspension was filtered through a 0.45-µm polycarbonate filter, and then the analysis followed the AOX analysis procedure described above. One replicate of each soil sample was analysed. Blanks were analysed using the same procedure but without addition of soil. All samples were clearly above the detection limit, which was approximately 1 µg Cl_{org} g⁻¹ (d.w.).

The total amount of chlorine (TX) was determined by adding 20 mg of sieved and milled soil (0.12 mm) to a small crucible followed by direct combustion in the AOX analyser. One replicate of each soil sample was analysed. Blanks were analysed by combustion of the crucibles without the addition of soil. All samples were clearly above the detection limit, which was approximately 1 µg Cl g⁻¹.

Cl_{in} and nitrate concentrations in runoff and precipitation

Cl_{in} concentration was determined using an MIC-2 ion chromatography system, with chemical suppression (Metrohm). The analyses were done according to the standard procedure for the determination of Cl_{in} concentration of water with low contamination levels. The water samples were thawed and filtered through 0.15-µm filter (Metrohm) and separated on a Metrosep A Supp 5 IC column (150 × 4.0 mm) (Metrohm) with a Metrosep A Supp 4/5 Guard pre-column (Metrohm). The ions were transported by means of an eluent comprising 0.0024 M Na₂CO₃ and 0.003 M NaHCO₃. The equipment was calibrated when the eluent was new, and a high and a low calibration standard were analysed approximately every 10 samples. The samples were clearly above the Cl_{in} detection limit of 0.01 mg l⁻¹.

Total organic carbon (TOC) concentration in runoff and precipitation

Total organic carbon concentration was analysed using a Shimadzu 5000 TOC Analyzer (Shimadzu). All samples were analysed in three replicates. Blanks comprising Milli-Q water and a reference standard were analysed every 10 samples.

Estimation of input and output fluxes and storage

Precipitation data for the catchment from the sampling period were too scattered to allow monthly extrapolations. Monthly and annual inputs of Cl_{in} to the catchment by means of wet deposition were estimated by combining precipitation amount data from a nearby meteorological station (Simonstorp) with precipitation chemistry data (1983–1999) from the three closest meteorological stations in the Swedish precipitation monitoring network, the Sjöängen (58°46' N, 14°18' E, *n* = 172, 120 m a.s.l.), Aspveten (58°48' N, 17°23' E, 1985–1999, *n* = 180, 20 m a.s.l.), and Norra Kvill (57°49' N, 15°34' E, 1985–1999, *n* = 165, 261 m a.s.l.) stations. Inverse

distance-weighted interpolation (Eq. 1) was used to estimate the wet deposition of Cl_{in} in the catchment (Helsel and Hirsch 2002). The interpolation method assumes that values closer to the stations are more representative of the values to be estimated than values further away are. This is appropriate for Cl_{in} , as it is influenced by the distance from the coast and hence should be more influenced by the Aspveten and Norra Kvill samples, as they were taken closer to the east coast. Weightings change according to the linear distance of the samples from the catchment; the elevation of the sites does not affect the weightings, as it is not believed to have a major impact.

$$z(\chi_p) \equiv \frac{\sum_{i=1}^n z(x_i) \cdot \frac{1}{d^k}}{\sum_{i=1}^n \frac{1}{d^k}}$$

where, $z(\chi_p)$ is the interpolated value, n is the number of data values, $z(x_i)$ is the value at point i , d is the distance between points i and p , and k is the distance weighting. The interpolated average monthly concentrations were multiplied by the monthly precipitation obtained from the Simonstorp station, to yield monthly input fluxes and subsequently annual fluxes.

The Cl_{in} , Cl_{org} , and TOC output was estimated by interpolating the bi-weekly concentration measurements to arrive at daily concentration values, and by combining these with daily water discharge values to estimate monthly as well as annual fluxes.

The Cl_{in} , Cl_{org} storage of the catchment was estimated by multiplying the concentration in each soil core with the soil bulk density of each soil core and calculate the median area-based estimate the storage of all the soil cores in the catchment.

Statistics

Correlation between variables was tested using two-tailed Kendall's tau (threshold for accepting significance, 95% probability). The data displayed a monotonic relationship (non-linear), so Kendall's tau test instead of Pearson's r was

chosen to measure the strength of the correlation between the variables (Helsel and Hirsch 2002). Furthermore, Kendall's tau does not require a normal distribution among samples, is insensitive to extreme values, and does not presume a bivariate normal distribution. A post hoc analysis was done to determine the statistical power of the present study to detect a difference in concentration (5 and 10 $\mu\text{g Cl}_{\text{org l}}^{-1}$, 0.5 and 1 mg TOC l^{-1} , and 0.05 and 0.1 $\text{mg Cl}_{\text{in l}}^{-1}$) between two sampling occasions when using two, three, and five replicates (Cohen 1988).

Results

Hydrology

The total amounts of precipitation in 2003 and 2004 were 762 and 697 mm, respectively. Precipitation in 2003 exceeded the 30-year average (1951–1980, 696 mm), while the 2004 precipitation was close to the average. The amounts of precipitation occurring during the three sampling occasions from October 2004 to January 2005 were estimated to be 30 (0–10, min–max), 26 (0–7, min–max), and 21 (0–8, min–max) mm day^{-1} from the observations made at the Simonstorp meteorological station.

The average water discharge in the two observation years was 1.5 l s^{-1} . The total annual runoff of the catchment was approximately 200 mm in 2003 and 220 mm in 2004. The discharge increased by a factor of three in the late spring and late summer of 2003, in the early spring of 2004, and in the winter both years (Fig. 2). The water discharge was rather low in fall 2003 and summer 2004, but the flow could still be measured all year round.

Soil chemistry

Analysis of the soil samples showed that the soil in the catchment had a water content of approximately 30% and a total organic carbon content of approximately 50 $\text{mg C}_{\text{org g}}^{-1}$ soil d.w. (Table 1). The concentration of Cl_{org} in soil varied from 26 to 178 $\mu\text{g Cl}_{\text{org g}}^{-1}$ soil d.w., which was approx-

Table 1 Chemistry data for 16 soil cores (<40 cm depth) sampled in a grid over the catchment

Variable	Mean	Range (min–max)
Water content (%)	31	13–60
Organic carbon (mg C g ⁻¹ soil d.w.)	46	3–268
Organic chlorine (μg Cl _{org} g ⁻¹ soil d.w.)	87	26–178
Chloride (μg Cl _{in} g ⁻¹ soil d.w.)	40	9–131
Total nitrogen (mg N g ⁻¹ soil d.w.)	2.2	0.8–4.8

Organic carbon is calculated as l.o.i.*0.5

imately twice the Cl_{in} concentrations. The average chlorine-to-carbon ratios in the soil were 7 mg Cl_{org} g⁻¹ C_{org}, and varied from 1 to 12 mg Cl_{org} g⁻¹ C_{org}.

Precipitation chemistry

The pH of the rain samples collected near the catchment averaged 5.4 while the Cl_{in} content ranged from 0.6 mg l⁻¹ to 2.6 mg l⁻¹ (Table 2). The monthly concentrations of Cl_{in} obtained by interpolation ranged from 0.3 mg l⁻¹ to 1.3 mg l⁻¹. The concentrations increased in the autumn and remained high until late spring (Fig. 3). The concentration of Cl_{in} measured in the catchment was within the range, except for the samples obtained in January (Table 2). Among the three rain sampling occasions, the concentrations of Cl_{org}, TOC, and NO₃⁻ were lowest in the January samples, while Cl_{in} concentrations were highest in January.

Runoff chemistry

The runoff water temperature was lowest in March/April at 3.5°C and highest in September at 9.8°C in both 2003 and 2004. The water leaving the catchment had an annual average pH of 5.0 and 5.3 in 2003 and 2004, respectively (Table 3). The pH varied between 4.7 and 5.9 over the 2-year period, with a peak approaching 6.0 occurring in September in both years. Cl_{in} concentrations were relatively stable during both observation years and even though the runoff varied by a factor of nine, the concentration of Cl_{in} generally varied by a factor of only between 2.1 and 2.9.

Both the TOC and Cl_{org} concentrations in the runoff generally varied by a factor of approximately two, though extremes were occasionally reached during the observation period for min–max values of 2.6–17.0 mg l⁻¹ and 12–99 μg l⁻¹, respectively (Fig. 4). The values were in general approximately four to six times the concentrations measured in precipitation. In both years, the concentration of Cl_{org} started to increase in August, peaked in November, and decreased thereafter. TOC concentrations, however, display no such pattern.

Visual inspection of the graphs in Fig. 4 suggests that the concentrations of the studied variables somewhat follow the water discharge. In general, high concentrations of Cl_{org} and TOC were observed during periods of high water discharge, while the opposite pattern was observed for Cl_{in} concentration and pH. However, statistical analyses reveal that none of the

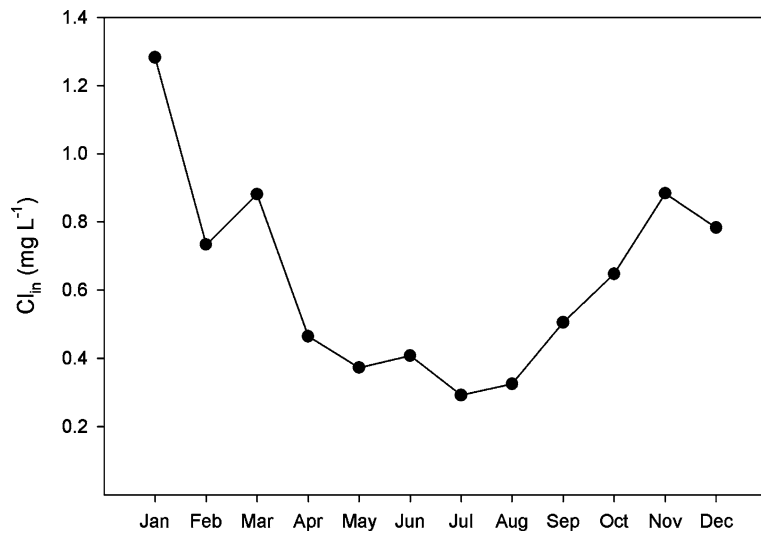
Table 2 Detected concentration and estimated input of Cl_{org}, Cl_{in}, TOC, pH, and NO₃⁻ in precipitation collected in precipitation samplers placed in an open field 300 m outside the studied catchment

	Precipitation concentrations				Input transport (g m ⁻¹ yr ⁻¹)	
	Date 1 (n = 9) ^a	Date 2 (n = 7) ^a	Date 3 (n = 3) ^a	Total average	2003	2004
pH	4.9 (4.6–5.1)	5.8 (4.8–6.0)	^b	5.4	–	–
Cl _{in} (mg l ⁻¹)	0.6 (0.6–0.7)	0.7 (0.7–0.8)	2.3 (1.8–2.6)	1.2	0.9	0.8
TOC (mg l ⁻¹)	2.2 (1.6–2.7)	1.7 (1.2–2.3)	1.0 (0.8–1.1)	1.6	1.2	1.1
Cl _{org} (μg l ⁻¹)	7 (5–9)	5 (4–7)	5 (3–7)	6	0.005	0.004
NO ₃ ⁻ (mg l ⁻¹)	2.3 (2.1–2.5)	1.5 (1.4–1.6)	0.88 (0.86–0.90)	1.6	1.2	1.1

^a Samples for Date 1 were taken in October 2004, Date 2 in November 2004, and Date 3 in January 2005

^b Not measured

Fig. 3 Interpolated Cl_{in} concentrations for the observed catchment. Interpolation was done by inverse distance-weighted interpolation from the three closest meteorological stations in the Swedish precipitation monitoring network (the Aspvreten, Sjöängen, and Norra Kville stations)



variables is strongly correlated with the water discharge. Kendall's tau correlation analysis of the 2-year data yielded a weak positive correlation between water discharge and TOC concentration ($\tau = 0.375$, $P < 0.001$) and an even weaker correlation between water discharge and Cl_{org} concentration ($\tau = 0.106$, $P < 0.001$). Similarly, a negative correlation was observed between water discharge and chloride concentration ($\tau = -0.264$, $P < 0.001$) and pH ($\tau = -0.216$, $P = 0.035$).

As revealed by statistical analysis, the correlations between concentration and water discharge are not strong. Still, it is notable that the highest concentrations of Cl_{org} and TOC concur with the highest runoff values. However, dividing the dataset into wet and dry periods suggests different Cl_{org} concentration patterns. During wet periods of high water discharge (above 0.7 l s^{-1}) the

concentrations remain quite stable. In contrast, during dry periods (below 0.7 l s^{-1} , denoted as base flow), the concentrations of Cl_{org} and TOC are clearly influenced by discharge peaks, and can increase by up to four times during a water discharge peak, as shown in the rain event study. During a rain event in late July 2003, the Cl_{in} concentration decreased to almost half the average concentration, whereas the Cl_{org} and TOC concentrations increased to at least twice the average levels. Two days before the sampling day it rained heavily, precipitation totalling 12 mm on the first day and 25 mm on the next. The runoff increased from 0.8 l s^{-1} the week before the rain event to 3.4 l s^{-1} on the day of sampling. Scrutinizing the data even more closely reveals that TOC concentration generally peaks during a high-flow event and is most often accompanied

Table 3 Runoff water chemistry (total of 53 sampling occasions, six replicates sampled on each occasion) at the weir during the 2003–2004 sampling period

	Runoff chemistry		
	2003 ($n = 28$)	2004 ($n = 25$)	Volume-weighted mean
Q (l s^{-1})	1.4 (0.4–3.7)	1.5 (0.4–3.7)	-
pH	5.3 (4.8–5.9)	5.0 (4.7–5.9)	-
Cl_{in} (mg l^{-1})	2.4 (1.4–2.9)	2.5 (1.9–2.9)	2.5
TOC (mg l^{-1})	5.6 (3.1–17.0)	5.6 (2.6–10.6)	6.5
Cl_{org} ($\mu\text{g L}^{-1}$)	38 (23–99)	33 (12–59)	39
NO_3 (mg l^{-1})	0.1 (<0.1–0.4)	0.1 (<0.1–0.4)	0.1

Mean value of the sampling period, range (minimum and maximum), and volume-weighted means

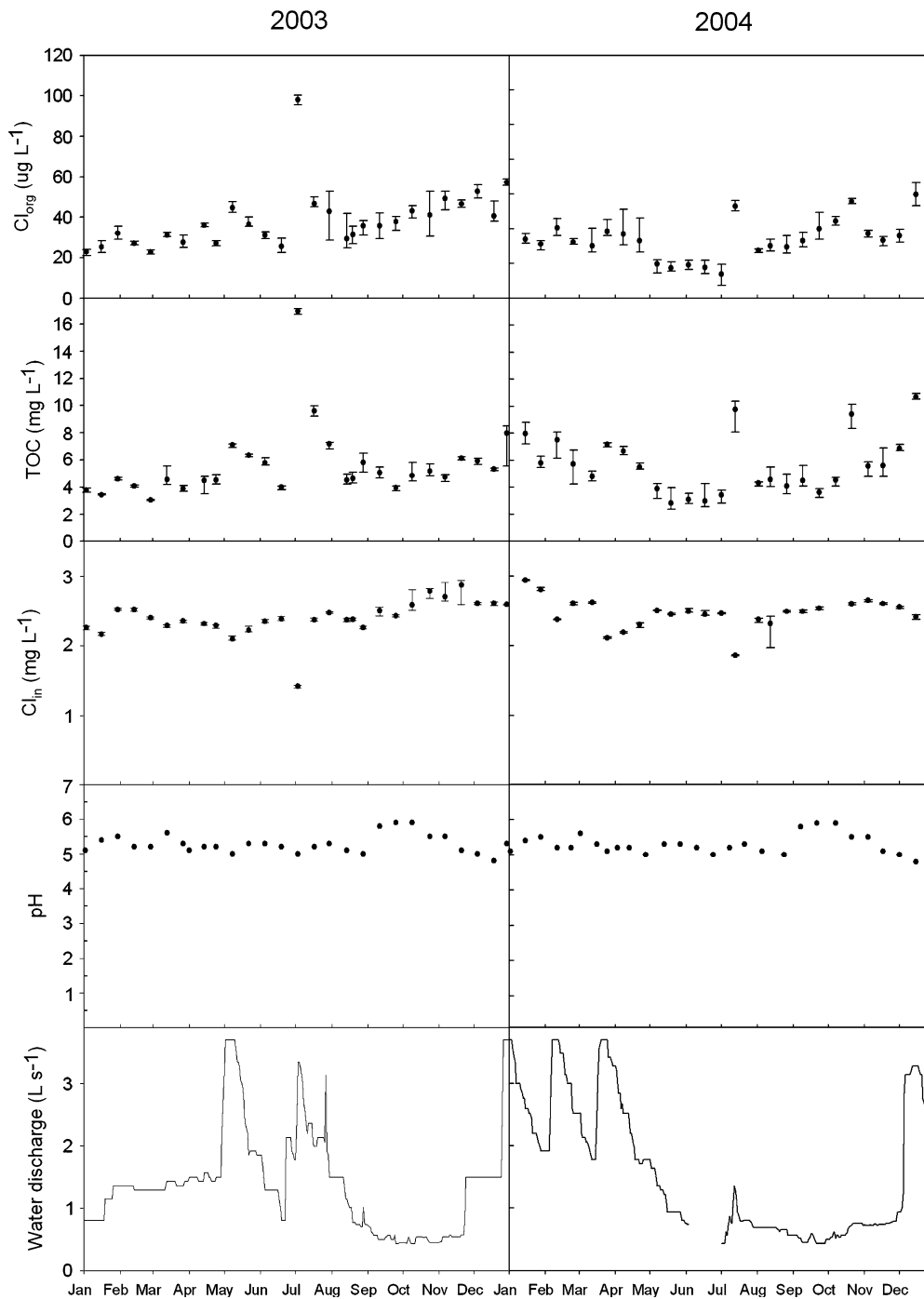


Fig. 4 Runoff concentrations (minimum, average, maximum) of Cl_{org} (organically bound chlorine measured as AOX), TOC (total organic carbon), Cl_{in} (chloride), pH, and water discharge in the 2003 and 2004 observation years

by a peak in Cl_{org} and a decrease in Cl_{in} . This is most evident under low-flow conditions, like those during the extreme occasions in July 2003

and July 2004 when the Cl_{in} concentration decreased considerably and the concentration of TOC and Cl_{org} increased by a factor of four.

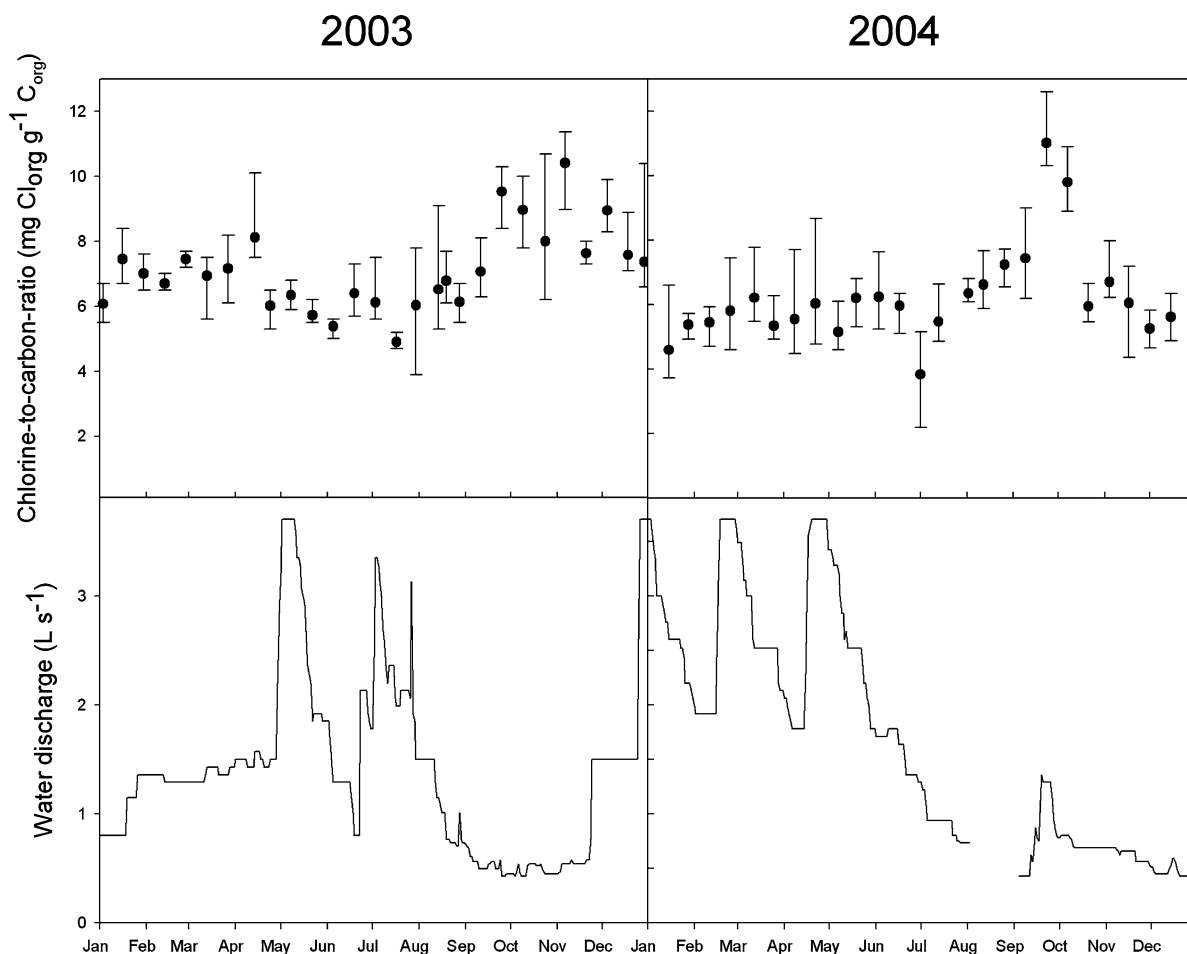


Fig. 5 Estimated chlorine-to-carbon ratios ($\text{mg Cl}_{\text{org}} \text{g}^{-1} \text{C}_{\text{org}}$) and water discharge in 2003 and 2004. Note that the ratio starts to increase in July, peaks in October–November, and then declines in December

Degree of organic matter chlorination

The Cl_{org} concentration co-varied with TOC ($\tau = 0.498$, $P < 0.001$), i.e., high TOC concentrations often coincided with high Cl_{org} concentrations. Even though these concentrations were correlated, the chlorine-to-carbon ratio varied from 3.4 to $10.3 \text{ Cl}_{\text{org}} \text{g}^{-1} \text{TOC}$ during the period with an average of $6.6 \text{ mg Cl}_{\text{org}} \text{g}^{-1} \text{TOC}$ (Fig. 5). A clear seasonal pattern was observed, in which chlorine-to-carbon ratios increased starting in July, peaked in October, decreased in November and December, and then held steady or slightly decreased from January to July.

Observations during a rain event

During the observed rain event in August 2003, the TOC concentrations increased from 4 mg l^{-1} to 8 mg l^{-1} as the water discharge increased, while Cl_{org} concentrations decreased by a few micrograms per litre. The increase in TOC concentration concurring with the slight decrease in Cl_{org} concentration generated a clear decrease in the chlorine-to-carbon ratio with increasing water discharge. A rapid decrease in chlorine-to-carbon ratio from $11 \text{ mg Cl}_{\text{org}} \text{g}^{-1} \text{C}_{\text{org}}$ was followed by a period when the chlorine-to-carbon ratio varied from sample to sample between 4 and $6 \text{ mg Cl}_{\text{org}} \text{g}^{-1} \text{C}_{\text{org}}$. After

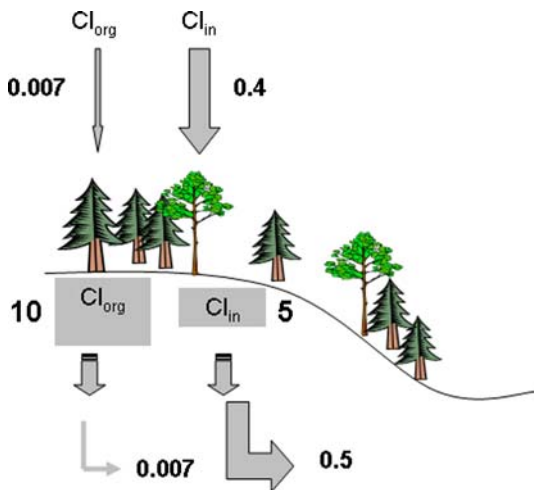


Fig. 6 Overall chlorine budget for the observed catchment (58°44' N, 16°21' E). Area-based storage is estimated from soil core samples (<40 cm depth). Input is estimated by combining daily precipitation amounts measured at Simonstorp (5 km NW of the catchment) with monthly interpolated concentrations from three meteorological stations (Sjöängen, Norra Kvill, and Aspöreten) situated 60–110 km from the catchment. Output is estimated from daily runoff measurements in the catchment in combination with interpolated bi-weekly runoff concentrations. Flux and storage units are $\text{mg m}^{-2} \text{yr}^{-2}$ and gm^{-2} , respectively

1 day, when the water discharge had reached the level of the day before the rain started, the chlorine-to-carbon ratio was also at the same level as before the rain event, approximately $7 \text{ mg } Cl_{org} \text{ g}^{-1} C_{org}$.

Chlorine budget estimates

The estimated annual inputs of Cl_{in} via wet deposition for 2003 and 2004, based on the interpolated data, were 0.42 and 0.43 g m^{-2} , respectively (Fig. 6). The annual wet deposition of Cl_{org} was estimated to be 0.007 and $0.006 \text{ gm}^{-2} \text{yr}^{-1}$ in 2003 and 2004.

Based on interpolated data, the estimated output of Cl_{in} in 2003 and 2004 via runoff was approximately 0.48 and 0.54 g m^{-2} , respectively, whereas the output of Cl_{org} via runoff was estimated to 0.008 and $0.007 \text{ g m}^{-2} \text{yr}^{-1}$ in 2003 and 2004, respectively. The rain-event study indicates that interpolation based on bi-weekly sampling might influence the estimated transport of both Cl_{in} and Cl_{org} . In order to evaluate

whether this might be the case in the present study, we estimated the transport during the 10-day period between the sampling occasions on August 19 and August 28, 2003 in two different ways; interpolation with and without the rain-event data. The Cl_{in} and Cl_{org} fluxes with the rain-event data gave transports from the catchment of 1.66 kg and 19.7 g , respectively whereas exclusion of the rain-event data gave 1.72 kg and 19.0 g . The comparison shows that the transport of Cl_{in} during this particular 10-day period was overestimated and the transport of Cl_{org} underestimated, by ca. 4% when excluding the rain-event data. Hence, in cases when numerous short-term rain-events take place, transport estimates might be incorrect also on annual basis. However, taking into account that the annual transport of Cl_{in} from the studied catchment was ca. 100 kg and the transport of Cl_{org} was ca. $1,800 \text{ g}$ the annual rain-event influence on Cl_{in} and Cl_{org} transport appears to be negligible since the number of rain-events taking place between sampling occasions were only three in 2003 and four in 2004. In conclusion, non-accounted for rain-events are not likely to have had a significant influence on the annual transport of Cl_{in} and Cl_{org} of the present study.

A dry deposition estimate, based on the assumption that Cl_{in} is neither lost or retained in the catchment and thus assuming steady-state, renders a dry deposition of 0.08 and 0.12 g m^{-2} in 2003 and 2004, respectively. The effect on the dry deposition estimate if Cl_{in} is retained in or released from soil is further elaborated upon in the discussion.

The storage of Cl_{org} and Cl_{in} in the topsoil was estimated to be 10 and 5 g m^{-2} , respectively by multiplying the soil concentration with the soil density. In summation, the annual input of Cl_{in} via wet deposition was slightly less than the estimated output of Cl_{in} via runoff. Thus, the input versus output of Cl_{in} was almost balanced, and Cl_{org} transport is within the margin of error of Cl_{in} transport. The total chlorine ($Cl_{org} + Cl_{in}$) storage in the topsoil is approximately 30 times larger than the transport of Cl_{in} , while the Cl_{org} storage is twice as large as the Cl_{in} storage. Hence, the major input and output of chlorine is inorganic and the major pool in the soil is organic.

Table 4 Post hoc analysis to determine the statistical power of the present study to detect a difference in concentrations of Cl_{org} , Cl_{in} , and TOC between two sampling occasions when using two, three, and five replicates (Cohen 1988)

	Effect size for respective compound							
	Cl_{org} ($\mu\text{g L}^{-1}$)		Cl_{in} (mg L^{-1})		TOC (mg L^{-1})		$\text{Cl/C ratio (mg Cl}_{\text{org}} \text{ g}^{-1} \text{ C}_{\text{org}})$	
	5	10	0.05	0.1	0.5	1	1	1.5
Replicates	Power (%)							
2	14	36	54	73	63	79	47	64
3	27	74	64	82	69	88	59	79
5	51	97	71	91	78	95	73	92

The standard deviation is $3.5 \mu\text{g Cl}_{\text{org}} \text{ l}^{-1}$, $0.05 \text{ mg Cl}_{\text{in}} \text{ mg l}^{-1}$, $0.4 \text{ mg TOC l}^{-1}$, and $0.9 \text{ mg Cl}_{\text{org}} \text{ g}^{-1} \text{ C}_{\text{org}}$

Methodological considerations

The average standard deviation among replicates on each sampling occasion was $3.5 \mu\text{g Cl}_{\text{org}} \text{ l}^{-1}$, $0.4 \text{ mg TOC l}^{-1}$, $0.05 \text{ mg Cl}_{\text{in}} \text{ l}^{-1}$, and $0.9 \text{ mg Cl}_{\text{org}} \text{ g}^{-1} \text{ C}_{\text{org}}$. The variation of TOC concentration increased with increased concentration, but Cl_{org} and Cl_{in} showed no such tendency. A post hoc analysis indicates that when five replicates were used to analyse Cl_{org} concentrations in runoff water, the present study had a power of 97% to detect a difference of $10 \mu\text{g l}^{-1}$ between two sampling occasions, when the alpha (significance level) was set to 0.05 and the standard deviation of Cl_{org} was $3.5 \mu\text{g l}^{-1}$. If the number of replicates is reduced to three or two, as often recommended in the methodology literature, the power decreases to 64% and 54%, respectively (Table 4). In sum, to achieve a high statistical power one will need five replicates to detect a difference of $0.1 \text{ mg Cl}_{\text{in}} \text{ l}^{-1}$, $10 \mu\text{g Cl}_{\text{org}} \text{ l}^{-1}$, and $1.5 \text{ mg Cl}_{\text{org}} \text{ g}^{-1} \text{ C}_{\text{org}}$ between two sampling occasions. Hence, our study suggests that at least five replicates are needed on each sampling occasion if the goal is, for example, to detect changes in the Cl_{org} and Cl_{in} concentrations in runoff from the studied catchment of $10 \mu\text{g Cl}_{\text{org}} \text{ l}^{-1}$ and $0.1 \text{ mg Cl}_{\text{in}} \text{ l}^{-1}$.

Discussion

A small flux of Cl_{in} and a large pool of Cl_{org} under near steady-state conditions

The results of the present study suggest that the storage of Cl_{org} is considerably larger than the

storage of Cl_{in} , which is in line with the few earlier studies conducted in the temperate region (Öberg and Grön 1998; Johansson et al. 2003a). The storage of Cl_{org} in the temperate region has to the best of our knowledge previously only been estimated for the top 60 cm of a spruce forest soil in Denmark (Öberg and Grön 1998) and the top 20 cm of forest soils in southeast Sweden (Johansson et al. 2003a), and these studies gave storages of 60 and $8 \text{ g Cl}_{\text{org}} \text{ m}^{-2}$, respectively. Cl_{in} is generally determined in water, so the total storage in soil is therefore rarely reported. The study of a spruce forest soil in Denmark mentioned above did not include Cl_{in} , but the other study did and reports Cl_{in} storage of $2 \text{ g Cl}_{\text{in}} \text{ m}^{-2}$. Other studies have focussed on the concentrations of Cl_{in} and Cl_{org} in soil without making pool estimates, and these studies repeatedly support the findings that the concentration of Cl_{org} is considerably larger than the storage of Cl_{in} in the top layer of forest soils in the temperate region (Rodstedth et al. 2003; Johansson et al. 2004). A study in a sub-tropical forest soil in southeast China supports the hypothesis that organic matter is a limiting factor for the occurrence of Cl_{org} and that the concentration of Cl_{org} is low in soils with low organic matter content (Asplund and Grimvall 1991; Johansson et al. 2004). In contrast, the concentration of Cl_{in} depends mainly on deposition, which in turn depends on the distance from the sea. Hence, the relative distribution of Cl_{in} versus Cl_{org} varies from site to site. The site we studied is situated in an area of moderate Cl_{in} deposition and contains rather high organic matter content in the top layer. In line with the above reasoning, both the concentration and storage of

Cl_{org} is considerably larger than the storage of Cl_{in} .

In contrast, the *transport* of chlorine ($\text{Cl}_{\text{org}} + \text{Cl}_{\text{in}}$) is approximately 30 times smaller than the total storage ($\text{Cl}_{\text{org}} + \text{Cl}_{\text{in}}$) of chlorine in the soil and the transport of Cl_{org} is negligible in relation to the transport of Cl_{in} . As discussed in an earlier paper, this implies that the pool of Cl_{org} in soil originates from transformed Cl_{in} either in/on plants or in the soil itself (Öberg et al. 2005). Several studies indicate that Cl_{in} may be transformed biotically in soil (Clutterbuck et al. 1940; Hunter et al. 1987; Gribble 1996; Verhagen et al. 1996; Öberg et al. 1997), while others demonstrate that abiotic transformation may also take place (Keppler et al. 2000; Hamilton et al. 2003). Some recent studies suggest that transformation, biotic or abiotic, may take place in decaying leaves even before they leave the tree (Reina et al. 2004). In addition, there are indications that a simultaneous transformation of Cl_{org} into Cl_{in} also takes place in soil (Öberg and Sandén 2005; Bastviken et al. 2006).

The situation under near steady-state conditions, despite the small transport, large pool, and complex biotic and abiotic transformation processes, resembles those of the biogeochemical cycling of, for example, carbon, nitrogen, and sulphur in soil (Schlesinger 1997). Actually, both sulphur and nitrogen have previously been used as internal tracers of water movement, which worked surprisingly well since near steady-state conditions generally prevail (Moldan and Cerny 1994). The practice of using sulphur as an internal tracer was abandoned in the 1970s due to the uncertainty caused by changes in the storage. It is tempting to suggest that we are now facing a similar situation with Cl_{in} , as evidence increasingly suggests that it is actually not inert in soil.

The results of the present study show that the concentrations of Cl_{org} in runoff water are low as compared to the concentration of Cl_{in} and that the major output consequently is Cl_{in} which also has been discussed in a previous study (Öberg and Sandén 2005).

Retention or precipitation of compounds in the soil has been described previously for organic carbon. It is well documented that organic matter is transported from topsoil in groundwater

recharge areas, and that most of the organic matter that subsequently precipitates at lower levels is eventually mineralized, even though the turnover rate of the various fractions ranges from months to perhaps thousands of years (Schlesinger 1997). TOC concentrations are generally higher in topsoil leachate and generally lower in deeper soil layers (Michalzik et al. 2001). It is well known that concentrations of Cl_{org} in surface water and in soil generally increase with increased TOC concentration (Enell et al. 1989; Asplund and Grimvall 1991; Johansson et al. 2003a). Since the Cl_{org} is related to organic matter in both runoff water and in the catchment soil, it appears likely that Cl_{org} from topsoil behaves similarly to the organic matter. Based on the above reasoning, it has been hypothesized that part of the Cl_{org} present in topsoil is leached to deeper soil layers and that most Cl_{org} formed in soil is retained there until it is degraded and mineralized (and released as Cl_{in}), while only a small part of the Cl_{org} is leached to surface waters.

Estimating the dry deposition

We found the annual input and output of Cl_{in} to be almost in balance (Fig. 6). According to prevailing theory, based on the assumption that Cl_{in} moves unaffected through soils, the Cl_{in} deposited in a catchment via wet and dry deposition is transported out of the catchment via runoff (Eriksson 1960). Wet deposition is measured using procedures similar to those used in the present study, whereas dry deposition is either deduced as runoff minus wet deposition (e.g. Juang and Johnson 1967) or measured as throughfall (i.e., water trickling through canopies) minus wet deposition (Hultberg and Grennfelt 1992). Dry deposition is considered to be of the same magnitude as wet deposition. The wet deposition found in the present study was similar to that previously reported for the larger Stubbetorp catchment, whereas the runoff we found was considerably lower (0.5 as compared to $0.7 \text{ g m}^{-2} \text{ yr}^{-1}$) (Maxe 1995). The previous study suggested a dry deposition of $0.3 \text{ g m}^{-2} \text{ yr}^{-1}$ using the output minus input approach. In the present study, the discrepancies between Cl_{in} input and output were found to amount to approximately $0.1 \text{ g m}^{-1} \text{ yr}^{-1}$.

The sub-catchment we studied has a higher content of pine than the whole catchment does, which could lower the dry deposition—though it would appear unlikely for the dry deposition to be as small as $0.1 \text{ g m}^{-2} \text{ yr}^{-1}$. Another possibility is that the transformation of Cl_{in} into Cl_{org} is larger in the sub-catchment than in the larger catchment, which implies a net Cl_{in} retention in the soils, but this possibility remains speculative, since the factors influencing these processes are largely unknown.

Imbalances between input and output of Cl_{in} in a catchment are generally explained by dry deposition, based on the assumption that Cl_{in} is inert in soil, i.e. the input by wet and dry deposition should equal the output (Eriksson 1960; Juang and Johnson 1967). Imbalances can also be explained by mineral weathering (Peters 1991), but the Cl_{in} content in minerals is less than 0.005% in the area where the observed catchment is situated (Melkerud et al. 1992) and therefore a minor contributor to runoff Cl_{in} . The estimates of dry deposition in the catchment are of a similar size as previously estimated in the catchment (Maxe 1995). Past research suggests that imbalances also may be explained by formation (uptake of Cl_{in}) or decomposition (release of Cl_{in}) or chlorinated organic matter in both soil and biomass. It is indisputable that soil and biomass processes have an affect on the chlorine balance (Öberg et al. 2005), although the rate remains uncertain and subsequently the influence on the present budget.

High concentrations of Cl_{org} and TOC during dry period high flow

The runoff concentrations of TOC and Cl_{org} varied considerably more than the concentration of Cl_{in} did. Based on existing understandings of hydrological patterns, some general conclusions can be drawn regarding periods when runoff is dominated by water with a long water residence time (base flow) and periods when water with a long water residence time is mixed with newly entered precipitation or snow melt (high flow) (Brutsaert 2005). Runoff under base-flow conditions generally consists of deeper groundwater that has spent a comparatively long time in the catch-

ment. This is because runoff in dry periods originates from old groundwater mixed with soil water stored near streams or areas saturated with water, and the latter can undergo rapid transport to the outlet during a rain event dramatically changing the proportions of old ground water versus surficial soil water (Brutsaert 2005). In the present study, the concentrations of TOC and Cl_{org} observed in runoff in periods of low flow (below 0.7 l s^{-1} , denoted as base flow) were clearly more influenced by rain events than they were in periods of high flow. These observations are in line with previous studies that report similar patterns (Bishop et al. 1990). These patterns are considered to be due to the fact that runoff water during dry-period rain events is strongly influenced by surficial soils with higher organic matter concentrations, resulting in higher amounts of dissolved soil organic matter and higher TOC as well as higher Cl_{org} concentrations in runoff.

Increasing chlorine-to-carbon ratios in runoff water during high-flow

In the present study, we found that the TOC concentration increased while the chlorine-to-carbon ratio decreased during the observed rain event. The former observation is in line with general hydrological knowledge, suggesting that the origin of the water during the rain event was mostly from surficial soil layers rather than from deeper soil layers. It is likely that the high concentrations of TOC observed in runoff under high-flow conditions may only derive from surficial soils near a stream or wet area, where the soil water is hydrologically connected to the output (Bishop et al. 2004). Hence, it is likely that very small areas are responsible for the peaks in TOC concentration, while larger areas are responsible for the levels between such peaks. The observation that the chlorine-to-carbon ratio decreased during the rain-event and thus with decreasing soil depth is consistent with previous studies which suggest that the chlorine-to-carbon ratio in organic matter increases with soil depth (Öberg and Grön 1998). High chlorine-to-carbon ratios were generally observed under low-flow conditions when the water originated from deeper soil layers.

Seasonal changes in the chlorine-to-carbon ratio

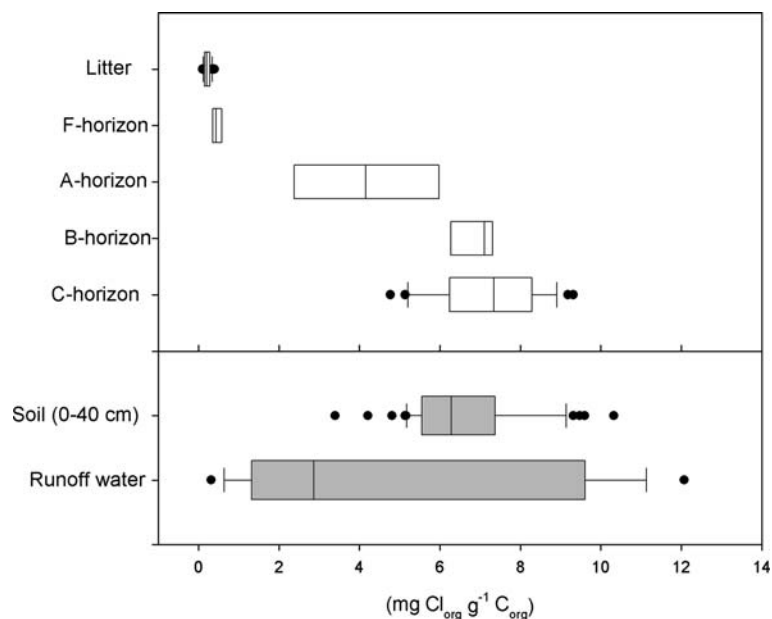
Our results suggest that the degree of chlorination of the organic matter in runoff varies over the seasons (Fig. 5). Organic matter became increasingly chlorinated in the autumn in 2003 and 2004. There are several plausible explanations of the observed pattern, two of which we will discuss in more detail below; these two explanations are that differing soil water origins (i) render differences in the chlorine-to-carbon ratio and (ii) increase the chlorination and/or decrease the dechlorination of organic matter.

As mentioned above, previous research suggests that chlorine-to-carbon ratios increase with soil depth (Öberg and Grön 1998). This pattern may be due to that organic matter with elevated chlorine-to-carbon ratios is leached from the topsoil to deeper soil layers or that the highly chlorinated organic matter is more resistant to decay, and therefore is in greater abundance in the older soil organic matter deeper in the profile. So far, studies of the vertical distribution of Cl_{org} have been confined to coniferous forest soil in the temperate region. The results of these studies are compiled in Fig. 7, which suggest that the chlorine-to-carbon ratio in such forests is below $0.1 \text{ mg Cl}_{\text{org}} \text{ g}^{-1} \text{ C}_{\text{org}}$ in the litter, approximately 1 mg

$\text{Cl}_{\text{org}} \text{ g}^{-1} \text{ C}_{\text{org}}$ in the organic layer, and between 5 and $10 \text{ mg Cl}_{\text{org}} \text{ g}^{-1} \text{ C}_{\text{org}}$ in the B-horizon and in deeper layers. Thus, one may hypothesize that runoff water originates from soil layers with lower chlorine-to-carbon ratios in the winter and spring and from layers with higher chlorine-to-carbon ratios in the late summer and fall.

Observations of increasing chlorine-to-carbon ratios in soil organic matter in the late summer and autumn are consistent with the results of a previous study, which showed a net increase in the degree of chlorination of coniferous forest soil litter in such periods (Öberg et al. 2005; Öberg and Sandén 2005). It is well known that chlorinated organic compounds can be microbially produced (Neidleman and Geigert 1986; Gribble 1996), that many soil microorganisms can produce enzymes that catalyse the formation of reactive chlorine species (e.g., Clutterbuck et al. 1940; Hunter et al. 1987), and that litter-degrading fungi, for example, may produce chlorinated organic matter (Öberg et al. 1996; de Jong and Field 1997; Gribble 2003). However, it is still unclear to what extent such processes actually take place in the field, even though recent studies suggest that the extensive and rapid transformation of Cl_{in} into Cl_{org} takes place in soil (Bastviken et al. 2006). Nevertheless, an increasing amount of evidence supports the hypothesis of

Fig. 7 Distribution of chlorine-to-carbon ratios in different compartments: litter, F-horizon, A-horizon, B-horizon, C-horizon, soil (0–40 cm), and runoff water. All data in the upper figure were compiled from Klosterhede in Denmark (Öberg and Grön 1998), and the data in the lower figure from the present study



Johansson et al. (2000), that enzymatic formation of reactive chlorine species (such as HOCl) enables the degradation of soil organic matter and results in the formation of chlorinated organic matter as a by-product (Ortiz-Bermúdez et al. 2003; Reina et al. 2004). In addition, it has been reported that abiotic chlorination processes may take place in soil (Keppler et al. 2000; Hamilton et al. 2003). Irrespective of the underlying process, the key question is whether the transformation of Cl_{in} to Cl_{org} in soil is mirrored in the runoff.

Based on the above findings, the following hypothesis is formulated as an explanatory framework for the observed increase in chlorine-to-carbon ratios in late summer and autumn. Fresh plant litter, which contains relatively high concentrations of easily degradable compounds, enters the soil compartment in the fall (Paul and Clark 1996). Hence, the activity of litter- and lignin-degrading organisms increases at this time. The increased activity of such organisms renders increased enzymatic formation of reactive chlorine, which in turn results in the oxidation, fragmentation, and chlorination of the organic matter, i.e., an increased chlorine-to-carbon ratio in the organic matter, which subsequently is leached from the soil and transported from the catchment with the runoff.

Further work is needed to test these hypotheses. The results of the study, considered together with results of previous research, suggest that the turnover of chlorine in soils is extensive and potentially important for natural chlorine cycling in general, which must be taken into account if one wishes to increase the understanding of the cycling of anthropogenic chlorine compounds in the environment, such as addition of road-salt.

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References

- Alexandersson H (2003) Correction of precipitation according to simple climatological principles. Swedish Meteorological and Hydrological Institute, Norrköping
- Asplund G, Grimvall A (1991) Organohalogens in nature. More widespread than previously assumed. *Environ Sci Technol* 25:1347–1350
- Asplund G, Christiansen JV, Grimvall A (1993) A chloroperoxidase-like catalyst in soil: detection and characterization of some properties. *Soil Biol Biochem* 25(1):41–46
- Asplund G, Grimvall A, Jonsson S (1994) Determination of the total and leachable amounts of organohalogens in soil. *Chemosphere* 28(8):1467–1475
- Baes C, Sharp R, Sjöoreen A, Shor R (1984) A review and analysis of parameters for assessing transport of environmentally released radionuclides through agriculture. Oak Ridge National Laboratory, Oak Ridge
- Bastviken D, Sandén P, Svensson T, Ståhlberg C, Magonakis M, Öberg G (2006) Chloride retention and release in a boreal forest soil – effects of soil water residence time and nitrogen and chloride loads. *Environ Sci Technol* 40:2977–2982
- Bishop K, Grip H, O'Neill A (1990) The origins of acid in runoff in a hillslope during storm events. *J Hydrol* 116:35–61
- Bishop K, Seibert J, Köhler S, Laudon H (2004) Resolving the double paradox of rapidly mobilized old water with highly variable responses in runoff chemistry. *Hydrol Process* 18:185–189
- Blomqvist G (2001) De-icing salt and the roadside environment: air-borne exposure, damage to Norway spruce and system monitoring. Ph.D. Thesis
- Brady N, Weil R (2002) The nature and properties of soils. New Jersey, Pearson Education Inc
- Brutsaert W (2005) Hydrology: an introduction. Cambridge University Press, New York
- Chen J, Wheeler H, Lees M (2002) Identification of processes affecting stream chloride response in the Hafren catchment, mid-Wales. *J Hydrol* 264:12–33
- Christophersen N, Neal C (1990) Linking hydrological, geochemical, and soil chemical processes on the catchment scale: an interplay between modeling and field work. *Water Resour Res* 26(12):3077–3086
- Clutterbuck PW, Mukhopadhyay SL, Oxford AE, Rastriick H (1940) Studies in the Biochemistry of microorganisms. *Biochem J* 34:664–677
- Cohen J (1988) Statistical power analysis for the behavioral sciences. Lawrence Erlbaum Associates, Inc., Hillsdale, New Jersey
- Cook P, Jolly I, Leany F, Walker G, Allan G, Fifield L, Allison G (1994) Unsaturated zone tritium and chlorine 36 profiles from southern Australia: their use as tracers of soil water movement. *Water Resour Res* 30(6):1709–1719
- Cox M, Fraser P, Sturrock G, Siems S, Porter L (2004) Terrestrial sources and sinks of halomethanes near Cape Grim, Tasmania. *Atmos Environ* 38(23):3839–3852
- de Jong E, Field J (1997) Sulfur tuft and turkey tail: biosynthesis and biodegradation of organohalogen by basidiomycetes. *Annu Rev Microbiol* 51:375–414

- Dimmer C, Simmonds P, Nickless G, Bassford M (2001) Biogenic fluxes of halomethanes from Irish peatland ecosystems. *Atmos Environ* 35:321–330
- Enell M, Kaj L, Wennberg L (1989) Organiskt bundet klor (AOX) i Västerdalälven 1988. Stockholm, Institutet för vatten- och luftvårdsforskning (IVL)
- Eriksson E (1960) The yearly circulation of chloride and sulfur in nature; meteoerological, geochemical and pedological implications. Part II. *Tellus* 12:63–109
- EU (1996) Water Quality – Determination of adsorbable organically bound halogens (AOX). Approved April 1996:1485
- Graedel T, Keene W (1996) The budget and cycle of earth's natural chlorine. *Pure Appl Chem* 68(9):1689–1697
- Gribble G (1996) Naturally occurring organohalogen compounds – a comprehensive survey. In: Herz W, Kirby G, Moore R, Steglich W, Tamm C (eds) *Progress in chemistry of organic natural products*. Springer, Berlin
- Gribble G (2003) The diversity of naturally produced organohalogens. *Chemosphere* 52:289–297
- Grim R (1968) Clay mineralogy. New York, McGraw-Hill
- Grön C (1995) AOX in groundwater. In: A. Grimvall and E. de Leer (eds) *Naturally-produced organohalogens*. Dordrecht, Kluwer Academic publishers
- Hamilton JTG, McRoberts WC, Keppler F, Kalin RB, Harper DB (2003) Chloride methylation by plant pectin: an efficient environmetally significant process. *Science* 301:206–209
- Hedin LO, Armesto JJ, Johnson AH (1995) Patterns of nutrient loss from unpolluted, old-growth temperate forests – evaluation of biogeochemical theory. *Ecology* 76(2):493–509
- Helsel D, Hirsch R (2002) *Statistical methods in water resources*. Elsevier Science Publishers, Amsterdam
- Hjelm O, Johansson M-B, Öberg-Asplund G (1995) Organically bound halogens in coniferous forest soil – distribution pattern and evidence of In Situ production. *Chemosphere* 30(12):2353–2364
- Hoekstra EJ, Duyzer JH, de Leer EWB, Brinkman UAT (2001) Chloroform – concentration gradients in soil air and atmospheric air, and emission fluxes from soil. *Atmos Environ* 35:61–70
- Hultberg H, Grennfelt P (1992) Sulfur and seasalt deposition as reflected by throughfall and runoff chemistry in forested catchments. *Environ Pollut* 75(2):215–222
- Hunter JC, Belt A, Sotos LS, Fonda ME (1987) Fungal Chloroperoxidase method. United States Patent
- Johansson E, Ebenå G, Sandén P, Svensson T, Öberg G (2001) Organic and inorganic chlorine in Swedish spruce forest soil: influence of nitrogen. *Geoderma* 101:1–13
- Johansson E, Krantz-Rulcker C, Zhang B, Öberg G (2000) Chlorination and biodegradation of lignin. *Soil Biol Biochem* 32:1029–1032
- Johansson E, Sandén P, Öberg G (2003a) Organic chlorine in deciduous and coniferous forest soil in southern Sweden. *Soil Sci* 168:347–355
- Johansson E, Sandén P, Öberg G (2003b) Spatial patterns of organic chlorine and chloride in Swedish forest soil. *Chemosphere* 52:391–397
- Johansson E, Zhang Björn X, Hu Z, Sandén P, Öberg G (2004) Organic chlorine and chloride in submerged paddy soil: a case study in Anhui province, southeast China. *Soil Use and Management* 20:144–149
- Juang F, Johnson N (1967) Cycling of chlorine through a forested watershed in New England. *J Geophys Res* 72(22):5641–5647
- Kaczmarczyk A, Niemirycz E (2005) Adsorbable organic halogens (AOX) in Polish rivers – levels and changes. *Acta Hydrochim Hydrobiol* 33(4):324–336
- Keppler F, Biester H (2003) Peatlands: a major sink of naturally formed organic chlorine. *Chemosphere* 52(2):451–453
- Keppler F, Eiden R, Niedan V, Pracht J, Schröder H (2000) Halocarbons produced by natural oxidation processes during degradation of organic matter. *Nature* 403:298–301
- Laniewski K (1998) Halogenated organic matter in precipitation. Linköping, Linköping University, Thesis
- Laternus F, Fahimi I, Gryndler M, Hartmann A, Heal MR, Matucha M, Schöler HF, Schroll R, Svensson T (2005) Natural formation and degradation of chloroacetic acids and volatile organochlorines in forest soil – challenges to understanding. *Environ Sci Poll R* 12(4):233–244
- Lee R (1997) ^{36}Cl transport and fate in soil. Imperial College, London
- Lee R, Shaw G, Wadey P, Wang X (2001) Specific association of ^{36}Cl with low molecular wight humic substances in soil. *Chemosphere* 43:1063–1070
- Lockwood P, McGarity J, Charley J (1995) Measurement of chemical weathering rates using natural chloride as a tracer. *Geoderma* 64:215–232
- Lovett GM, Likens GE, Buso DC, Driscoll CT, Bailey SW (2005) The biogeochemistry of chlorine at Hubbard Brook, New Hampshire, USA. *Biogeochemistry* 72(2):191–232
- Löfgren S (2001) The chemical effects of deicing salt on soil and stream water of five catchments in southeast Sweden. *Water Air Soil Poll* 130:863–868
- Maxe L (1995) Effects of acidification on groundwater in Sweden: hydrological and hydrochemical processes. Report 4388. Stockholm, Swedish Environmental Protection Agency
- Melkerud P-A, Olsson M, Rosén K (1992) Geochemical atlas of Swedish forest soils, Rapport i skogsekologi och skoglig marklära nr 65. SLU, Uppsala
- Michalzik B, Kalbitz K, Park J-H, Solinger S, Matzner E (2001) Fluxes and concentrations of dissolved organic carbon and nitrogen – a synthesis from temperate forests. *Biogeochemistry* 52:173–205
- Moldan B, Cerny J (1994) Biogeochemistry of small catchments. A tool for environmental research. John Wiley & Sons Ltd., Chichester
- Mulder J, Christophersen N, Haus M, Vogt R, Andersen A, Andersen D (1990) Water flow paths and hydrochemical controls in the Birkenes catchment as

- inferred from a rainstorm high in seasalts. *Water Resour Res* 27:2919–2928
- Myneni S (2002) Formation of stable chlorinated hydrocarbons in weathering plant material. *Science* 295:1039–1041
- Neal C, Kirchner JW (2000) Sodium and chloride levels in rainfall, mist, streamwater and groundwater at the Plynlimon catchments, mid-Wales: inferences on hydrological and chemical controls. *Hydrol Earth Sys Sci* 4(2):295–310
- Neidleman SL, Geigert J (1986) Biohalogenation. John Wiley and Sons, Chichester
- Nyberg L, Rodhe A, Bishop K (1999) Water transit times and flow paths from two line injections of ^3H and ^{36}Cl in a microcatchment at Gårdsjön, Sweden. *Hydrol Process* 13:1557–1575
- Ortiz-Bermúdez P, Srebotnik E, Hammel K (2003) Chlorination and cleavage of lignin structures by fungal chloroperoxidases. *Appl Environ Microbiol* 69(8):5015–5018
- Paul EA, Clark FE (1996) Soil microbiology and biochemistry. Academic Press, San Diego
- Peters N (1991) Chloride cycling in two forested lake watersheds in the west-central adirondack mountains, New York, USA. *Water Air Soil Pollut* 59:201–215
- Reina RG, Leri AC, Myneni SCB (2004) ClK-edge x-ray spectroscopic investigation of enzymatic formation of organochlorines in weathering plant material. *Environ Sci Technol* 38(3):783–789
- Rodstedth M, Ståhlberg C, Sandén P, Öberg G (2003) Chloride imbalances in soil lysimeters. *Chemosphere* 52:381–389
- Schlesinger W (1997) Biogeochemistry. An analysis of global change. Academic Press, San Diego
- Sheppard S, Evenden W, Amio B (1993) Investigation of the soil-to-plant pathway for I, Br, Cl and F. *J Environ Radioactiv* 21:9–32
- Standardization (1995) Water quality – determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulfate ions, using liquid chromatography of ions – Part 1: Method for water with low contamination (ISO 10304-1:1992), European Committee for Standardization, Brussel
- Stringer R, Johnston P (2001) Chlorine and the environment. Kluwer Academic Publishers, Dordrecht
- Thunqvist EL (2004) Regional increase of mean chloride concentration in water due to the application of deicing salt. *Sci Tot Environ* 325(1–3):29–37
- Verhagen FJM, Schwats HJ, Kuyper TW, Wijnberg JBPA, Field JA (1996) The ubiquity of natural adsorbable organic halogen production among basidiomycetes. *Appl Microbiol Biotechnol* 45:710–718
- Winterton N (2000) Chlorine: the only green element – towards a wider acceptance of its role in natural cycles. *Green Chem* 2:173–225
- Öberg G (2002) The natural chlorine cycle – fitting the scattered pieces. *Appl Microbiol Biotechnol* 58:565–581
- Öberg G (2003) The biogeochemistry of chlorine in soil. In: G Gribble (ed) The handbook of environmental chemistry. The natural production of organohalogen compounds. Springer-Verlag
- Öberg G, Grön C (1998) Sources of organic halogens in a Danish spruce forest soil. *Environ Sci Technol* 32:1573–1579
- Öberg G, Sandén P (2005) Retention of chloride in soil and cycling of organic matter-bound chlorine. *Hydrol Process* 19:2123–2136
- Öberg G, Brunberg H, Hjelm O (1997) Production of organically bound chlorine during degradation of birch wood by common white-rot fungi. *Soil Biol Biochem* 29(2):191–197
- Öberg G, Holm M, Sandén P, Svensson T, Parikka M (2005) The role of organic-matter-bound chlorine in the chlorine cycle: a case study of the Stubbetorp catchment, Sweden. *Biogeochemistry* 75:241–269
- Öberg G, Nordlund E, Berg B (1996) In situ formation of organically bound halogens during decomposition of Norway spruce needles: effect of fertilization. *Can J For Res* 26:1040–1048