

Chlorine Transport in a Small Catchment

Teresia Svensson



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Cover: Mirror of the water at the spring at Stubbetorp in March 2006.
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Abstract

It is generally known that chlorine compounds are ubiquitous in the environment. In recent years, researchers have concluded that chlorine is part of a biogeochemical cycle in soil involving an interaction between chloride (Cl_{in}) and organic-matter-bound chlorine (Cl_{org}). Even though there is indisputable evidence that Cl_{org} is formed naturally, there are actually few simultaneous field measurements of Cl_{org} and Cl_{in} . Previously stipulated conclusions with respect to underlying processes and transport estimates have thus been deduced from rather few concentration measurements. It is well known that the chemical composition in soil and runoff water varies widely over time and in space. The main objective of the thesis is to investigate the on-site variation of Cl_{in} , Cl_{org} and VOCs in runoff water in order to (i) construct a chlorine budget on a catchment scale to visualize the relative contribution of Cl_{in} , Cl_{org} , and VOCs; (ii) more reliably estimate how and why the concentrations of Cl_{in} , Cl_{org} , and VOCs in runoff water vary; and (iii) analyze the influence of various environmental variables on the transport.

The present thesis highlights the on-site variation and fluxes of Cl_{in} , Cl_{org} , and VOCs in a small forested catchment in southeast Sweden. Field flux data collected during a two-year period and a constructed overall chlorine budget were evaluated. The results show that the storage is dominated by Cl_{org} whereas the transport is dominated by Cl_{in} and that the storage is far much larger than the transport. Still, input and output is nearly in balance for all investigated chlorine species. It is interesting to note that these observations resemble observations made for carbon, nitrogen and sulphur; i.e. a large storage, small transport, complex biogeochemical cycling processes at hand but still close to steady state conditions with respect to output-input balances. It appears as if topsoil acts as a sink for Cl_{in} , while deeper soil acts as a source of Cl_{in} . In addition, the results of the thesis suggest that on-site variation depend on seasonal variations. These variations are to some extent caused by water discharge, but also by water residence time, internal chlorination/dechlorination of organic matter, and different soil water origins. Furthermore, both a net retention and a net release of Cl_{in} were observed in laboratory studies. The study indicates that simultaneous retention and release of Cl_{in} takes place in soil, which probably has an impact on the Cl_{in} import and export fluxes. Finally, the results show for the first time that tetrachloromethane can be emitted from laboratory incubated soil, and that soil nitrogen concentrations has quite different effects on the emission rates of chloroform and tetrachloromethane.

The results of the thesis, considered together with results of previous research, suggest that the turnover of chlorine in soils is extensive and potentially important for 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.

Keywords: catchment, chloride, chlorine, chloroform, organic chlorine, runoff water, soil, VOCs

Sammanfattning

De senaste decenniernas forskning har påvisat att en omfattande bildning och nedbrytning av klororganiska föreningar sker i mark. Bildning av sådana föreningar sker genom att klorid binds in i organiskt material. Denna naturliga bildning har rönt uppmärksamhet dels för att många klorerade ämnen är giftiga och dels för man tidigare trott att alla klororganiska ämnen uteslutande kommer från mänsklig verksamhet. Huvudmålet för föreliggande avhandling var att (i) uppskatta transporten av klorerade föreningar i nederbörd och avrinningsvatten, (ii) diskutera de klorerade föreningarnas ursprung med utgångspunkt från hur deras förekomst varierar i avrinningsvatten, (iii) undersöka hur transporten av klorid (salt) påverkas av olika faktorer och (iv) studera hur frisättningen av flyktiga klorerade föreningar från mark påverkas av kväve.

Avhandlingen bygger på en klorbudget som konstruerats utifrån fältstudier som genomförts i ett litet skogsbeklätt avrinningsområde i sydöstra Sverige. Dessutom har laboratoriestudier genomförts med jord som inhämtats från samma område. Resultaten visar att lagret av klor i marken är betydligt större än flödena och att det främst består av organiska ämnen medan flödet domineras av klorid (salt). Detta tyder på att en stor del av kloriden deltar i en biogeokemisk cykel vilket strider mot gängse uppfattning att klorid rör sig opåverkat genom mark. Hypotesen är att de översta marklagren fungerar som en sänka för klorid genom att omvandlas till organiskt bundet klor. De djupare jordlagren fungerar däremot som en kloridkälla genom att det klorerade organiska materialet transporterats med regnvatten från de ytligare till de djupare liggande lagren för att så småningom brytas ner, varvid klorid frisätts. Ovan beskrivna hypotes stöds av laboratoriestudierna där man kunnat notera att det sker såväl en fastläggning som en frisättning av klorid i mark. Resultaten från avhandlingen tillsammans med resultat från tidigare studier tyder på att en stor del av den klorid som finns i avrinningsvatten kommer från förmultnande organiskt material och att klorid med andra ord inte följer regnvattnets väg genom marken, vilket man tidigare trott. Studierna tyder alltså på att klorid till viss del "gör en omväg" med en tidsfördröjning på troligen åtskilliga upp till hundratals år. Vidare tyder studierna på att flyktiga klorerade föreningar som kloroform och tetraklormetan bildas i mark och att tillsats av kväve orsakar en minskning av kloroform och en ökning av tetraklormetan.

Avhandlingen visar tydligt att det är nödvändigt att rikta uppmärksamhet mot klors biogeokemi i mark och då inte minst mot de processer som påverkar transporten av klor från de övre marklagren till grundvatten och ytvatten om vi ska öka förståelsen av hur klorerade ämnen som tillförts naturen genom mänskliga aktiviteter beter sig.

Nyckelord: avrinningsområde, avrinningsvatten, flyktiga klorerade föreningar klor, klorid, kloroform, organiskt klor, mark

Ett varmt tack till

Först av allt vill jag tacka *Gunilla Öberg*, min handledare, för allt stöd jag har fått under min doktorandtid. Jag har framförallt uppskattat dina konstruktiva idéer, kommentarer till texter, problemlösande, entusiasm, kunskap och inte minst sällskap på intressanta konferensresor.

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List of papers

This thesis is based on the following papers, referred in the summary by their Roman numerals (I-V) and are appended to the thesis.

- I. 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.
- II. Svensson T., Sandén P., Bastviken B., Öberg G. Chlorine transport in a small catchment in southeast Sweden during two years. *Manuscript*.
- III. Svensson T., Laturus F., Sandén P., Öberg G. Chloroform in runoff water – a two-year study in a small catchment in southeast Sweden. *Submitted*.
- IV. Bastviken D., Sandén P., Svensson T., Ståhlberg C., Magounakis M., and Öberg G. (2006) Chloride retention and release in a boreal forest soil: effects of soil water residence time and nitrogen and chloride loads. *Accepted in Environmental Science & Technology*.
- V. Svensson T., Laturus F., Öberg G. Influence of nitrogen on the release of volatile organochlorines from coniferous forest soil: a laboratory study. *Manuscript*.

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1 Introduction

Chlorine is ubiquitous in the environment and one of the most common elements on the surface of the earth (Graedel and Keene 1996). Chlorine occurs in different species such as chloride (Cl_{in}), volatile chlorinated organic compounds (VOCs) such as chloroform, non-volatile compounds such as trichloroacetic acids, and organically bound in larger non-specific compounds such as humic and fulvic acids (Winterton 2000). A large variety of chlorine species have been detected in (i) water compartments such as surface water, ground water, and precipitation; (ii) air compartments such as aerosols, atmosphere, and soil air; and (iii) terrestrial compartments such as vegetation, organisms, soil, and sediments (Eriksson 1960; Asplund and Grimvall 1991; Hoekstra and Leer 1994; Grön 1995; Laniewski, Borén et al. 1995; Gribble 1996; Keene, Khalil et al. 1999; Haselmann, Laturus et al. 2002; Johansson, Sandén et al. 2003a).

The chemical composition of surface waters is a subject that has been under debate for at least 100 years. Prior to 1950, it was believed that the chemical composition of surface water was determined by catchment characteristics (Öberg and Bäckstrand 1996). In the mid-1950s, Eriksson introduced the hypothesis that surface water chemistry to a large extent was determined by precipitation chemistry (Eriksson 1955). His thesis was supported by extensive data on Cl_{in} and sulphur in precipitation and surface water. It has since then been generally accepted that Cl_{in} in surface water reflects its chemical composition in precipitation, on the assumption that Cl_{in} moves unaffected through soils (Schlesinger 1997). However, more recent research suggests that Cl_{in} participates in a complex biogeochemical cycle, which gives cause to re-evaluate the understanding that Cl_{in} is inert in soil and that Cl_{in} in surface water reflects its chemical composition in precipitation.

One of the pillars of the biogeochemical chlorine cycle is that surface water, in addition to Cl_{in} , contains various forms of organic chlorine (Cl_{org}): chlorinated organic matter, non-volatile chlorinated organic compounds and chlorinated volatiles (VOCs). Since the end of the 1980s, there have been numerous measurements of the total amount of organically bound chlorine (measured as AOX, adsorbable organic halogens) (Wigilius, Allard et al. 1988; Asplund and Grimvall 1991; Grimvall, Borén et al. 1991; Grön 1995; Kaczmarczyk and Niemirycz 2005). These studies show that

organic chlorine is ubiquitous in surface waters. The Cl_{org} in surface waters originates in part from anthropogenic sources (pulp-bleaching, solvents, pesticides, etc.) and in part from natural sources. It seems that the major part of the naturally occurring organic chlorine in surface water originates from the surrounding soil (Asplund and Grimvall 1991). Parts of the Cl_{org} are volatiles, such as chloroform, which have been detected in surface waters, polluted as well as unpolluted (Kostopoulou 2000; Laturnus, Lauritsen et al. 2000). Measurements of VOCs are scattered and time-series are rare. The origin of the VOCs in surface water as well as the relationship between occurrence of VOCs, Cl_{org} , and Cl_{in} is unclear, but it appears that the various chlorine species are related by a variety of transformation processes in soil.

1.1 The scope of the thesis

The work presented in this thesis focuses on fluxes and dynamics of chlorinated organic compounds and chloroform in runoff water. The main objective of the thesis is to investigate the on-site variation of Cl_{in} , Cl_{org} and VOCs in runoff water in order to (i) construct a chlorine budget on a catchment scale to visualize the relative contribution of Cl_{in} , Cl_{org} , and VOCs; (ii) more reliably estimate how and why the concentrations of Cl_{in} , Cl_{org} , and VOCs in runoff water vary; and (iii) analyze the influence of various environmental variables on the transport. The investigations were carried out in a small forested catchment in southeast Sweden in combination with laboratory studies. The following questions are addressed in this thesis, with the related research reported in Papers I through V as indicated:

What is the relative contribution of Cl_{in} , Cl_{org} , and VOCs in various pools and fluxes in the chlorine cycle?

- Paper I describe and evaluate fluxes and pools of chlorine by constructing a chlorine budget of a small forested catchment.

What is the on-site variation of Cl_{in} , Cl_{org} , and VOCs?

- Field flux and storage data were collected during a two-year period in a small forested catchment in southeast Sweden. The temporal variation and fluxes of Cl_{org} , Cl_{in} , and VOCs are the subject of Papers II and III, and the spatial variation and storage of Cl_{org} and Cl_{in} are the focus of Papers I and II. The chlorine species concentration variation and the budget estimates were used to evaluate possible chlorine sources.

What decides abundance and transport patterns of soil chlorine species?

- Paper IV examines the influence of water residence time as well as nitrogen and Cl_{in} load on Cl_{in} retention in soil, as observed and evaluated in laboratory incubated intact soil cores. Paper V describes observations on the influence of nitrogen on the release of VOCs from laboratory incubated soil.

2 Current scientific knowledge

2.1 Occurrence of chlorine

Chlorine (Cl_{in} and Cl_{org}) is found almost everywhere in the environment: in water, air, and terrestrial compartments. The concentrations vary between compartments, but the average concentrations of Cl_{in} are generally larger than the concentrations of Cl_{org} (Table 1). For example, the Cl_{in} concentration in various waters is measured in $mg L^{-1}$, while Cl_{org} is measured in $\mu g L^{-1}$ and VOCs in $ng L^{-1}$ (Eriksson 1960; Asplund and Grimvall 1991; Enell and Wennberg 1991; McCulloch 2003). In soils with a relatively large content of organic matter, Cl_{org} concentrations are two to four times the concentrations of Cl_{in} (Johansson, Sandén et al. 2003a). The cause of the widespread occurrence of Cl_{org} in surface waters and soil has been under debate since the end of the 1980s.

Table 1. Cl_{in} , Cl_{org} and chloroform concentrations in various waters, primarily in Sweden. Chloroform is one of the most frequently detected volatile chlorinated organic compounds (VOC) in surface water.

	Cl_{in} ($mg L^{-1}$)	Cl_{org} ($\mu g L^{-1}$)	Chloroform ($ng L^{-1}$)
Rain water	0.2-3.5 ^a	1-5 ^d	11-97 ^g
Groundwater	10-300 ^b	5-24 ^c	5-1600 ^h
Surface water (lakes and rivers)	0.74-11 ^c	5-200 ^f	4-3800 ⁱ

(a) Minimum and maximum concentrations obtained from 6 precipitation stations in different regions of Sweden 1983-1998 (Kindbohm, Svensson et al. 2001)

(b) Minimum and maximum concentrations from 20,100 wells (dug wells and drill wells) in Sweden sampled during 1984-1986 (Bertills 1995)

(c) Concentrations (10th and 90th percentiles) obtained from analyses of Swedish lakes during 1983-1994 (Wilander 1997)

(d) Minimum and maximum concentrations in rain and snow at 7 sites in Sweden (Laniewski, Boren et al. 1999; Laniewski, Dahlen et al. 1999)

(e) Minimum and maximum concentrations in groundwater from 14 wells in Denmark (Grön 1995)

(f) Minimum and maximum concentrations in 135 lakes (Asplund and Grimvall 1991) and rivers in Sweden (Enell and Wennberg 1991)

(g) Minimum and maximum concentrations of chloroform obtained from precipitation measurements in Germany 1988-1989 (Schleyer, Renner et al. 1991; Schleyer 1996)

(h) Minimum and maximum concentrations obtained from groundwater measurements at one site in Denmark (Laturmus, Lauritsen et al. 2000)

(i) Minimum and maximum concentrations compiled from rivers and lakes in Belgium, Canada, France, Germany, The Netherlands, Switzerland, UK, USA (McCulloch 2003).

2.1.1 Point sources

Chlorine may originate from natural sources such as sea salt deposition but also from anthropogenic sources, which are either well-identified point sources or more diffusive sources. One commonly discussed problem is that Cl_{in} is applied as a road salt and thereby enters soils and surface waters, which may cause problems for groundwater, vegetation, and soil structure (Blomqvist 2001; Löfgren 2001; Thunqvist 2004). Moreover, industrial activities like production of solvents and by-products of paper bleaching, drinking water chlorination, and pesticide use cause dispersal of Cl_{org} in the atmosphere, water, and soil (Stringer and Johnston 2001). For example, the concentrations of Cl_{org} , measured as adsorbable organic halogens (AOX), in surface water can reach $1000 \mu\text{g L}^{-1}$ downstream from a pulp mill (Häsänen and Manninen 1989) and chloroform, which is a common by-product of water chlorination and pulp bleaching, can reach concentrations above regulatory limits for drinking water in pulp-mill effluents (Juuti, Vartiainen et al. 1996).

2.1.2 Atmospheric deposition

Prior to the mid-1950s, the chemical composition of surface waters was considered to be a result of physical land-use history in combination with the geochemical, hydrological, and features of the surrounding area (Öberg and Bäckstrand 1996). In the mid-1950s, it was suggested that the chemical composition of rivers mirrors the chemical composition of precipitation (Eriksson 1955). The arguments were based on extensive Cl_{in} and sulphate data and implied that these compounds originated from oceans, as the oceans produce sea salt aerosols when the waves break the ocean's surface (Eriksson 1960). The aerosols are carried away with the winds to the atmosphere and are either transported back to the sea or deposited on land by precipitation that washes out Cl_{in} from the atmosphere. Gases and particles can also contain Cl_{in} ; they can either be deposited directly on the ground or stick to the crown of trees or washed with the precipitation to the soil. The input of Cl_{in} by gases and particles is called “dry deposition” compared to “wet deposition”, which is deposition of Cl_{in} by rain. The deposition to soil is generally higher in forested areas than over open land because atmospheric particles are attached to vegetation (Eriksson 1960) and possible leaching from the vegetation (Brady and Weil 2002). The prevailing understanding since at least the mid-1950s is that the deposited Cl_{in} is inert in soil and rapidly transported through the soils to the surface waters and rivers and back to the

sea. In the late 1980s, it was revealed that large amounts of Cl_{org} were present in soil and surface water and that Cl_{in} appeared to participate in a complex biogeochemical cycle. This has opened up a discussion on the inertness of Cl_{in} in soil.

It is well known that precipitation, in addition to Cl_{in} , also contains Cl_{org} (Enell and Wennberg 1991; Grimvall, Borén et al. 1991; Laniewski, Borén et al. 1995). Measurements of individual halogens in organic matter derived from precipitation have revealed that most of the organically bound halogens detected as AOX are chlorinated compounds (Laniewski, Boren et al. 1999). Brominated compounds are widespread but less prevalent, and organically bound iodine has only been detected at sites close to the sea (Laniewski, Boren et al. 1999).

Characterization of the Cl_{org} present in rain and snow has shown that the major part of Cl_{org} is found in fractions of relatively polar and non-volatile to semi-volatile compounds, in particular organic bases and acids (Laniewski, Boren et al. 1999). Chloroacetic acids can occasionally explain some percentage of the Cl_{org} in precipitation (von Sydow 1999), while the relative contribution from volatile organochlorines (VOCl) usually is smaller, with concentrations often even lower, in ppt ($ng\ L^{-1}$) levels (Schleyer 1996).

Very little is known about the origin of the Cl_{org} in precipitation. Known industrial pollutants, such as flame retardants (e.g. chlorinated alkyl phosphates) and pesticides (e.g. lindane) are typically present at ppt levels (Stringer and Johnston 2001), i.e. in concentrations about three orders of magnitude less than observed AOX concentration. In addition, throughfall contains higher concentrations of Cl_{org} than precipitation only; a study conducted at Klosterhede in northwest Denmark suggests that Cl_{org} in throughfall mainly originates from internal sources rather than from dry deposition (and thus external) sources (Öberg, Johansen et al. 1998).

2.1.3 Weathering

As mentioned previously, Cl_{in} has long been believed to participate in geochemical processes only, i.e. transported from oceans via soil back to the oceans again, being only negligibly affected by the cycling. Therefore riverine Cl_{in} has likewise in the past been considered to originate from the atmosphere only, despite possible weathering processes during the pathway through the soil (Eriksson 1960; Schlesinger 1997). There are limited analyses of Cl_{in} in rocks in Sweden, but acid bedrocks such as

granite contains low amounts of Cl_{in} , and the highest amounts are found in alkaline bedrocks (Melkerud, Olsson et al. 1992). Acidic minerals can be considered to have a lower chemical weathering rate than alkaline minerals. The weathering rate has been estimated for a small stream at Hubbard Brook with bedrock consisting of mainly granite. Approximately 2 % of the Cl_{in} stream output originates from weathering, which can be considered as small compared to the atmospheric contribution (Lovett, Likens et al. 2005).

2.1.4 Soil and vegetation processes

The widespread occurrence of Cl_{org} in lakes and its co-occurrence with organic matter has raised the question of whether Cl_{org} in surface water originates from surrounding environments rather than from deposition (Asplund and Grimvall 1991). The concentration of Cl_{org} in organic soil is in most cases higher than Cl_{in} (Johansson 2000). In fact, the percentage of chlorine in soil organic matter (0.01-0.5 %), is almost the same percentage as phosphorous (0.03-0.2 %) and slightly less than nitrogen (1-5 %) and sulphur (0.1-1.5 %) (Öberg 1998). The soil is mainly composed of high molecular weight substances, usually larger than 1000 Dalton (Hjelm and Asplund 1995) and the composition of Cl_{org} is similar to soil organic matter.

As summarized below, a number of studies suggest that Cl_{in} is transformed to Cl_{org} in soil and vegetation. Increasing evidence points in the direction that the processes are mainly biotic, but there are indications also of abiotic processes taking place (Keppler, Eiden et al. 2000; Hamilton, McRoberts et al. 2003).

Numerous studies show that a large number of specific Cl_{org} compounds are formed naturally by various organisms (Neidleman and Geigert 1986; Gribble 1996). Over 3000 different Cl_{org} compounds are known to be produced naturally (Gan, Yates et al. 1997). In addition, it seems that vegetation forms Cl_{org} compounds in fresh and senescent and humified plant material (Myneni 2002; Hamilton, McRoberts et al. 2003; Reina, Leri et al. 2004).

Researchers have also established that VOCs are formed in soil (Harper 1985; Varner, Crill et al. 1999; Haselmann, Ketola et al. 2000; Khalil and Rasmussen 2000; Rhew, Miller et al. 2000; Dimmer, Simmonds et al. 2001; Rhew, Miller et al. 2001; Laturnus, Haselmann et al. 2002; Cox, Fraser et al. 2004). Natural emission of chloroform and chloromethane has been estimated to equal to or even surpass

industrial emissions (Laternus, Haselmann et al. 2002; Montzka and Fraser 2003). Terrestrial ecosystems and boreal forest soils in particular seem to produce significant amounts of chloroform. The underlying processes of formation of Cl_{org} and VOCs are still a matter of discussion. Both biotic and abiotic processes are suggested formation pathways (Harper 1985; Öberg, Brunberg et al. 1997; Hoekstra, Verhagen et al. 1998; Haselmann, Ketola et al. 2000; Keppler, Eiden et al. 2000; Haselmann, Laternus et al. 2002; Hamilton, McRoberts et al. 2003), and it seems to suggest both a specific and un-specific formation by micro-organisms (Clutterbuck, Mukhopadhyay et al. 1940; Harper, Kennedy et al. 1988; Verhagen, Schwats et al. 1996; Öberg, Brunberg et al. 1997). In conclusion, there is considerable evidence that a natural formation of Cl_{org} and VOCs takes place in soil, but questions still remain on the importance of soil to the occurrence of Cl_{org} and VOCs in surface water and transport of the same.

2.2 Biogeochemical cycling of chlorine

It is widely believed that chlorine does not participate in biological processes, and that it is present in the environment only as Cl_{in} . The past decade of studies has revealed that Cl_{in} participates in a complex biogeochemical cycle (Asplund and Grimvall 1991; Winterton 2000; Lee, Shaw et al. 2001; Myneni 2002; Öberg 2002), involving for example, formation and degradation of Cl_{org} (consumption and release of Cl_{in}), volatilization, leaching and precipitation (Asplund, Christiansen et al. 1993; Öberg and Grön 1998; Dimmer, Simmonds et al. 2001; Hoekstra, Duyzer et al. 2001; Johansson, Ebenå et al. 2001; Rodstedth, Ståhlberg et al. 2003; Öberg and Sandén 2005) (Figure 1). Despite the emerging picture of chlorine cycling in soil, very little is known of the underlying processes and key environmental factors that control the occurrence and transport. In fact, the general understanding is still that the biogeochemical cycling and chemistry of chlorine is simple, with Cl_{in} the dominant if not the only species of importance. According to textbooks, Cl_{in} is virtually biologically and chemically inert in the environment and is assumed to act conservatively with respect to water—a view which is still commonly reiterated in leading scientific journals. Over the last decade, however, more and more data have been published that contradict this hypothesis (Hanes 1971; Larsson and Jarvis 1999; Nyberg, Rodhe et al. 1999; Viers, Dupre et al. 2001; Chen, Wheeler et al. 2002; Kauffman, Royer et al. 2003), and it has recently been suggested that formation and mineralization of Cl_{org} might explain the deviation from expected Cl_{in} behavior.

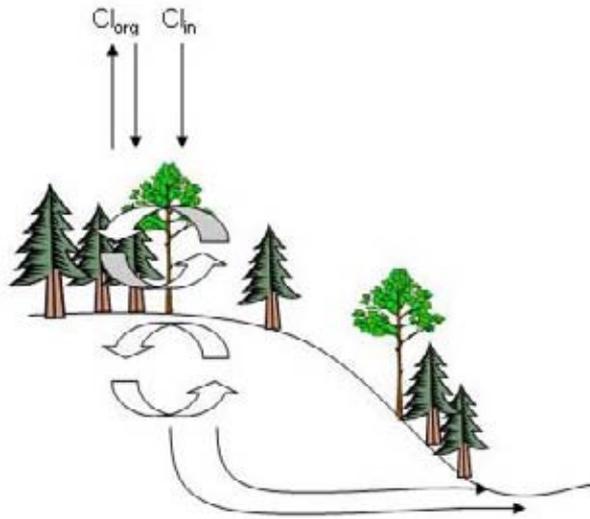


Figure 1. Conceptual picture of the biogeochemical cycling of chlorine in a forested catchment.

3 Methods

This thesis is based on catchment studies (Papers I-III), laboratory controlled soil lysimeters (Paper IV), and soil incubations (Paper V). All water and soil samples were collected at a forested site in southeast Sweden. This section describes some general aspects of the chosen methods. More detail on methods can be found in the original papers.

3.1 Outline of catchment methodology

A catchment is an area of land from which rainwater or snow melt drains into a reservoir, pond, lake, river, or stream. It is defined by a water divide (a boundary between catchments). Precipitation falling on the catchment (input) is drained through the soils to the water outlet or leaves the catchment by evapotranspiration (output) (Brutsaert 2005). Elements deposited on the catchments are subject to a variety of processes such as water transport (if soluble in water) and microbial, chemical, and geological processes. Catchment studies allow continuous observations to study fluxes and mass balances, which can provide insight to processes within the catchment. This information can thereafter be used for modeling, e.g. predicting runoff concentrations. As there is no previous information of simultaneous monitoring of Cl_{in} , Cl_{org} and chloroform, long-term estimates of variation in catchment output are therefore valuable for future modeling. The proper way to estimate mass output from a catchment is by the use of continuous water discharge and runoff concentration measurements. For example, retention of compounds can be observed by making input-output budgets such as Cl_{in} retention (e.g. Likens 1995). In the present thesis, a small forested catchment with no direct industrial impact or road salt effects represents the study object.

3.1.1 Site description

The studies were carried out within the Stubbetorp catchment, which is situated in a forested mountain area in southeast Sweden (58°44' N, 16°21' E), or within one of its sub-catchments, hereafter denoted as the Stubbetorp south sub-catchment (Figure 2). The Stubbetorp catchment has previously been described in Maxe (1995). In Paper I, the entire Stubbetorp catchment is studied, whereas Papers II and III focus on the

Stubbetorp south sub-catchment. In Papers IV and V, soil samples were collected in the northwestern part of the Stubbetorp catchment.

The highest hills in the Stubbetorp catchment are 130 metres above sea level, and the distance to the Baltic Sea is approximately 50 km. There are no known point sources in the area; the distance to larger roads where road salt is applied is 5 km downstream, which implies that there is no direct road salt or other external effects. It should be noted that the water divide in Figure 2 was estimated by assuming the general flow direction from elevation levels and taking account of the estimated Stubbetorp catchment area. Water samples for Paper II and III were sampled at the spring (Figure 2); there are no visible streams in the Stubbetorp south catchment area, but there are small wet areas in the upper catchment. The water from the spring flows into a mire and eventually reaches a stream where sampling was done for Paper I. The topography of the area is broken, and the bedrock, gneissic granite, and mineral chemical composition in soil is poor in Cl_{in} (Maxe, 1995). The only Cl_{in} containing mineral in the soil is apatite with a Cl_{in} content of 2 % and is assumed to occur to a maximum of 0.2 % in the soil (Melkerud, Olsson et al. 1992). Coniferous forest with pine (*Pinus sylvestris* (L.)) and Norway spruce (*Picea abies* (L.)) is the dominant vegetation.

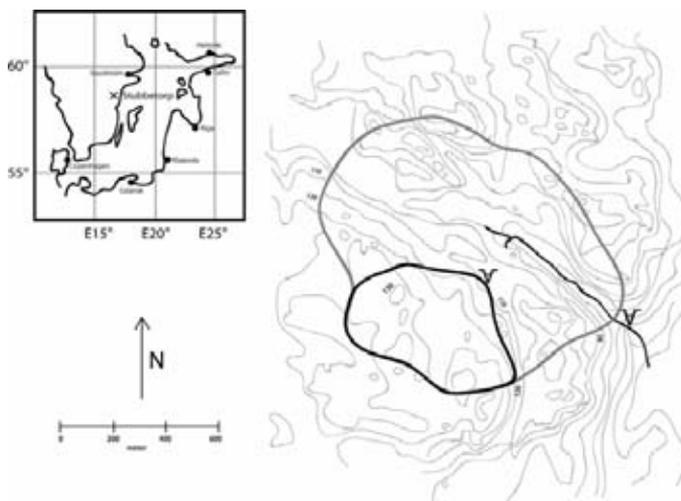


Figure 2. The Stubbetorp catchment area in southeast Sweden (58°44'N, 16°21'E) is approximately 0.87 km². Precipitation samples for Papers II and III were collected 300 m north of the catchment. Runoff samples for Paper I were collected at a weir at the outlet of the Stubbetorp catchment. Runoff samples for Papers II and III were collected at the “spring”, the outlet of Stubbetorp south catchment (the marked area in the southern part). Soil sampling for Papers I and II was done in the Stubbetorp catchment. Soil for the laboratory studies in Papers IV and V was collected in the northwestern part of the catchment.

3.1.2 Study outline

A chlorine budget for the Stubbetorp catchment (Maxe 1995) based on best available estimates was constructed to highlight what was previously known about terrestrial chlorine cycling (Paper I). Chlorine pool sizes, inputs (wet and dry deposition of Cl_{in} and Cl_{org} , respectively), and outputs (transport to runoff water of Cl_{in} and Cl_{org} and transport to the atmosphere of Cl_{org}) were estimated. The estimates showed that the Cl_{in} flux and the pool sizes of Cl_{in} and Cl_{org} were most robust in the sense that the estimates were based on a large number of samples in the specific catchment providing information about the variability in time and space. The other fluxes (transport of Cl_{org} to groundwater and atmosphere) were less robust since the best available estimates were based on data from other catchments or from laboratory studies, and typically these data did not include temporal or spatial variability. For example, the output (via runoff) estimate of Cl_{org} from the catchment was based on one concentration measurement extrapolated to an annual flux. This is a major concern since the Cl_{org} pool in the soil was approximately twice as large as the pool of Cl_{in} , and the total export of chlorine from the topsoil (15 cm) was dominated by Cl_{org} (Rodstedth, Ståhlberg et al. 2003). Therefore, in Paper II, the output of Cl_{org} and Cl_{in} was simultaneously measured during a two-year period to gain robust data concerning the natural variation in order to estimate the Stubbetorp south sub-catchment output.

There is strong evidence that chloroform is naturally formed in soil (Laternus, Haselmann et al. 2002), and evidence suggests that it is transported from soil to air and surface waters. However, there are few concentration measurements in surface waters. Hence, to acquire robust data, the output of chloroform and some additional VOCs to runoff water were observed through bi-weekly sampling during the same two-year period. The results were used to visualize the natural variation of concentrations in stream water and to make reliable estimations of the transport from soil to runoff water (Paper III). In addition, input via wet deposition of VOCs was observed in part during a period of four months.

3.1.3 Soil sampling for storage estimates

Soil samples were collected in May 2003 in the Stubbetorp catchment to determine the storage of Cl_{in} and Cl_{org} (Papers I and II). In order to obtain a representative sample of the storage in the catchment, the catchment was divided into a grid with 49 nodes by eight lines in the north-south direction and eight lines in the west-east direction located approximately 130 m apart. The soil core samples were collected with a metal soil cylinder, 7 cm diameter and to depths of 40 cm (61% of the nodes) and 30 cm or less (38% of the nodes). The whole soil core was homogenized. Further sample treatments of the soil core are described in the section on chemical analyses (Section 3.3).

3.1.4 Precipitation sampling for input estimates

Precipitation has been measured continuously since 1951 by the Swedish Meteorological and Hydrological Institute (SMHI) at Simonstorp station, 5 km west of the catchment. The long-term actual mean precipitation for the period 1951–1980 is 696 mm yr^{-1} , compensated for losses in the measurement by SMHI's correction factors (Eriksson 1983). The precipitation was measured within the catchment during 1986–1990 and the actual precipitation was 688 mm yr^{-1} (Maxe 1995). A more detailed description of the hydrochemistry in the catchment can be found in Maxe (1995). For 2003 and 2004 the monthly precipitation was estimated by daily values obtained from Simonstorp.

Precipitation data from the catchment collected in 2003 and 2004 were too scattered to allow monthly extrapolations. Monthly and annual input of Cl_{in} by wet deposition to the catchment were estimated by combining wet deposition data from the nearby meteorological station (Simonstorp) with precipitation chemistry data (1983–1999) from the three closest stations at approximately 60–120 km distance in the Swedish precipitation monitoring network (Paper II). The concentrations from the three stations were interpolated to yield concentrations data for Stubbetorp. Input via wet deposition of Cl_{in} was estimated by multiplying the interpolated concentration data with the precipitation amount measured at the meteorological station at Simonstorp. To sum up, the estimated input of Cl_{in} is rather robust on a time-scale of a year, but on a monthly basis the uncertainties are larger.

Precipitation samples were collected nearby the catchment (app. 300 m north) in order to measure the content of Cl_{org} and VOCs in rain on six occasions between October 2004 and September 2005. The precipitation collectors (n=9) were placed according to environmental monitoring standards in Sweden (Naturvårdsverket 2003), at a certain distance from each other and surrounding vegetation, which can increase the input by washout of the needles or leaves i.e. include dry deposited compounds on vegetation. Precipitation was collected on six occasions and stored in a refrigerator (ca. 4°C) in most cases for a maximum of 6 h and in a few cases for a maximum of 24 h before analyses of VOCs, or stored in a freezer for the remaining chemical analysis.



Figure 3. Precipitation sampling at Stubbetorp. Nine collectors were placed at least 3.5 m apart and at a height of 160 cm. (photo: Frank Laturmus)

3.1.5 Runoff sampling for output estimates

In 1987, a stainless steel V-notch weir was installed at the outlet of Stubbetorp south sub-catchment to measure the water discharge (Figure 4). The weir was installed directly at a spring and not in a stream. The water level was continuously registered by the aid of a gauge (A. Ott, Kempton) and the flux was calculated from a discharge rating curve and based on daily average discharge values. In Stubbetorp south sub-catchment, the water discharge has previously been continuously measured with daily records for the ten years 1987–1997 (Maxe 1995) and for Papers II and III in this thesis during 2003–2004.



Figure 4. Runoff sampling for Papers II and III at the spring, where the water discharge was measured by a V-notch weir with a gauge (in the box at the right picture) measuring the water table. (photo: Teresia Svensson)

Water samples for chemical analyses of Cl_{org} , Cl_{in} , TOC, and VOCs of runoff were collected upstream of the weir in Stubbetorp south sub-catchment in order to avoid air bubbles in the water samples, every second week from January 2003 to December 2004. Five to six samples were collected, one after another, every 30 seconds (given a total time between the first sample and the last of three minutes) on each occasion. The samples for Cl_{org} , Cl_{in} , and TOC were collected in PE bottles (app. 500 ml, high-density polyethylene, WWR International), pre-rinsed carefully with RO-water. VOCs samples were collected in glass flasks (app. 120 mL), which were pre-cleaned with MQ-water and hexane/acetone (1:1) mixture five times each and stored at 70°C until used for sampling. Prior to sampling, all bottles were rinsed three times with the runoff water. Thereafter, the flasks were filled with the water and the glass flasks were capped without headspace with aluminum caps with a septum (butyl PTFE (polytetrafluoroethylene), WWR International) and transported to the laboratory within 1 h and treated as the precipitation samples.

In addition to the bi-weekly samplings, runoff samples were collected during a rain event in August 2003 when approximately 23 mm rain fell over two days. Water samples were collected on three occasions: one sample was collected on the first occasion, one week before the water level started to rise due to the rain event; the second occasion was approximately 14 hours after the rain started. The water level had risen 3 mm (corresponds to an increase of 0.05 L s^{-1}) and samples were collected

every 10th minute with a total of 17 samples; an additional sample was collected during the third sampling occasion which took place one day after the rain had stopped, when the water level was back to the level before the rain event.

3.2 Outline of laboratory soil incubations

The soil samples for the soil lysimeter study in Paper IV and the soil headspace incubations in Paper V were collected in the Stubbetorp catchment described above. The sampling area is situated in a discharge area of the catchment, where the average groundwater table is less than 0.5 m below soil surface.

3.2.1 Soil lysimeter study

The soil lysimeter study was designed to investigate the influence of water residence time as well as nitrogen and Cl_{in} load on Cl_{in} retention in intact soil cores. Undisturbed soil cores (15 cm soil depth, cross-sectional area 80 cm²) were collected at the field site. The zero tension lysimeters were incubated in climate chambers mimicking the field conditions by controlling temperature and humidity. The lysimeters were irrigated with artificial rain twice a week, corresponding to concentrations in precipitation in the Stubbetorp area; the lysimeters were mounted so the water could freely leach out of the soil as previously described by Rodhstedt et al. (2003). The study was designed as a factorial experiment with three factors and two levels each (2³-factorial design). The soil lysimeters were treated with three factors; Cl_{in} , nitrogen, and rain, which were applied as high or low for each factor (Table 2). In sum, this experimental design provided eight different treatment combinations. Each combination was carried out in three replicates, resulting in a total of 24 soil lysimeters. Lysimeter treatments represented high and low levels of water, nitrogen (added as NH_4NO_3), and Cl_{in} (added as NaCl) load (high and low levels corresponding to the west and east coasts of Sweden, respectively).

Table 2. The factorial design for Paper IV. These amounts correspond to the low and high precipitation levels, inorganic nitrogen deposition, Cl_m wet deposition on the east and the west coasts of southern Sweden, respectively. There were eight treatment combinations, and each combination had three replicates, i.e. 24 soil lysimeters.

Factor	Level	
	Low	High
Water load (mm)	483	1449
Cl_{in} ($mg\ m^{-2}\ yr^{-1}$)	1449	4346
Nitrogen ($mg\ m^{-2}\ yr^{-1}$)	579	1931

3.2.2 Soil incubation study

The soil incubation study was designed to investigate the impact of nitrogen on the VOCl release from soil and intended to be a first report on possible effects of N fertilization on VOCl release. The litter layer was removed and soil was collected from the O-horizon (10 cm depth), sieved (2 mm mesh), and homogenized before being incubated in glass flasks (15 g w.w.) with different amounts of nitrogen (added as NH_4NO_3) added for two incubations periods of four days and six weeks, respectively. The present study was designed such that the nitrogen amendments corresponded to fairly realistic numbers for nitrogen deposition in southern Sweden and silvi-fertilization according to the Swedish National Board of Forestry (National board of forestry 1991). We estimated the additions by using the soil bulk density estimated in a previous study on soil from the same site (Rodstedth, Ståhlberg et al. 2003). In sum, the additions should correspond to 13 to 312 $kg\ N\ ha^{-1}$, which is slightly higher than the yearly deposition of nitrogen in the region (7-10 $kg\ N\ ha^{-1}$ in 2002) (Persson, Ressner et al. 2004) and approximately to one generation fertilization application to a mature forest soil recommended by the National Board of Forestry for Mid-Sweden (<300 $kg\ ha^{-1}$) (National board of forestry 1991). A typical fertilizer dose in Swedish silviculture is 150 $kg\ N\ ha^{-1}$ given as ammonium nitrate with addition of some dolomite, two to four times at intervals of about 10 years (Nohrstedt 2001). Both blanks (incubation with no soil added) and reference samples (incubation with soil added with solution without nitrogen) were used to identify VOCl background and soil release.

3.3 Chemical analyses

3.3.1 ...in water samples

Water temperature and pH were measured on the sampling occasions in the field with a digital thermometer and a field pH meter (PHM202 pHmeter, Radiometer Copenhagen).

3.3.1.1 Cl_{org}

The water samples were analyzed for Cl_{org} as AOX (adsorbable organic halogen, (EU 1996). In short, the organic compounds in the water sample were adsorbed on activated carbon, washed with an acidified nitrate solution to remove remaining Cl_{in}. Thereafter the sample was combusted at 1000°C in an oxygen atmosphere and the formed halides were titrated with silver ions with microcoulometric titration with an AOX instrument (ECS3000, Euroglas). The AOX method used to detect Cl_{org} actually measures the sum of chlorine, bromide, and iodine but 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. Therefore, Cl_{org} is used as the sum of organically bound chlorine; if other halides are present in considerable amounts, the method will overestimate the Cl_{org} in the samples. There were previous concerns that Cl_{in} might interfere with the AOX measurements and thereby overestimate the Cl_{org}, but that is not significant unless there are high Cl_{in} concentrations such as in brackish waters (Asplund, Grimvall et al. 1994).

TOC, Cl_{in}, and nitrate

The total amount of organic carbon in water was analyzed using a Swedish standard method (SS EN 1484) using a Pt-catalyzed and high temperature oxidation (Schimadzu TOC-5000 Analyser). A sub-set of samples (n=4) were analyzed during both base-flow and high-flow for differences between filtered (0.45 µm pre-rinsed filters) and unfiltered samples. The difference between the pair of samples was within the sample variation, suggesting that the particulate fraction was negligible in relation to the dissolved organic matter fraction. Cl_{in} in water samples were determined by ion chromatography with chemical suppression (MIC-2, Metrohm), according to standard procedure for determination of Cl_{in} of water with low contamination (European

Committee for Standardization 1995). In short, water samples were filtered (0.15 μm filter, Metrohm) and separated on an anion column and detected with a conductivity meter.

VOCl_s

The study in Paper III focused on chloroform (CHCl_3), but the samples were also scanned for other VOCl_s previously reported to be found in environmental samples (e.g. tetrachloromethane (CCl_4), trichloroethene (C_2HCl_3) and tetrachloroethene (C_2Cl_4), dichloromethane (CH_2Cl_2), bromochloromethane (CH_2BrCl), chloriodomethane (CH_2ClI), dibromochloromethane (CHBr_2Cl). Chloromethane (CH_3Cl) was not studied since the method and column available at our laboratory did not allow a reliable separation and identification of chloromethane in the samples analyzed.

The concentration of VOCl_s in water samples was analyzed with a purge-and-trap method, i.e. similar to the EPA method 502.2 (EPA 1995). In short, 100 mL of water was purged with helium for 15 minutes and trapped on a cold trap and thereafter released by heating the cold trap with boiling water; the compounds were introduced to the GC column and analyzed with an electron capture detector. A more detailed description of the method is given by Laturnus et al. (2000). For a detailed description of column and temperature program see Paper III. As the concentration of the VOCl_s was low, care was taken with regard to (i) variation in the method, (ii) background levels, and (iii) possible degradation during storage. The variation in method was analyzed by spiking pre-purged sample water; possible laboratory air contamination was managed by heating the purge flask between each analysis until blank levels were reached. Two different sample treatments were used in order to decrease the variation among samples. Before May 2003, all the samples were stored in the dark and at room temperature until they were analyzed within a total time of approximately 7 hours. After May 2003, the samples were kept in a refrigerator until analysis and heated in a water bath to 25°C before analysis; all these samples were analyzed within 6 hours. In general, the average coefficient of variation (CV) in samples decreased from 22% to 15% for chloroform with the new sample treatment. We believe that the samples were subjected to microbial and/or contamination processes that influenced

the samples during storage at room temperature; however, there are no indications that the change in procedure had an impact on the concentrations (Paper III).

3.3.2 ...in soil samples

The concentration of Cl_{org} (TOX) in solid samples was analyzed according to Asplund et al. (1994). This method is similar to the method of analyzing sludge or contaminated soils and sediments. In short, a sieved and milled soil sample is washed with an acidic nitrate solution to remove remaining Cl_{in} , and the sample follows the procedure for AOX analysis described above.

The total amount of chlorine (TX) was determined by adding sieved and milled soil to a small crucible followed by direct combustion in the AOX instrument. Cl_{in} was calculated as TX minus TOX and represents an alternative method of determining Cl_{in} in soil rather than measuring Cl_{in} in water soil leachate by, for example, potentiometric titration (Johansson, Ebenå et al. 2001). Both methods are insensitive to a specific halogen, but show differences in leachability. There is a risk of overestimation of Cl_{in} by using TX-TOX because TX analyzes not only Cl_{org} and porewater Cl_{in} but possibly also mineral Cl_{in} . Higher Cl_{in} concentrations were found for the TX-TOX method compared to the potentiometric method; however, mineral Cl_{in} can possibly be partly leached due to the low pH used for removing Cl_{in} from the soil prior to TOX measurement. Hence, since the concentrations of Cl_{org} are often much larger than Cl_{in} , it is of less importance when comparing soil pools. However, further studies need to be carried out on different soil types to investigate the potentials and drawbacks of these two methods.

3.3.3 ...in headspace samples

Determination of VOCs in headspace samples for the laboratory incubated soil is reported in Paper V. The headspace glass flasks were flushed with helium, and VOCs were trapped on a cold trap followed by the same analysis procedure as for VOCs in water. A more detailed description of the method is given by Haselmann et al. (2000). It should be noted that the analysis of soil headspace used for flux estimations should be treated with caution as we have no information of spatial and temporal variation in the field.

3.4 Statistical analyses

In Paper III, possible seasonal impacts on chloroform concentrations were assumed to depend partly on water discharge, which also generally varied with the season, and on other factors affected by the season (e.g. temperature and microbial activity in the soil). To try to separate effects of water discharge and other seasonal factors, a simple linear regression was made by using chloroform in runoff as the dependent variable and water discharge as explanatory variable. The residual variation over time that could not be explained by water discharge was used to determine the effect of other seasonal factors (Helsel and Hirsch 2002).

In Paper IV, to evaluate the influence of water residence time and of Cl_{in} and nitrogen loads, we used two-way ANOVA in line with the factorial design of the experiment (Sokal and Rohlf 1995). For tests of correlations or linear relationships we used Kendall's tau and the Kendall–Theil robust line tests to avoid producing biased results because of single outliers or extreme values in the dataset (Helsel and Hirsch 2002). The significance level chosen when interpreting results was set to 5%.

To test whether there was a significant release of VOCs from the soil, i.e. a difference between VOC concentrations in reference and blank samples, a Mann-Whitney rank sum test was used instead of a t-test in Paper V. The Mann-Whitney rank sum test does not require normal distribution in samples containing an unknowable number of observations, and is insensitive to both extreme values and different variance (heteroscedasticity). In addition, the Mann-Whitney rank sum test was used to test the difference between the VOC-release effect in soil with and without added ammonium nitrate. A correlation analysis was performed to test whether the addition of ammonium nitrate co-varied with observed VOC concentrations. The data had a monotonic (non-linear) relationship, so Kendall's tau instead of Pearson's r was chosen to measure the strength of the correlation between the variables (Helsel and Hirsch 2002). Kendall's tau does not require a normal distribution among samples; it is insensitive to extreme values, and does not presume a bivariate normal distribution. The significance level was set to 5%. Kendall's tau was also used to test if there were significant correlations between the runoff and soil variables in Paper II and III.

4 Cl_{in} and Cl_{org} storage and fluxes

On the basis of the results obtained in Papers I and II, it is clear that chlorine both enters and leaves the catchment primarily as inorganic (Cl_{in}) (Figure 5). It is further shown that (i) the storage of both Cl_{in} and Cl_{org} are larger than the transport of the same on a catchment level, but (ii) the storage is dominated by Cl_{org} despite the fact that the transport into and out of the catchment is dominated by Cl_{in} . The storage of Cl_{org} is approximately twice as large as the Cl_{in} in the upper 40 cm of the soil at the investigated site (Paper I). It is further shown that input via precipitation and output via runoff for Cl_{in} and Cl_{org} were of similar size. The input and output of Cl_{org} was nearly in balance on a time scale of a year, while there were some discrepancies in the Cl_{in} and chloroform input and output budget. In Paper I, approximately $0.3 \text{ g } Cl_{in} \text{ m}^{-2} \text{ yr}^{-1}$ of the output cannot be explained by wet deposition and $0.1 \text{ g } Cl_{in} \text{ m}^{-2} \text{ yr}^{-1}$ in Paper II. Output of chloroform is approximately 6 times the input via wet deposition (Paper III), and the results imply a source additional to wet deposition (Figure 6).

Previous rain, soil, and surface water measurements imply that Cl_{org} is more widespread than earlier assumed (Asplund and Grimvall 1991; Grön 1995; Laniewski, Dahlen et al. 1999; Johansson, Sandén et al. 2003a; Biester, Keppler et al. 2004). The results of the present thesis are the first estimates of transport of Cl_{org} and Cl_{in} to runoff water. The results call for a discussion in relation to three issues: (i) What are the uncertainties in the calculated estimates of storage and fluxes? (ii) Why is there such a large storage of Cl_{org} in soil as the major input is Cl_{in} ? and (iii) Why is the major output inorganic despite the fact that the largest storage of chlorine in soil is Cl_{org} ?

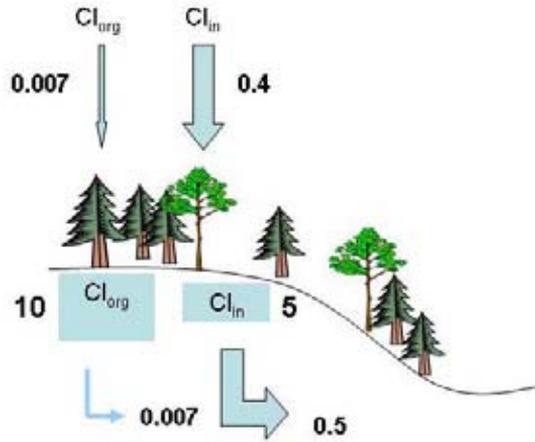


Figure 5. Overall chlorine budget for the observed Stubbetorp south catchment (58°44'N, 16°21'E). Input and output is estimated for this study by combining data on precipitation amount at Simonstorp, interpolated concentration from three meteorological stations (Sjöängen, Norra Kvill, Aspvreten), and runoff measurements in the catchment. Dry deposition of Cl_{in} is denoted with a question mark in the figure.

4.1 Estimates of Cl_{in} and Cl_{org} pool and fluxes

The estimates of Cl_{in} flux and the pool sizes of Cl_{in} and Cl_{org} in Paper I and Cl_{org} output flux in Paper II are robust in the sense that the estimates were based on a large number of samples in the specific catchment, providing information about the variability in fluxes with time and for storage in space regarding the studied catchment.

The soil storage data of Cl_{in} and Cl_{org} are based on 49 soil cores in the Stubbetorp catchment, sampled at one occasion. The concentrations of Cl_{org} in soil in the catchment are in the lower Cl_{in} of previously reported Cl_{org} concentrations in soil (Öberg and Grön 1998; Johansson 2000). Previous studies suggest that the concentrations of Cl_{org} decrease with depth along with organic matter (Hjelm, Johansson et al. 1995). Hence, the lower concentrations obtained in the present study are most likely due to the fact that samples were collected to a larger depth, while in the study by Johansson et al. (2003b), the humic layer (O-horizon) which reached a maximum depth of 30 cm was chosen. The total storage in the catchment was likely

more representative since when turning the concentrations into storage estimates, the storage of organic chlorine should include as much of the soil profile as possible, and not only the topsoil, in order to make a correct estimate of the soil storage of Cl_{org} . The area estimations of the storage of chlorine in soil inform us that the amount of Cl_{org} is more prevalent than Cl_{in} in forest soil in the catchment, which is in line with previous studies (Öberg and Grön 1998; Öberg 2003; Johansson, Sandén et al. 2003b).

Input of Cl_{in} was obtained from precipitation samples collected in the actual catchment, comprising 5 years of Cl_{in} sampling of precipitation (Maxe 1995), while Cl_{org} input was estimated from other sites' concentrations measurements, which still agree well with the three precipitation sampling occasions in the catchment in 2004 (Paper II). The Cl_{in} output data were taken from measurements in runoff during a 5-year period in Paper I and in Paper II from measurements in runoff in the Stubbetorp south sub-catchment, while Cl_{org} output data were obtained with a similar sampling interval as for Cl_{in} in the Stubbetorp sub-catchment (Paper II). Hence, the output of Cl_{org} can be considered as equally robust as Cl_{in} output at least in the Stubbetorp south sub-catchment.

4.1.1 Estimating dry deposition

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, Olsson 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.

There are large uncertainties in estimating dry deposition as the methods are based on indirect measurements, either by assuming that Cl_{in} is inert in soil (e.g. Juang and Johnson 1967) or by subtracting open field deposition from throughfall deposition (Hultberg and Grennfelt 1992). The former is questioned at present since it seems that

Cl_{in} is not inert in soil, i.e. Cl_{in} takes part in soil processes on its way to the runoff (Rodstedth, Ståhlberg et al. 2003; Öberg and Sandén 2005). So far, such statements are rather new and need further study, but it seems that the soil is a sink of Cl_{in} and if so, the dry deposition is probably underestimated and calls for a re-evaluation (Paper I). The latter is problematic as throughfall may not only derive from dry deposited Cl_{in} , but also leaching from the vegetation itself, which will overestimate the dry deposition (Brady and Weil 2002). Therefore, in Paper I, the dry deposition was re-estimated by including estimated soil sinks of Cl_{in} in a catchment. From the constructed budget, there are transformations of Cl_{in} to Cl_{org} in soil and in biomass, although the rates remain uncertain. Therefore, the dry deposition in the catchment earlier estimated at $0.3 \text{ g } Cl_{in} \text{ m}^{-2} \text{ yr}^{-1}$ must be larger. The Cl_{in} sink in biomass and topsoil ($0.3 \text{ g } Cl_{in} \text{ m}^{-2} \text{ yr}^{-1}$) followed by a source in deeper soil ($0.2 \text{ g } Cl_{in} \text{ m}^{-2} \text{ yr}^{-1}$) renders a dry deposition of approximately $0.4 \text{ g } Cl_{in} \text{ m}^{-2} \text{ yr}^{-1}$.

In summation, (i) the estimate wet deposition of Cl_{in} in the catchment is considered as robust, but the estimated dry deposition should be used with caution since there are large uncertainties in assessing a reliable method, and ii) the uncertainties for Cl_{org} input are comparably large, but the relative contribution of Cl_{org} to the chlorine input is small, and the constructed budget takes into account a great portion of the spatial and temporal variation within the catchment.

4.2 Origin of chlorine in soil

Cl_{in} in soil originates from sea salt deposition but also from internal sources like weathering of bedrock (Schlesinger 1997). Despite the fact that Cl_{in} is very water soluble and therefore easily transported through soils, Cl_{in} in soil may be retained by ion-exchange processes (i.e. held and exchanged on the positively charged soil colloids), which may explain some of the Cl_{in} storage in soil (Brady and Weil 2002). However, it is generally assumed that the majority of the deposited Cl_{in} is transported through soil unaffected, with only a minor influence of Cl_{in} soil adsorption (Brady and Weil 2002). Cl_{in} is thought to only be bound electrostatically and therefore easily reversible and to equilibrate fast with the soil solution.

For Cl_{in} we can easily assume that the major source of Cl_{in} in soil during past years is deposition, with a minor portion originating from bedrock, but the origin of Cl_{org} in soil it is not as clear. The input of Cl_{org} by deposition is significantly smaller than the

deposited Cl_{in} (Paper I and II). Previous estimates show that deposition of Cl_{org} cannot explain the storage in soil (Asplund and Grimvall 1991). The concentration in precipitation of Cl_{org} (measured as AOX) is rather low (in $\mu g L^{-1}$) and Cl_{org} contains non-volatile, dissolved organic compounds with a molecular weight of less than 1000 D (Enell and Wennberg 1991; Laniewski, Borén et al. 1995). Cl_{org} in soils (measured as TOX) consists primarily of high molecular weight organic matter (Hjelm and Asplund 1995).

The results of the present study in combination with previous studies imply that a considerable turnover of Cl_{in} to Cl_{org} may still take place in the vegetation or the soil i.e. Cl_{in} is deposited on the vegetation or the soil and subjected to a transformation to Cl_{org} . In time, the chlorine transformation will lead to a buildup of a large storage of Cl_{org} in soil, caused to a small extent by a small input by Cl_{org} deposition but predominantly by Cl_{in} transformation in soil to Cl_{org} . In Paper IV, we observe that Cl_{in} is retained in soil followed by a release. Studies by Reina et al. (2004) suggest that a considerable transformation of Cl_{in} to Cl_{org} takes place in senescent plant leaves. Recent results in a ^{36}Cl tracer experiment suggest a considerable incorporation of Cl_{in} into organic matter, which occurs between 2°C and 37°C, is largest at 20°C, and not detectable above 50°C (Bastviken, Thomsen et al.). On the basis of the temperature-dependent incorporation, Bastviken et al. suggest that biotic processes are responsible for the incorporation; however, there are also known abiotic processes involved in Cl_{org} formation in soil. There is indisputable evidence that several soil organisms can form Cl_{org} (Clutterbuck, Mukhopadhyay et al. 1940; Harper 1985; Neidleman and Geigert 1986; Gribble 1996; Hoekstra, Verhagen et al. 1998). Other studies indicate that an abiotic formation of Cl_{org} takes place in soil (Keppler, Eiden et al. 2000; Fahimi, Keppler et al. 2003; Hamilton, McRoberts et al. 2003), however; the present thesis does not provide evidence to distinguish between biotic and abiotic processes responsible for either storages or fluxes, but instead discusses the abundance and occurrence.

The results of the present study in combination with previous studies suggest that part of the Cl_{org} in soil is biodegradable (Öberg 1998), which may be mineralized and leached out of the soil, but another part is more stable and less easily leached (Hjelm and Asplund 1995), which will add to the Cl_{org} pool in soil. The transformation of Cl_{in} to Cl_{org} in soil is probably a process that has occurred over a long time since Cl_{org}

appears to be present in soil organic matter in all types of environments such as peat, paddy soils, forests, and pastures (Asplund, Grimvall et al. 1989; Keppler and Biester 2003; Biester, Keppler et al. 2004). These authors suggest a natural formation of Cl_{org} over a long time, which results in an accumulation of Cl_{org} . Such accumulation is likely to happen in forest soils also. Soil organic matter in forests originates from plant tissue that is decomposed over a long period (Schlesinger 1997), and chlorination of organic matter has probably occurred over the same period. Hence, it can be concluded from Papers I and II that the soil pool of Cl_{org} , which is larger than the flux of Cl_{in} , probably is an effect of transformation of Cl_{in} to Cl_{org} in the past and possibly at present, as is supported by previous work.

4.3 Chloroform imbalances

A rough chloroform budget was calculated which showed that the annual input was $1 \mu\text{g m}^{-2} \text{yr}^{-1}$ and output was $6 \mu\text{g m}^{-2} \text{yr}^{-1}$ (Figure 6). The estimate of chloroform output is more solid than the input since the former is based on bi-weekly estimates over a period of two years, whereas the input is based on three sampling occasions (Paper III). However, the average concentrations of chloroform in precipitation (Paper III) are in the lower range of those previously detected in other areas (Class and Ballschmiter 1986; Schleyer, Renner et al. 1991). Earlier studies of chloroform concentrations in rain vary across sampling sites, but to our knowledge there are no concentration measurements made in remote areas or nearby the catchment. Class and Ballschmiter reported concentrations of chloroform of 25 ng L^{-1} and Schleyer reported concentrations of $11\text{-}17 \text{ ng L}^{-1}$ in southern Germany (Class and Ballschmiter 1986; Schleyer, Renner et al. 1991), but the concentration of chloroform at other sites characterized by highly dense population can reach 100 ng L^{-1} and in some cases up to 1010 ng L^{-1} , in TriCity in Poland (Polkowska 2004). The concentrations in precipitation observed in the catchment are in the lower range, and the conclusion we can draw is that the input is slightly lower compared to other studies and to run-off detected in Paper III.

Possible sources of chloroform in runoff are dry deposition and surrounding soil as there are no known point sources in the area that can contribute. There is no information of dry deposition of chloroform, but it is not doubted that chloroform is formed naturally in soil (Laternus, Haselmann et al. 2002; Laternus, Fahimi et al.

2005). Different soil types, such as forest soils, salt marshes, temperate wetlands, and rice paddies have been investigated and found to release VOCs (Haselmann, Ketola et al. 2000; Khalil and Rasmussen 2000; Laturnus, Lauritsen et al. 2000; Rhew, Miller et al. 2000; Dimmer, McCulloch et al. 2001; Hoekstra, Duyzer et al. 2001; Rhew, Miller et al. 2001). Forest soil, especially spruce forest soil, is assumed to contribute up to 25% of the total natural global emission of VOCs from soil (Laturnus, Haselmann et al. 2002), although the mechanisms (biotic or abiotic) behind the formation of chloroform are still under debate. Chloroform is assumed to be formed by a chloroperoxidase-mediated reaction (Laturnus, Mehrtens et al. 1995), but still there is no conclusive evidence of such formation. Hence, the soil most likely renders a net flux of chloroform from soil to atmosphere, and the fluxes of chloroform to runoff in Paper III are probably small compared to chloroform flux to the atmosphere from forested terrestrial ecosystems in other studies.

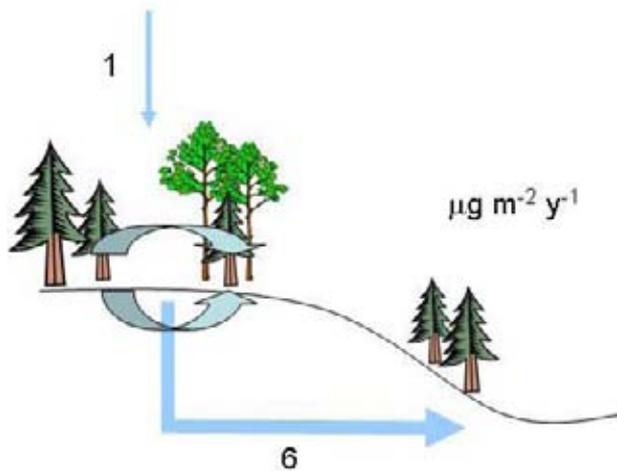


Figure 6. This figure presents input by wet deposition and output of chloroform in the catchment. The input was estimated from rain water sampling on six occasions combined with daily precipitation amounts, and the annual output was estimated by combining daily water discharge measurements with interpolated bi-weekly concentration measurements. Note that the fluxes strongly vary with e.g. water discharge during dry periods. The input was assumed to be solely wet deposition as the net flux of chloroform are regarded as directed to the atmosphere. Therefore the flux data indicate that chloroform is formed in soil and transported to groundwater or becomes part of an internal cycling in the forest ecosystem.

5 Origin of Cl_{in} in surface water

The budget calculations in Paper I suggest that a considerable portion of Cl_{in} in soil is transformed to Cl_{org} and subsequently leached to deeper soil layers where a net mineralization of Cl_{org} takes place in soil, preferably in deeper soil layers. Recent estimates suggest that degrading organic matter is a major source of Cl_{in} in runoff rather than precipitation (Öberg and Sandén 2005). The estimate in Paper I that the loss of Cl_{org} through runoff is small to negligible in relation to other fluxes, i.e. wet deposition and topsoil leaching, is supported in Paper II. Furthermore, within an observation period of 142 days both a net retention and net release of Cl_{in} was observed in soil lysimeter leachate (Paper IV). All in all, the results suggest that the considerable turnover of Cl_{in} to Cl_{org} and the large Cl_{org} pool can be further mineralized again and release Cl_{in} for transport to runoff water and eventually to surface waters.

5.1 Cl_{org} retention in soil

The concentration of both organic matter and Cl_{org} is considerably lower in runoff than in topsoil water (Paper I and II). In addition the transport of Cl_{org} is larger from topsoil to deeper soil than from soil to runoff water (Figure 7). Consequently, it seems that a part of the large amount of Cl_{org} present in topsoil is leached to deeper soil layers, and a majority is retained there or degraded during the downward transport in the soil profile, while only a small part is leached to runoff waters.

Retention or precipitation in soil has previously been described for organic matter. 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). TOC is generally higher in topsoil leachate but generally lower in deeper soil layers (Michalzik, Kalbitz et al. 2001). Organic matter is leached from topsoil, and the soil organic matter is precipitated or mineralized in deeper soil horizons. The mobile organic matter is leached further downwards in the soil horizon and in runoff the organic matter is generally lower than in topsoil water (Michalzik, Kalbitz et al. 2001).

It has previously been described that concentrations of Cl_{org} in surface water and in soil generally increase with increased TOC concentration (Paper II, (Asplund and Grimvall 1991; Enell and Wennberg 1991; Johansson, Sandén et al. 2003b). Since we see a correlation of Cl_{org} to organic matter in runoff (Paper II) and know that concentrations of Cl_{org} decrease down the soil profile, Cl_{org} probably behaves similarly to the organic matter, i.e. is leached from surficial soil and precipitates and mineralizes in deeper soil. Based on this reasoning, it has been suggested that of the Cl_{in} that is deposited on soil, some part passes through the soil unaffected, but another part undergoes a transformation to Cl_{org} and travels down the soil profile until it is mineralized and Cl_{in} is released and enters runoff waters (Öberg and Sandén 2005). The latter pathway may delay the output of Cl_{in} and adversely affect Cl_{in} budgets; however, this is a hypothesis that has to be further investigated to assess its importance.

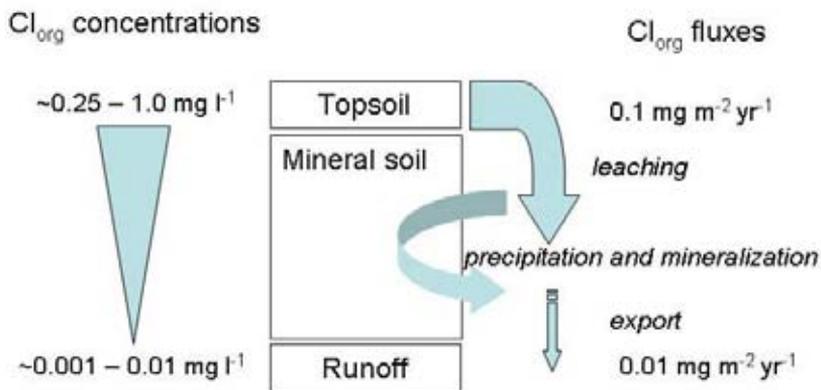


Figure 7. Cl_{org} transport in soil. Concentrations data and flux estimations for top-soil are based on data from Rodhstedt et al. 2003 and for run-off from Paper III.

As previously described, soil can act as a sink and as a source of Cl_{in} . That was further proved in Paper IV, where a retention and release of Cl_{in} occurred in soils, and that rates may be considerable high relative to the load of Cl_{in} and water. During the observed experimental period, the soil in lysimeters acted as a net sink for Cl_{in} in the beginning and a net source in the end. It was not possible to distinguish between actual retention and release rates, therefore net retention and net release terms were used. The observed decrease in Cl_{in} concentration at the start was explained by

chlorination of soil organic matter or ion exchange. Previous studies suggest that release of Cl_{in} occurs in deeper soil layers and not in topsoil layers, but the results in Paper IV suggest that both processes are on-going in topsoil. As of yet, there is not sufficient data to explain shifts from soil net retention to net release of Cl_{in} in soil. Such shifts could be due to the retention processes being hampered, the release processes being favored, or a combination of both. Possible hypotheses are that availability of easily degraded organic matter decreases with time (i.e. the organic matter becomes more refractory with time due to selective microbial degradation) or that the concentration of molecular oxygen (O_2) is decreased due to microbial activity. Microbial soil organic matter chlorination most likely requires oxic conditions, but dechlorination of some chlorinated pollutants is favored by anoxic conditions (Fetzner 1998; van Pee and Unversucht 2003). Hence, both net retention and net release of Cl_{in} can occur in topsoil, but net retention is probably stimulated in topsoil, where the organic matter and oxygen are available in sufficient amounts, compared to deeper soil layers, which hamper the net retention and increase the mineralization and net release of Cl_{in} .

The chemical signature of runoff waters seems also to be dependent on the deposition of Cl_{in} and water residence time. The factorial study (Paper V) suggests that a high Cl_{in} deposition (corresponding to three times the deposition at the catchment) and a long water residence time (corresponding to slightly lower than the annual precipitation in the area) render high initial net retention followed by higher net release rates than with low Cl_{in} deposition and increased annual precipitation (corresponding to at least twice the annual precipitation in the area for the catchment site). In contrast to previous studies, Paper V suggests that nitrogen has no effect on the Cl_{in} transformation rates in soil. At least, one can conclude that any potential influence caused by the elevated nitrogen amendment was hidden by the influence of other variables. Other factors such as Cl_{in} input and water residence time apparently had a larger influence in the conducted experiment than the amendment of nitrogen did.

6 Chemical composition of chlorine in runoff water

One of the major results in this thesis is that chlorine species in runoff water in part originates from precipitation and in part originates from the surrounding soils (Paper I). Further, the observed output via runoff of Cl_{in} , Cl_{org} , and chloroform is to some extent caused by the size of water discharge, but the data also suggest that it is probably also due to dissimilar soil water transport processes until the chlorine compounds reach the outlet and runoff water. Cl_{in} , Cl_{org} , and chloroform in runoff react differently to changes in water discharge (Papers II and III) (Figure 8). Cl_{in} shows the smallest variation (a magnitude of two) and chloroform the largest (a magnitude of ten) with Cl_{org} in between (a magnitude of eight). It is also clear that the water discharge cannot solely explain the concentration changes observed in runoff. Water that becomes runoff water originates from different sources and is subsequently subjected to different kinds of environments and processes until it reaches the catchment outlet. As further developed below, I suggest that some of the origin of the different chlorine species and pathways yielding specific runoff variations may be reflected in the chemical signature of runoff water observed in the outlet of the catchment in Papers II and III.

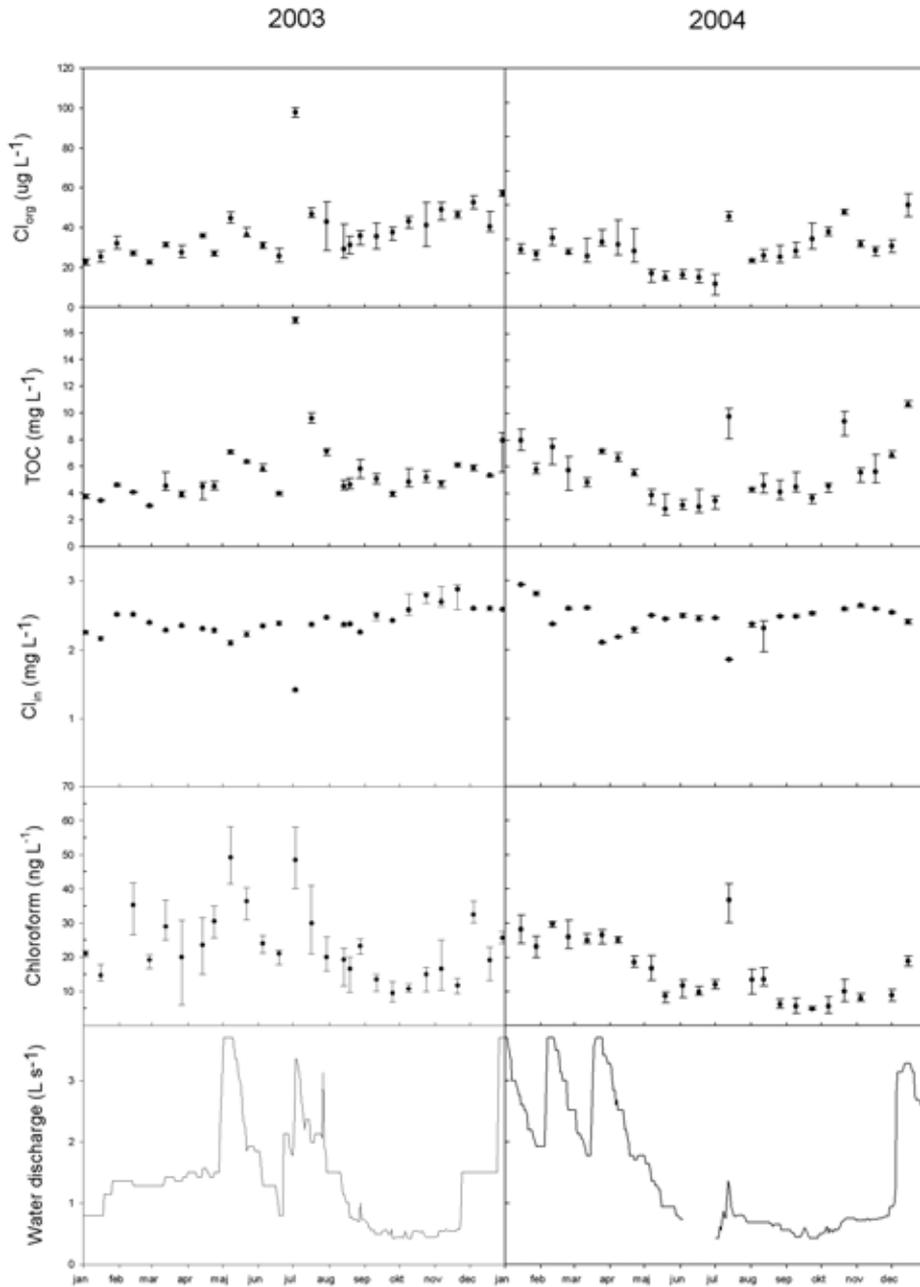


Figure 8. Runoff concentrations (minimum, average, maximum, n=5-6) of Cl_{org} (organically bound chlorine measured as AOX), TOC (total organic carbon), Cl_{in} (chloride), chloroform and water discharge during observation years 2003 and 2004.

Cl_{in} , Cl_{org} , and chloroform in runoff may originate from precipitation. Cl_{in} has previously been described as originating mainly from deposition, but also from soils with minerals of high chlorine content (Eriksson 1960). Cl_{org} and chloroform may originate from precipitation but also from soil, which is assumed to form Cl_{org} and chloroform. Hence, the observed chlorine species in runoff water may originate from deposition but probably also from vegetation or soil formation.

6.1 Seasonal runoff variations

During different periods over a year the runoff can have different chemical signatures often attributed to different water flow paths (Brutsaert 2005). Despite extensive research of hydrological and hydrochemical studies, several questions remain to be answered, such as how the water chemistry is transformed along the flow paths in the catchment and how old water and newly entered water actually contribute to observed runoff water (Peters 1991; Viers, Dupre et al. 2001; Kirchner 2003; Bishop, Seibert et al. 2004). Water reflecting surface soils are often rich in dissolved organics and have a low pH (Bishop, Grip et al. 1990). Such water is usually of short residence time and comprises a large component of storm runoff in the outlet. The water transit time varies from one rain event to another. The wetter the soil is and the higher the groundwater table, the larger will be the fraction of short residence time in the runoff. Water draining deep soils is conventionally thought to have a longer residence time and is characterized by high concentration of weathering products and high alkalinity (Brutsaert 2005).

In the studied catchment, there are different periods when the runoff is dominated by water with a long water residence time (in this case denoted as base flow) and water with long water residence time also mixed with newly entered precipitation or snow melt (high flow) (Brutsaert 2005). Periods when the water has a comparably long time in the catchment are denoted as dry periods, with a water discharge below approximately 0.7 L s^{-1} . Periods when water has a comparably short time in the catchment are denoted as wet periods, with a water discharge above approximately 0.7 L s^{-1} . Dry periods occur mainly during summer and autumn and wet periods during winter and spring. Consequently, it is a complex mixture of water representing different water flow pathways through the soil that we observe in runoff water.

6.2 Cl_{in} variations in runoff

I next discuss the observed runoff variations in Cl_{in} concentration. The results in Paper II show that the Cl_{in} concentrations were in most cases stable, except for dry-period rain events when Cl_{in} concentrations decreased. The observed variations can have at least two different plausible explanations: (i) relatively old water with a long water residence time and high Cl_{in} concentration is diluted during a rain event by the new water from precipitation with relatively low Cl_{in} concentration, and/or (ii) a rise in groundwater level towards the soil surface will cause a mobilization of soil water from different soil depth, with similar Cl_{in} concentration independent of soil depth.

The latter explanation is based on lateral flow of water that is eventually connected to the flow to the stream, which is a very common explanation for water movement in agricultural soils (Larsson, Jarvis et al. 1999). The concentration of Cl_{in} is generally higher in soil water than in precipitation, but the lateral soil distribution of Cl_{in} concentrations is almost evenly distributed in organic soils (Peters 1991; Hjelm, Johansson et al. 1995). In such a model, the lateral soil chemistry distribution is important if the soil layers are hydrologically connected to the stream; otherwise they are not important for runoff chemistry. The former condition is based on the relative amount of water from groundwater and from newly-entered precipitation that is represented during a water discharge peak, which in several cases is enough to explain, for instance, the variation of Cl_{in} (e.g. Peters and Ratcliffe 1998). In such a model, the increased amount of water and the low concentration in rain contribute more to the decrease of Cl_{in} runoff during rain events than the soil water having long residence time and relative high Cl_{in} concentrations that also enter the outlet.

In Paper II, it seems that the concentration of Cl_{in} in runoff water is relative stable during the whole observation period, although during rain events in July 2003 and 2004 the Cl_{in} concentrations decreased dramatically. The results are consistent with a previous study (Peters and Ratcliffe 1998), describing two rain events at different seasons with different soil moisture conditions. The explanations of the different Cl_{in} behavior during dry and wet periods Cl_{in} concentrations rest on the explanation of old and new water mixing in runoff water (Peters and Ratcliffe 1998; Burns, McDonnell et al. 2001). They assume that the precipitation contributes more during dry periods than during wet periods. When the soil is relative dry, the runoff water is to a major degree reflected by precipitation and by water with little or no contact with the soil

matrix; by comparison, during wet periods the soil water more easily moves from the soil matrix to runoff due to higher water percolation. In Paper II, I assume that such a pattern occurred during the dry period rain events in 2003 and 2004. The relative steady concentration of Cl_{in} in runoff water during the observation period may be explained by an increased soil water transport resulting from an increase in the water table during rain events. Soil water from different soil depths is leached out, but the soil water Cl_{in} concentrations seems to be independent of soil depth and therefore there is no large decrease in Cl_{in} . In the Stubbetorp catchment, the Cl_{in} concentrations in soil water have previously been measured: they varied between 1.9–2.7 mg L⁻¹ at different soil depth (independently of soil depth 0–80 cm), with no obvious spatial trend (Maxe 1995). Hence, the variation of Cl_{in} concentrations in runoff is probably to a major degree a result of the soil conditions favoring water transport an occasionally a direct response to precipitation. The results are in line with previously observed damped behavior of Cl_{in} in stream water (Kirchner 2003; Bishop, Seibert et al. 2004), and further supports the hypothesis in Paper I, that Cl_{in} in surface waters originates from decomposed organic matter.

6.3 Cl_{org} and chloroform variations in runoff

The variation of Cl_{org} and chloroform concentrations in runoff can to some extent be explained by variation in water discharge, but periods can be identified in which the Cl_{org} and chloroform concentrations are influenced by runoff to a larger or smaller extent (Paper II and III). During dry periods, the concentrations were multiplied due to increased water discharge, whereas increased water discharge during wet periods had little or no impact at least for Cl_{org} . As described for Cl_{in} , during a dry-period rain event in August 2003, the runoff water can consist of newly entered precipitation water, old groundwater, and water influenced by stored soil water nearby the stream or areas saturated with water, which can undergo a rapid transport to the outlet during a rain event. Dissolved organic matter in runoff has been described to a large degree as originating from nearby streams rather than from areas further away (Bishop, Grip et al. 1990). Thus, high concentrations of Cl_{org} and chloroform during summer periods may be explained by an increased amount of topsoil-leached Cl_{org} and chloroform during summer rain events, compared to a larger contribution from deeper soils with smaller concentrations of TOC, Cl_{org} , and possibly chloroform during dry periods in between rain events. It is important to notice that the high concentrations of TOC

observed in runoff may only derive from surficial soils nearby a stream or wet area, where the soil water is hydrologically connected to the output (Bishop, Seibert et al. 2004).

Previous research suggests that the chlorine-to-carbon ratio increases with soil depth (Öberg and Grön 1998) and that this pattern is due to the fact that organic matter with elevated chlorine-to-carbon ratio is leached from topsoil to deeper soil layers (Öberg and Sandén 2005). The studies so far conducted on vertical distribution of Cl_{org} have been confined to coniferous forest soil in the temperate region. The results from these studies are compiled in Figure 9, which indicate that the chlorine-to-carbon ratio in litter in such forests is below $0.1 \text{ mg Cl}_{\text{org}} \text{ g}^{-1} \text{ C}_{\text{org}}$, around $1 \text{ mg Cl}_{\text{org}} \text{ g}^{-1} \text{ C}_{\text{org}}$ 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 as well as in deeper layers. On the basis of these results and those of the present study, it seems likely that the runoff water originates from deep soil layers with lower chlorine-to-carbon ratios during high flow from surficial layers with higher chlorine-to-carbon ratios during low flow. For example, for a rain event in August 2003, one may hypothesize that the chloroform originated from surficial soil because of rather low chlorine-to-carbon ratios in the runoff peak. At the beginning of this investigated rain event, the runoff water contained rather low chloroform concentration and had rather high chlorine-to-carbon ratios. The chloroform concentrations increased simultaneously when the chlorine-to-carbon ratios decreased. This is consistent with what is well known: that the discharge origin to a considerable extent depends on the amount of water present in soil, since runoff partly originates from surficial layers during high-flow conditions and from deeper soil layers during low-flow conditions.

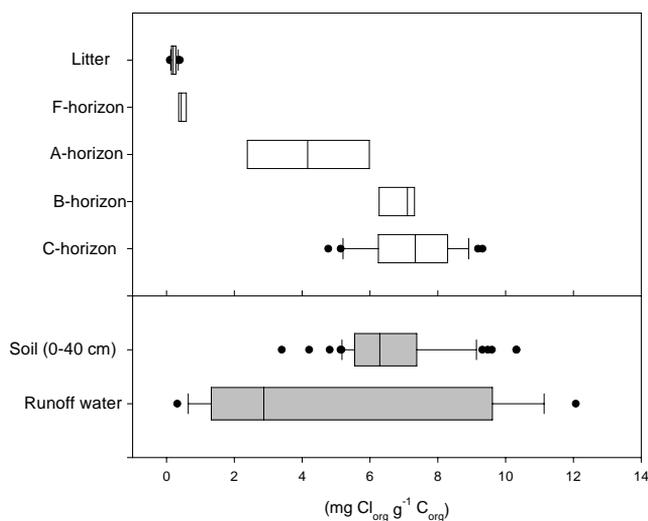


Figure 9. Distribution of chlorine-to-carbon ratios in different compartments; litter, F-horizon, A-horizon, B-horizon, C-horizon, soil (0-40 cm) and runoff water. All data in the upper figure are compiled from Klosterhede in Denmark (Öberg and Grön 1998), and the data in the lower figure from Stubbetorp south catchment (PaperII).

It is known that chloroform can be subjected to degradation in deeper soil layers and in ground water (Fetzner 1998) which, if given sufficient time, will probably decrease the chloroform output in runoff. Hence, the low concentrations of chloroform in runoff during base flow conditions are probably in part due to the fact that, due to its longer residence time, a larger portion of the chloroform is degraded during base-flow conditions as compared to saturated conditions. The peaks seen during base flow condition rain events may be due to the fact that the chloroform flushed out with the rainwater spends far too short a time in the soil to be subjected to degradation processes. Another possibility is that the chloroform concentrations in runoff are so low during base-flow conditions that the formed chloroform is emitted to air instead of being dissolved in soil water and transported to the outlet. The fact that comparably small amounts of chloroform are transported during base-flow condition rain events (in spite of the elevated concentrations) supports this hypothesis.

During periods with discharge above base flow, the chloroform concentrations were higher than during periods of base flow conditions and rain events did not always induce clear peaks in the chloroform concentrations. The residence time during

periods above base flow is shorter than during base flow conditions. Consequently, there is less time for evaporation and degradation processes to take place, thus rendering higher chloroform concentrations. The absence of chloroform peaks associated with specific rain events during high-flow periods is most likely a result of the fact that the amount of water present in soil during wetter periods is considerably larger than during drier periods. The water brought to the soil during a wet-period rain event will consequently have a small to negligible influence on the water residence time and soil water chemistry due to dilution than rain events do during drier periods (Brutsaert 2005). Hence, the observed pattern suggests that chloroform is formed in surficial soil layers and transported to the outlet during high-flow conditions as well as during dry period rain-events and lost through degradation or evaporation during drier periods due to longer soil water residence times.

7 Tetrachloromethane – naturally formed in soil?

The results from laboratory incubated soil (Paper V) imply unexpectedly that tetrachloromethane was released from the soil samples, which suggests that tetrachloromethane is naturally formed in the investigated soil (Paper V). In the same soil, chloroform was released, which was not surprising as emission of chloroform from various soil types has repeatedly been observed (Laternus, Haselmann et al. 2002). Tetrachloromethane in soil is generally agreed to originate from external sources such as industry, and soil is a sink of tetrachloromethane. However, there are previous soil air measurements suggesting a net emission of tetrachloromethane from soil (Hoekstra, Duyzer et al. 2001). The earlier observations of tetrachloromethane emission from soil were scattered, where soil was acting as a sink also, i.e. similar soil and ambient air concentrations (Hoekstra, Duyzer et al. 2001). Net emission of tetrachloromethane has previously been interpreted as a re-emission of previously deposited tetrachloromethane on the soil, which agrees well with the general belief that soil is a sink of tetrachloromethane (Haselmann, Ketola et al. 2000; Happell and Roche 2003). In addition, the results of the soil incubations also indicate a release of trichloroethene from soil. It is known that trichloroethene is emitted into the air by industrial production and fossil fuel combustion, while oceans are the single known natural source of this compound (Abrahamsson, Ekdahl et al. 1995; Khalil, Moore et al. 1999). Hence, the results of chloroform release and soil origin are supported by previous studies, while the origin of tetrachloromethane and trichloroethene are unknown.

The observation of higher tetrachloromethane concentrations in incubation flasks with soil, compared to incubation flasks without soil implies that the observed tetrachloromethane originated from the investigated soil. For tetrachloromethane, the background levels were significantly smaller than the observed concentrations in the flasks incubated with soil. The background concentrations of trichloroethene were rather high, which caused difficulties in interpretation of the results and the possibility of deducing whether or not the investigated soil was a source.

Previous studies suggest that, in addition to industrial sources, volcanoes, terrestrial plants, rice fields, and salt lake sediments may emit tetrachloromethane (Gribble 1996; Jordan 2000; Weissflog, Lange et al. 2005)(Gribble 1996; Jordan 2000;

Weissflog, Lange et al. 2005). However, before one can say without doubt that soil is a source of tetrachloromethane, Paper V needs the support of further studies investigating the potential soil release in relation to soil as a sink and possible contamination.

8 Main conclusions

This thesis has shown that:

- (i) storage of Cl_{in} and Cl_{org} on a catchment level is considerably larger than the transport of the same;
- (ii) the input via precipitation and output via runoff for the investigated chlorine species were of similar size in the investigated catchment;
- (iii) there is evidence that steady state is not at hand as it appears as if a major part of Cl_{in} brought to the catchment via precipitation is converted to Cl_{org} in topsoil and that Cl_{org} is converted to Cl_{in} in deeper soil;
- (iv) Cl_{in} in runoff originates mainly from decomposing organic matter;
- (v) the concentrations of Cl_{org} , Cl_{in} , and chloroform in runoff vary seasonally, which to some extent is caused by water discharge, but also probably by soil water transport processes;
- (vi) tetrachloromethane can be emitted from soil; and
- vii) soil nitrogen amendments cause a decrease in the emission of chloroform, and soil nitrogen amendments cause an increase in the emission of tetrachloromethane.

To gain increased understanding of the chlorine transport in catchments, further attention should be given to the chlorine biogeochemistry in soil in relation to processes that influence the transport of chlorine from topsoil to groundwater.

9 References

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