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Chlorine cycling and fates of ^{36}Cl in terrestrial environments

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Abstract

Chlorine-36 (^{36}Cl), a radioisotope of chlorine (Cl) with a half-life of 301,000 years, is present in some types of nuclear waste and is disposed in repositories for radioactive waste. As the release of ^{36}Cl from such repositories to the near surface environment has to be taken into account it is of interest to predict possible fates of ^{36}Cl under various conditions as a part of the safety assessments of repositories for radioactive waste. This report aims to summarise the state of the art knowledge on Cl cycling in terrestrial environments. The view on Cl cycling in terrestrial environments is changing due to recent research and it is clear that the chloride ion (Cl^-) is more reactive than previously believed. We group the major findings in three categories below according to the amount of data in support of the findings.

From the result presented in this report it is *evident* that:

- There is an ubiquitous and extensive natural chlorination of organic matter in terrestrial ecosystems.
- The abundance of naturally formed chlorinated organic compounds (Cl_{org}) frequently exceeds the abundance of Cl^- , particularly in soils. Thereby Cl_{org} in many cases dominates the total Cl pool.
- This has important implications for Cl transport. When reaching surface soils Cl^- will not be a suitable tracer of water and will instead enter other Cl pools (Cl_{org} and biomass) that prolong residence times in the system.
- Cl^- dominates import and export from terrestrial ecosystems while Cl_{org} and biomass Cl can dominate the standing stock Cl within terrestrial ecosystems.
- Both Cl and Cl_{org} pools have to be considered separately in future monitoring programs addressing Cl cycling.

Further, there are also *indications* (in need of confirmation by additional studies) that:

- There is a rapid and large uptake of Cl^- by organisms and an accumulation in green plant parts. A surprisingly large proportion of total catchment Cl (up to 60%) can be found in the terrestrial biomass.
- Emissions of total volatile organohalogens could be a significant export pathway of Cl from the systems.
- Some of the Cl_{org} may be very persistent and resist degradation better than average organic matter. This may lead to selective preservation of some Cl_{org} (with associated low bioavailability).
- There is a production of Cl_{org} in tissues of e.g. plants and animals and Cl can accumulate as chlorinated fatty acids in organisms.

Most other nevertheless important aspects are *largely unknown* due to lack of data. Key unknowns include:

- The development over time of major Cl pools and fluxes. As long as such data is lacking we cannot assess net changes over time.
- How the processes behind chlorination, dechlorination and transport patterns in terrestrial systems are regulated and affected by environmental factors.
- The ecological roles of the chlorine cycling in general.
- The ecological role of the microbial chlorination in particular.
- The chlorine cycling in aquatic environments – including Cl^- and Cl_{org} pools in sediment and water, are largely missing.

Given the limited present information available, and particularly the lack of data with a temporal dimension and the lack of process understanding, predictive models are challenging.

We also summarize currently available methods to study Cl in the environment.

Sammanfattning

Klor-36 (^{36}Cl), en radioisotop med en halveringstid på 301 000 år, förekommer i vissa typer av radioaktivt avfall. För att kunna förutse vad som händer om ^{36}Cl når markytan är det viktigt att veta hur klor kan omvandlas och transporteras i olika ekosystem. Denna rapport syftar till att sammanfatta kunskapsläget om klor i naturmiljöer med fokus på landmiljöer.

Synen på klor i naturen är under omfattande förändring till följd av de senaste decenniernas forskning. Det står nu helt klart att klorid (Cl^-) som tidigare betraktats som icke-reaktiv och totalt dominerande, istället är i hög grad reaktiv och inte alltid utgör den dominerande klorformen.

Utifrån de studier som presenteras i rapporten är det tydligt att:

- Det sker en omfattande naturlig klorering av organiskt material i många miljöer och inte minst i ytliga marklager.
- Mängden organiskt bunden klor (Cl_{org}) är i många miljöer betydligt högre än mängden Cl^- . Därmed dominerar Cl_{org} ofta det totala klorförrådet i exempelvis mark.
- Detta har stor inverkan på transporten av klor eftersom Cl_{org} till stor del finns i partikulärt organiskt material medan Cl^- är mycket vattenlösligt. Cl^- som når ytliga marklager är t ex inte lämpligt som spårämne för markvattenflöden såsom tidigare antagits. Cl^- kommer till stor del att bindas in till Cl_{org} -förrådet och därmed förlänga uppehållstiden i ekosystemen.
- Cl^- dominerar både importen och exporten från terrestra ekosystem medan Cl_{org} kan dominera stationära klorförråd i systemen.
- Framtida mätningar med syfte att klargöra kloromsättning och klorflöden behöver beakta Cl^- och Cl_{org} separat.

Därtill finns ett antal troligen viktiga indikationer som skulle behöva bekräftas av ytterligare studier. Dessa inkluderar att:

- Det sker ett snabbt och omfattande upptag av Cl^- av organismer och klor tycks ackumuleras i grön växtbiomassa. En stor andel av den totala klormängden i avrinningsområden (upp till 60% i en studie) har påträffats i den terrestra biomassa.
- Avgång av flyktiga klorerade kolväten kan vara en stor okänd exportväg för klor från ekosystem.
- En del Cl_{org} verkar vara betydligt mer motståndskraftigt mot nedbrytning än det genomsnittliga organiska materialet. Detta kan leda till att Cl_{org} bevaras selektivt i mark och därmed också mindre tillgängligt för mikroorganismer.
- Det sker en klorering av organiskt material i levande biomassa och klor kan ansamlas som klorerade fettsyror i organismer.

Övriga aspekter på klor i naturen är till stora delar okända. Centrala okända aspekter inkluderar:

- Hur klor-förråden utvecklas över tid. Detta är centralt för att förstå förändringar över tid och reglering i förråden.
- Reglering av klorerings-, deklorerings- och transportprocesser, samt hur dessa påverkas av olika miljövariabler och miljöförhållanden.
- Den ekologiska förklaringen till varför så många organismer utför klorering av organiskt material.
- Omsättning av klor i akvatiska system. Här saknas separata data gällande Cl^- och Cl_{org} både i sediment och i vattenfasen.

Rapporten fokuserar framför allt på terrestra aspekter av klorcykeln och innehåller också information om vanliga metoder för mätning av olika klorföreningar.

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Frequently used abbreviations

Cl	chlorine
Cl ⁻	chloride ion
Cl _{org}	total organochlorine
VOCl	volatile organochlorine
³⁶ Cl	chlorine-36; a radioisotope of Cl emitting primarily beta radiation
³⁶ Cl ⁻	chloride-36 ion
³⁶ Cl _{org}	organically bound chlorine-36
³⁵ Cl	chlorine-35; a stable isotope of Cl
³⁷ Cl	chlorine-37; a stable isotope of Cl
TX	total halogens; an operational definition based on an analysis method which strictly defined detect chlorine, bromine and iodine
TOX	total organic halogens; an operational definition based on an analysis method which strictly defined detect chlorine, bromine and iodine
AOX	adsorbable organic halogens; an operational definition based on adsorption on activated carbon prior to analysis.
EOX	Extractable organic halogens
d.m.	dry mass
HCl	hydrochloric acid

1 Introduction

Chlorine (Cl) is one of the 20 most abundant elements on earth. It is essential for life for various reasons. Chloride (Cl⁻), the only stable ionic form of Cl, is the major anion in blood and is present at concentrations of approximately 100 mmol L⁻¹ in plasma and interstitial fluid (Yunos et al. 2010). Cl⁻ participates in osmoregulation of cells (White and Broadley 2001), and is as an important electrolyte for regulation of muscle function and synaptic transmission in the neural system. The adult human dietary intake of Cl⁻ in the USA is 6–12 g d⁻¹ (Yunos et al. 2010). Cl⁻ also functions as an essential co-factor in enzymes involved in photosynthesis related to the oxidation of water by the PSII photosystem (Winterton 2000). Thereby, Cl is a critical nutrient and a suggested minimum requirement of Cl for crops is 1 g kg⁻¹ dry mass (d.m.) (White and Broadley 2001).

Many of the most debated organic pollutants, including the “dirty dozen” highly toxic and now internationally banned persistent organic pollutants, are chlorinated (Godduhn and Duffy 2003). Although natural halogenated organic compounds have been known since the late 19th century (Gribble 2003), this was forgotten in the environmental debate, and the dominating view was that chlorinated organic compounds (organochlorines; Cl_{org}) in the environment were primarily of anthropogenic origin and often toxic. It is now evident that there is also a large natural production of Cl_{org}. Nearly 5,000 naturally produced chlorinated organic compounds have been identified and chemically characterized, and their production has been associated with fungi, lichen, plants, marine organisms of all types, insects, and higher animals including humans (Gribble 2003, 2010, Öberg 2002). Some of these have well known physiological functions, including several important antibiotics (e.g. vancomycin). Others have important effects in the environments. For example volatile organochlorines (VOCl) enhance atmospheric ozone destruction (Winterton 2000). However, the ecological functions of most Cl_{org} in nature, and the reasons for its production, are largely unknown.

Another research area where Cl has been central is hydrology. Cl⁻ is the dominating chlorine pool globally, is highly soluble in water, and has a high enrichment factor when comparing oceanic and riverine concentrations (i.e. sea water concentrations are in the order of 2,500 times larger than freshwater concentrations; Winterton 2000). At the first glance this indicates that Cl⁻ is unreactive in the environment and this has been a prevailing view for a long time (e.g. White and Broadley 2001). Accordingly, Cl⁻ has been seen as an inexpensive and suitable tracer of soil and ground water movements (Herczeg and Leaney 2011, Hruška et al. 2012) and studies using Cl⁻ as a water tracer has been a foundation for contaminant transport models (e.g. Kirshner et al. 2000). However, as discussed below, there is now clear evidence that Cl⁻ is highly reactive in some environments.

Recently ³⁶Cl, a radioactive isotope with a half-life of 301,000 years, has attracted interest because of its presence in radioactive waste. The long half-life in combination with high mobility in the geosphere and the potential for substantial biological uptake creates a need for long-term risk assessments related to handling and storage of radioactive waste (Limer et al. 2009). Previous assumptions that ³⁶Cl in soils primarily occurs as ³⁶Cl⁻ and is highly soluble and unreactive has been questioned along with growing awareness of a more complex cycling of Cl in terrestrial environments.

Several aspects of Cl, including the physiological role (e.g. Yunos et al. 2010, White and Broadley 2001), the persistent organic pollutant perspective (e.g. Winterton 2000) and the global Cl cycle (Graedel and Keene 1996) have been summarized previously, and will not be the primary focus here. This text rather provides an update and supplement to previous reviews focusing on the terrestrial Cl cycling (e.g. Öberg 2002, Clarke et al. 2009). A primary motivation for this is the recent interest in ³⁶Cl behavior in soils (e.g. Sheppard et al. 1996, Limer et al. 2009, Van den Hoof and Thiry 2012).

2 Fundamental chemical aspects of chlorine

Cl is the 20th most abundant element on Earth (Winterton 2000). It has atomic number 17 and belongs to the halogen group in the periodic table. Cl has a high electron affinity and electronegativity and thereby molecular Cl is a strong oxidant. Consequently, molecular Cl is rare in nature and instead the inorganic ion from Cl⁻ which is highly soluble in water typically dominates in the hydrosphere and in minerals (but frequently not in soil as discussed below).

2.1 Cl isotopes and sources of ³⁶Cl

Cl occurs in nature as primarily two stable isotopes, ³⁵Cl (ca 76%) and ³⁷Cl (ca 24%). Besides those isotopes seven radioactive isotopes exist of which ³⁶Cl has a very long half-life, $3.01 \cdot 10^5$ years. The half-lives of the other six radioactive Cl isotopes are less than one hour; these isotopes are, therefore, not of interest in the context of Cl cycling in the environment. ³⁶Cl decays with a maximum energy of 709.6 keV either by emitting a beta particle (98.1%) or by electron capture (1.9%) resulting in the end products argon-36 (³⁶Ar) and sulphur-36 (³⁶S), respectively (Rodríguez et al. 2006, Peterson et al. 2007).

In the environment, ³⁶Cl is produced by natural nuclear reactions; in the atmosphere by the spallation of argon with cosmic ray protons, and in soil and rock by neutron activation of potassium, calcium and chlorine (White and Broadley 2001). The resulting radiological dose to individuals is calculated by the ratio of ³⁶Cl to stable chlorine (³⁶Cl/Cl) in the surface environment but it varies between geographical locations. The natural ³⁶Cl/Cl ratio is between 10^{-15} and 10^{-12} (Campbell et al. 2003). The dose can thereby differ by several orders of magnitude between coastal and inland areas due to the difference in concentration of stable Cl. ³⁶Cl/Cl ratios exceeding 10^{-12} (up to $2 \cdot 10^{-11}$) have been found in a 100 km² area in the Tokai-mura region, Japan, where four nuclear power reactors and one nuclear fuel reprocessing plant had been operated (Seki et al. 2007).

³⁶Cl was produced in large amounts by neutron activation of seawater upon nuclear weapon tests between 1952 and 1958 (Peterson et al. 2007). These peaks in ³⁶Cl have been used for dating ground water (Campbell et al. 2003, White and Broadley 2001). ³⁶Cl is also produced during nuclear power reactor operation due to neutron capture of stable ³⁵Cl that may be present at trace levels in core materials, graphite, coolant water, and construction materials such as steel and concrete (Fréchet and Degros 2005, Hou et al. 2007). In addition, ³⁶Cl can be produced in considerable amounts via spallation reactions of other concrete components, such as Potassium (K) and Calcium (Ca), primarily in fast reactors where high-energy particles such as fast neutrons are present (Aze et al. 2007). Although ³⁶Cl levels are typically low, the active uptake of organisms and high concentration ratios in plants relative to soils (Kashparov et al. 2007a, b, White and Broadley 2001) makes information about Cl cycling in soils and sediment layers including bioavailability and residence end exposure times relevant for risk assessments (Limer et al. 2009).

3 Major Cl reservoirs and large scale cycling

The largest Cl reservoirs on the earth's surface are the crust and the ocean (Graedel and Keene 1996; Table 3-1). Inorganic Cl by far dominates these reservoirs. Estimates for the other reservoirs are also largely based on Cl⁻ concentration measurements. This assumption of a general dominance of Cl⁻ is problematic for the pedosphere because Cl_{org} levels have been shown to range from 11 to near 100% of the total Cl pool in a large range of soil types (Gustavsson et al. 2012, Johansson et al. 2003a, Redon et al. 2011, 2013; see also Section 4 below). This means that the pedosphere Cl pool may be at least twice as large as proposed by Graedel and Keene (1996).

Graedel and Keene (1996) also propose fluxes between the reservoirs based on available data. These values are poorly constrained. For example, to balance the overall budget a yearly loss of 30 Tg Cl yr⁻¹ from the pedosphere (equivalent to 1.25‰ of the pedosphere reservoir) had to be assumed. This would lead to a rapid depletion of the pedosphere stock which is clearly unrealistic, and therefore this budget illustrates substantial lack of knowledge regarding large scale fluxes in combination with bias from ignoring Cl_{org} formation in terrestrial environments.

In the large scale inorganic Cl cycle mineral weathering contributes with Cl⁻ to freshwaters and later the ocean. The largest contribution of Cl⁻ to the atmosphere is sea salt aerosols while minor contributions include HCl from volcanic activity and biomass burning, mineral aerosols, and volatile organochlorines (VOCl_s) of natural or anthropogenic origin. Cl⁻ is transported to oceans and soils by wet and dry deposition (further described in Section 4 below).

Table 3-1. Major Cl reservoirs on earth, how they were estimated, and theoretical residence times based on data from Graedel and Keene (1996; corrected values for the cryosphere). Note that major pools of organic Cl are not considered and therefore the pedosphere reservoir is highly uncertain (see text for details).

Reservoir	Cl content (g)	Reservoir was estimated from:	Residence time (years)
Mantle	22×10^{24}	Meteorite Cl:Si ratio; mantle mass.	1.1×10^{13}
Crust	60×10^{21}	Meteorite Cl:Si ratio; crustal mass.	3.4×10^8
Oceans	26×10^{21}	Cl concentration; water volume.	4.3×10^6
Pedosphere	24×10^{15}	Average soil Cl ⁻ 100 mg kg ⁻¹ d.m. mean soil depth and density 2 m and 1.0 g cm ⁻³ . ^a	5.3×10^2
Freshwater	320×10^{15}	Average Cl ⁻ concentration in rivers and ground water; water volume.	1.5×10^3
Cryosphere	0.5×10^{15}	Cl ⁻ concentration in rain or snow; ice volume.	8.3×10^1
Troposphere	5.3×10^{12}	Concentrations of HCl, CH ₃ Cl and Cl ⁻ aerosols; troposphere volume.	8.8×10^{-4}
Stratosphere	0.4×10^{12}	Cl concentration; stratosphere volume.	1.3×10^1

^a Assumptions by Graedel and Keene (1996); no published references in support of these values provided.

4 Chlorine in terrestrial ecosystems

During the past decades there has been a rapid development towards improved qualitative understanding of the terrestrial Cl cycle. We are, however, far from being able to present a detailed quantitative picture due to two main reasons. The first one is due lack of data – in most cases the reported fluxes are extrapolated to whole ecosystems or regions based on a few measurements at specific points in time and space. Secondly, there is still lack of knowledge regarding some qualitative aspects of the biogeochemical Cl cycle, and the processes behind the Cl cycling (e.g. formation and degradation of Cl_{org}) as well as their regulation are still uncertain.

The terrestrial environment includes biomass, litter and surface soil layers (often characterized by higher content of organic/humic matter than below layers), mineral soil layers, and soil water. Figure 4-1 show these reservoirs and also fluxes of Cl to, from, and within the system.

4.1 Input of Cl to terrestrial ecosystems

4.1.1 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^- 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^- from the atmosphere. There is a clear pattern of decreasing wet deposition of Cl^- with increasing distance to the sea and with consideration to prevailing wind directions (Clarke et al. 2009). Gases and particles can also contain Cl^- ; 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^- by gases and particles is called “dry deposition” compared to “wet deposition”, which is deposition of Cl^- by e.g. rain and snow. The deposition to soil is generally higher in forested areas than over open land because atmospheric particles are intercepted by vegetation and there is also possible leaching from the vegetation.

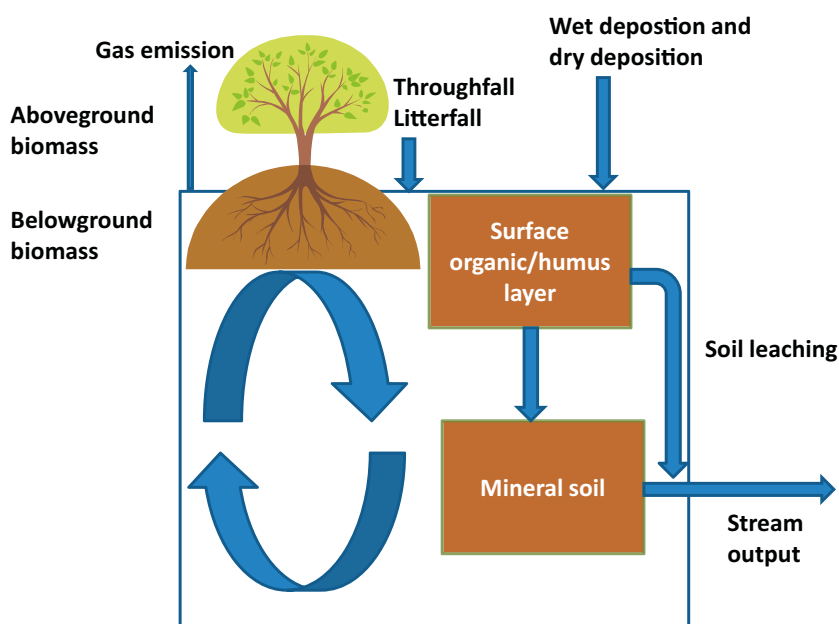


Figure 4-1. A schematic diagram of pools and fluxes of chlorine in terrestrial ecosystems.

The quantification of wet deposition of Cl^- can be done with high precision and is relatively well constrained but highly variable depending on distance to the sea (higher wet deposition close to the sea). In Europe wet Cl deposition varies from 0.5 to 220 $\text{kg ha}^{-1} \text{yr}^{-1}$ (Clarke et al. 2009). Dry deposition includes inputs Cl^- via gases, aerosols, and particles. Because dry deposition includes several forms of Cl and is affected by interception by surfaces such as tree canopies, the estimate of dry deposition is difficult to measure and considerable more uncertain but has been estimated to 15–73% (average 43%) of total deposition based on data from North America and Europe (Svensson et al. 2012).

It is well known that precipitation, in addition to Cl^- , also contains Cl_{org} (Enell and Wennberg 1991, Grimvall et al. 1991, Laniewski 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 et al. 1999) (see Section 7.1 for description of AOX analysis). Brominated compounds are widespread but less prevalent, and organically bound iodine has only been detected at sites close to the sea (Laniewski 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, particularly organic bases and acids (Laniewski et al. 1999). Chloroacetic acids can occasionally explain up to 6% of the Cl_{org} in precipitation (Laniewski et al. 1995, von Sydow et al. 1999, Svensson et al. 2007a), while the relative contribution from volatile organochlorines (VOCl_s) usually is smaller, with concentrations often at ppt (ng L^{-1}) levels (Schleyer 1996, Svensson et al. 2007b).

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 total AOX concentrations. 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 et al. 1998).

4.1.2 Weathering

As mentioned previously, Cl^- 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 biological processes or interactions with organic matter. Riverine Cl^- has likewise often been considered to originate primarily 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 rocks, but felsic bedrocks such as granite contains low amounts of Cl^- , and the highest amounts are found in mafic bedrocks (Melkerud et al. 1992) and obviously in halide rich evaporite minerals. 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, New Hampshire, USA, with bedrock consisting of mainly granite. Approximately 2% of the Cl^- stream output originated from weathering, which can be considered as small compared to the atmospheric contribution (Lovett et al. 2005).

Land rise in previously glaciated regions can result in soils that were originating as marine sediments and therefore are rich in Cl^- . Release of Cl^- from such marine deposits constitutes a special case with significant subsurface contribution of Cl^- to soils, water and organisms. In the Forsmark area, in central East Sweden, investigated thoroughly by SKB, leaching from marine deposits could have contributed up to 20% of the Cl^- exported from the area (Tröjbom and Grolander 2010).

4.1.3 Input from irrigation, fertilization and road de-icing

Anthropogenic Cl^- input from irrigation and fertilization can represent substantial inputs to terrestrial environments. Irrigation with low salinity water can contribute in the order of 1,000 $\text{kg ha}^{-1} \text{yr}^{-1}$ and thereby anthropogenic contributions can be the major Cl input in some areas (White and Broadley 2001). Irrigation of crops can also lead to accumulation of salt in soil (Rengasamy 2010). Cl is an essential element for plants (Broyer et al. 1954) and is known to be an important anion in crop production (Engel et al. 2001).

Since the start of de-icing of roads in mid-twentieth century, studies have shown increased Cl^- concentrations in both surface water and groundwater in the vicinity of roads. In the Laxemar-Simpevarp area in South East Sweden, 35–56% of the total Cl^- input was estimated to come from road salt (Tröjbom et al. 2008). Road salt effects can be chemical (e.g. induce ion exchange affecting acidification and metal and nutrient leaching; Löfgren 2001, Bäckström et al. 2004) or biological (e.g. effects on mussels and pond food webs; Todd and Kaltenecker 2012, Van Meter et al. 2011).

4.2 Gaseous efflux from terrestrial systems

Volatile organochlorines (VOCl) are produced in a wide variety of ecosystems such as wetlands, salt marshes and forests (Dimmer et al. 2001, Rhew et al. 2002, Albers et al. 2011), and in different climatic regions including boreal, temperate and tropical areas (Yokouchi et al. 2002, Rhew et al. 2008, Albers et al. 2011). Despite the growing knowledge in the field, data on VOCl emission rates are scattered and inconsistent. Budget and transport estimates on various scales are highly uncertain, partly because low concentrations of each specific VOCl make sampling and analyses challenging (Pickering et al. 2013; see Section 7 below). Furthermore, VOCl sources and sinks are not well understood, and continuous observations over time are scarce.

VOCl have been found in several terrestrial biomes such as tropical forest, grasslands, deciduous forest, taiga, tundra, and rice fields (Khalil et al. 1998, Varner et al. 1999, Laturus et al. 2000, Redeker et al. 2000, Haselmann et al. 2002, Dimmer et al. 2001, Hoekstra et al. 2001, Wang et al. 2007, Rhew et al. 2008). Most of the available information has been gathered in the northern hemisphere. Previous studies in terrestrial ecosystems have primarily considered seven different VOCl. The most commonly studied compounds are chloromethane (CH_3Cl) and chloroform (CHCl_3). Other VOCl compounds reported include CCl_4 (tetrachlorometane), $\text{C}_2\text{H}_3\text{Cl}$ (chloroethylene), CH_2Cl_2 (dichloromethane), CH_3CCl_3 (methyl chloroform), and $\text{C}_2\text{H}_3\text{Cl}_3$ (trichloroethane) (Haselmann et al. 2002, Hoekstra et al. 2001, Wang et al. 2007, Mead et al. 2008, Rhew et al. 2008). In addition, other halogenated compounds such as bromomethane, iodomethane trichlorofluoromethane (freon-11) and dichlorodifluoromethane (Freon-12) have also been reported to be released from terrestrial sources (Khalil and Rasmussen 2000, Rhew et al. 2000, Keppler et al. 2003, Varner et al. 2003).

Emissions are considered to be small compared to wet and dry deposition of Cl . However, a ^{36}Cl radio-tracer study indirectly indicated substantial release of VOCl in soils corresponding to $0.18 \text{ g Cl m}^{-2} \text{ yr}^{-1}$ or 44% of the annual wet deposition (Bastviken et al. 2009). This is a high number that needs validation, but interestingly it includes all possible VOCl in contrast to other estimates that measure specific VOCl compounds only. Previous studies showed average emission of chloroform and chloromethane corresponding to 0.13 and $0.04 \text{ g Cl m}^{-2} \text{ yr}^{-1}$, respectively, from a coniferous forest soil (Dimmer et al. 2001), or $< 0.01 \text{ g Cl m}^{-2} \text{ yr}^{-1}$ for chloroform from a Scots pine (*Pinus silvestris*) forest soil (Hellén et al. 2006). Other ecosystems also show VOCl emissions. For instance coastal salt marshes are releasing chloromethane indicating fluxes of $0.2\text{--}1.2 \text{ g m}^{-2} \text{ yr}^{-1}$ (Rhew et al. 2000). Given this, the formation of VOCl would not only represent a substantial proportion of the emission to the atmosphere but also a significant part of the chlorine cycle. In addition, such high fluxes might explain some of the observed Cl^- imbalances found in catchments in Europe and North America (Svensson et al. 2012).

4.3 Terrestrial reservoirs of chlorine

4.3.1 Soil

Total Cl typically range from 20 to $> 1,000 \text{ mg Cl kg}^{-1} \text{ d.m.}$ in non-saline soils (Table 4-1). The concentrations of Cl_{org} in surface soil layers are in most cases higher than Cl^- levels (Table 4-1). The dry mass fraction of Cl_{org} in surface soils (0.01–0.5%), is as large as for phosphorous (0.03–0.2%) and only slightly lower than nitrogen (1–5%) and sulphur (0.1–1.5%) (Öberg 2002). Measurements of bulk density, horizon thicknesses etc are often difficult to obtain for many studied soils and often affect total storage calculations more than concentration differences. Total storage is usually largest in the mineral soil layer because of its greater thickness compared to the organic surface layer, despite the fact that Cl_{org} concentrations are typically 2–5 times higher in the organic surface soil layer (Redon et al. 2011). The presently available data only separates organic and mineral soil layers and more

detailed discussions about specific soil profiles is therefore not possible at this point. The data in Table 4-1 indicate that total Cl levels are higher in soils with more organic matter while the percentage Cl_{org} is frequently higher and above 80% in mineral soils. Based on this information higher soil Cl levels may be connected with soil organic matter content, probably because soil chlorination processes stabilize Cl as Cl_{org} as proposed by Gustavsson et al. (2012). However, the available information is too scarce to be conclusive on a general basis.

The soil organic matter is mainly composed of high molecular weight substances, usually larger than 1,000 Dalton (Hjelm and Asplund 1995). Very few studies have tried to determine Cl_{org} content in different types of soil organic matter. Lee et al. (2001) concluded that the Cl_{org} was associated with organic matter with a molecular weight of < 10,000 Dalton, while most organic matter in the studied soil had higher molecular weight (> 10,000 Dalton). Bastviken et al. (2007, 2009) found that 1–10% of the Cl_{org} in coniferous soil was associated with water leachable fractions of the organic matter. Interestingly Redon et al. (2011) found that the Cl:C ratio in Cl_{org} increases with soil depth, ranging from 0.08 to 2.7 mg Cl_{org} g⁻¹ C in the humus layer and from 0.6 to 6.1 mg Cl_{org} g⁻¹ C in mineral soil (0–40 cm). Johansson et al. (2001) also report increasing Cl:C ratios with soil depth. Hence, some of the chlorinated organic molecules can be resistant to degradation and selectively preserved compared to average soil organic matter.

4.3.2 Sediment

Analysis of sediment Cl_{org} have focused on contamination from industrial activities. There is a large body of literature on specific chlorinated pollutants (e.g. PCBs and DDTs). Among the bulk Cl_{org} measures, adsorbable organic halogens (AOX; see Section 8 about description of analytical techniques) have been used to study sediment pore waters, but such efforts in non-contaminated sediments are relatively rare. There has also been a suggestion to avoid AOX analyses for sediment pore waters when it was discovered that it cannot discriminate between natural and anthropogenic Cl_{org} (Müller 2003). Extractable organic halogens (EOX; extraction of sediments with cyclohexane–isopropanol under sonication) yielded concentrations of 5–70 mg kg⁻¹ sediment (probably dry mass sediment but this was unclear) in the upper 2 cm of Bothnia bay sediments in a pulp and paper mill contamination area (Pöykiö et al. 2008). Another study reported Cl_{org} concentrations of < 10 to 843 µg Cl g⁻¹ organic matter in seven non-polluted inland water sediments (Suominen et al. 1997). The analysis methods differed (AOX and EOX after various extractions) which makes comparisons uncertain. Analyses using similar methodology as for soils (TOX; see Section 8 for description) appear to be largely missing and therefore Cl and Cl_{org} levels in sediments are presently unclear.

4.3.3 Water

In contrast to soils, Cl^- concentrations generally exceed Cl_{org} concentrations in water. For example, the Cl^- concentration in various waters is measured in mg L⁻¹, while Cl_{org} is typically measured in µg L⁻¹ and VOCl_s are in the range of ng L⁻¹ (Table 4-2) (Eriksson 1960, Asplund and Grimvall 1991, Enell and Wennberg 1991, McCulloch 2003). This means that the atmospheric deposition of Cl_{org} is in the order of 1000-fold lower than deposition of Cl^- and thereby often assumed to be negligible from a bulk Cl perspective. While ground water has the highest Cl^- concentrations in comparison with rain water and surface waters, Cl_{org} and VOCl concentrations can be highest in surface waters (Table 4-2). The environmental quality criteria with regard to Cl^- levels in groundwater published by Swedish food agency use a Cl^- threshold level of 100 mg L⁻¹.

4.3.4 Biomass

The Cl^- content of plant biomass varies among plant species. For plant growth a general Cl^- requirement of 1 mg g⁻¹ d.m. has been suggested, but deficiency symptoms have been observed at 0.1–5.7 mg g⁻¹ d.m., while toxic levels between 4–50 mg g⁻¹ d.m. have been reported (White and Broadley 2001). This means that extrapolations across species and locations are highly uncertain. Plant Cl_{org} content has been estimated to 0.01–0.1 mg g⁻¹ d.m. (Öberg et al. 2005), but this is based on scattered measurements from beech leaves, spruce needles, sphagnum moss and bulk samples of grass and the variability between species and plant parts are unknown at present.

Table 4-1. Examples of total Cl and the fraction Cl_{org} in various soils. Soil depth is denoted by soil layer (e.g. humus and mineral layers) or by distance from soil surface.

Ecosystem, country	Total Cl (mg kg ⁻¹)	Cl _{org} (%)	Soil layer or depth	Reference
Coniferous forest, Sweden	99–274	67–73	humus	Gustavsson et al. 2012
Conif. forest, Sweden	154	86	humus	Bastviken et al. 2009
Conif. forest, Sweden	331	95	humus	Bastviken et al. 2007
Conif. forest, Sweden	127	69	humus + mineral	Svensson et al. 2007b
Conif. forest, Sweden			humus	Öberg and Sandén 2005
Conif. forest, Sweden	369–458	81–85	humus	Johansson et al. 2003a, Johansson et al. 2003b
Conif. forest, Sweden	310	68	humus	Johansson et al. 2001
Conif. forest, Denmark	206–772	67–85	humus	Albers et al. 2011
Conif. forest, China	45	38	15 cm	Johansson et al. 2004
Conif. and deciduous forests, France ^a	45–1,041	40–100	humus	Redon et al. 2011
Mixed deciduous forest, Sweden	224	85	humus	Johansson et al. 2003a, Johansson et al. 2003b
Mixed forests ^a	34–340	89	mineral, 0–30 cm	Redon et al. 2013
Conif. and deciduous forests, France ^a	25–210	29–100	mineral 0–10 cm	Redon et al. 2011
Pasture, Sweden	46–65	85–90	5–15 cm	Gustavsson et al. 2012
Grassland, France ^a	13–1,248	83	mineral, 0–30 cm	Redon et al. 2013
Agricultural soil, France ^a	19–100	87	mineral, 0–30 cm	Redon et al. 2013
Agricultural soil, Sweden	45–49	84–89	5–15 cm	Gustavsson et al. 2012
Paddy soil, China	38	34	15 cm	Johansson et al. 2004
Peat bog, Canada	30–1,177	43–84	Surface – 6 m	Silk et al. 1997
Peat bog, Chile	366–1,084	82–93	Surface – 2 m	Biester et al. 2004

^a Includes study sites at different distances to the sea.

Table 4-2. Chloride (Cl⁻), organochlorines (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 ⁻ (mg L ⁻¹)	Cl _{org} (µg L ⁻¹)	Chloroform (ng L ⁻¹)
Rain water	0.2–3.5 ^a	1–15 ^d	11–97 ^g
Groundwater	10–300 ^b	5–24 ^e	5–1,600 ^h
Surface water (lakes and rivers)	0.74–11 ^c	5–200 ^f	4–3,800 ⁱ

(a) Minimum and maximum concentrations obtained from 6 precipitation stations in different regions of Sweden 1983–1998 (Kindbohm 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 et al. 1998, 1999), combined with typical range given in Öberg et al. (1998).

(e) Minimum and maximum concentrations in groundwater from 14 wells in Denmark (Grøn 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 et al. 1991, Schleyer 1996).

(h) Minimum and maximum concentrations obtained from groundwater measurements at one site in Denmark (Laternus 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).

In another study, standing stock Cl in trees in a pine forest in Belgium, based on measurements of different plant parts, were estimated to 4.7 and 5.5 kg Cl ha⁻¹ for wood plus leaves, and roots, respectively (Van den Hoof and Thiry 2012). This study also found that fresh leaves had the highest Cl concentration (0.59 mg g⁻¹ d.m.) corresponding to 35% of the Cl in the trees and that Cl_{org} accounted for less than 10% of the Cl in the leaves and the bark but constituted 20% of the total biomass Cl of the whole tree.

Interestingly, monitoring of total Cl in various landscape compartments, including soil, sediment, water, and biomass, in the Forsmark area indicated that the terrestrial biomass Cl pool dominated over the other pools and accounted for in the order of 60% of the total catchment Cl (Tröjbom and Grolander 2010). Cl was substantially enriched in biomass compared to other comparable elements (e.g. bromine and iodine) and nutrients (nitrogen, phosphorus, potassium, calcium). It is known that Cl is an essential element, but this level of enrichment indicates that the roles of Cl for organisms may not be fully understood, and that a large part of potential contaminant ³⁶Cl reaching terrestrial parts of the landscape will be taken up by biota. The pool of Cl in the limnic biota was negligible compared to Cl pools in sediments and water.

Another interesting finding is reported by Tröjbom and Nordén (2010). In a comparison between two areas in central East Sweden and South East Sweden, Forsmark and Laxemar-Simpevarp, respectively, total Cl:C ratios in the green parts of terrestrial plants were 10-fold higher in the Forsmark area for unknown reasons. In the Forsmark area the green parts of rooted terrestrial plants also had a 10-fold higher total Cl:Br ratio compared to heterotrophs, most dead biomass, sea water and soils. Altogether, this indicates active uptake and accumulation of Cl in green parts of terrestrial plants.

4.3.5 Litter

Litter is represented by detached dead or dying plant biomass. Simultaneous leaching of Cl⁻ and formation of Cl_{org} has been shown in litter (Myneni 2002). A recent study of senescent leaves from white oak (*Quercus alba*) showed Cl⁻ and Cl_{org} contents of 335 and 165 mg kg⁻¹, respectively (Leri and Myneni 2010). In this study Cl fractions were quantified with X-ray absorption near-edge structure (XANES) spectroscopy. This enabled the discoveries that (1) total Cl_{org} content in the leaves increased during the senescence and gradual degradation, (2) aliphatic Cl_{org} was present a stable levels over time and seems contributed by plant processes and stable to degradation, and (3) that water soluble aromatic Cl_{org} was first leached from the leaves followed by later accumulation of non-soluble aromatic Cl_{org} during senescence.

Spruce needle litter in Denmark contained 51–196 (median 101) µg Cl_{org} g⁻¹ d.m. (Öberg and Grøn 1998). In a study of 51 different forest sites in France with both coniferous and broad leaf tree species total Cl content in the litter was 46–528 (median 147) mg kg⁻¹ d.m. and the percentage Cl_{org} was 11–100% (median 40%; Redon et al. 2011). Again, available data suggest substantial variability within and between species and locations.

4.4 Translocation within systems and hydrological export

There are scattered indications of extensive internal cycling of Cl in terrestrial ecosystems. For example, the annual root uptake of Cl by Scots pine (*Pinus silvestris*) was found to be 9-fold larger than Cl demand by the tree (Van den Hoof and Thiry 2012). The excess Cl was returned primarily as Cl⁻ in throughfall and to some extent by litterfall. Similarly, a study integrating data from 27 forests of different types in France show that throughfall was highly variable between different forests, but on an average twice as high as the total atmospheric Cl deposition (41 and 20 kg ha⁻¹ yr⁻¹, respectively; Redon et al. 2011). For comparison the average Cl in litterfall in these systems ranged from 0.1 to 2.5 kg ha⁻¹ yr⁻¹. Again this indicates that tree Cl uptake can be much greater than the net internal demand to supply growth of new biomass. This cycling, if being a general pattern, will prolong Cl residence times in the systems. The reasons for excess uptake of Cl relative to needs is unknown but could be related with evapotranspiration if Cl⁻ enters the plant with the water without discrimination.

There is also an extensive cycling of Cl in soils. In the upper soil layers microbial activity results in formation of Cl_{org} from Cl⁻ (i.e. chlorination; e.g. Bastviken et al. 2009, Öberg et al. 2005). Measured rates in incubations from 14 sites varied from 1.4–90 ng Cl g⁻¹ d.m. d⁻¹ or, expressed as fraction of the Cl⁻ pool being transformed to Cl_{org} per day, from 0.0002 to 0.003 d⁻¹) (Gustavsson et al. 2012).

Table 4-3. Examples of estimated soil organic matter chlorination rates.

Source	Type of study and experiment time	Specific chlorination (d ⁻¹)	Mass-based rate (ng Cl _{org} g ⁻¹ C _{org} d ⁻¹)	Area-based rate (kg Cl ha ⁻¹ yr ⁻¹)
Lee et al. 2001	Lab: arable soil; 11 weeks	0.00199	–	–
Silk et al. 1997	Lab: peat; 8 weeks	0.00066	–	–
Bastviken et al. 2007	Lab: forest soil; 78 days	0.00029	20	–
Bastviken et al. 2009	Lab: forest soil; 6 months	0.0007–0.0034	78–311	–
Gustavsson et al. 2012	Lab: conif. forest soil. 4 months	0.00094–0.0014	37–90	–
Gustavsson et al. 2012	Lab: pasture soil. 4 months	0.00021–0.00074	3.5–4.9	–
Gustavsson et al. 2012	Lab: agricultural soil. 4 months	0.00032–0.00055	2.6–5.0	–
Öberg et al. 1996	Field experiment: spruce litter	–	1,002	0.5
Öberg and Grøn 1998	Field study: spruce litter	–	1,469–7,517	0.35
Öberg 2002	Lysimeter mass balance	–	–	2.7
Öberg et al. 2005	Mass balance of catchment	–	–	2.0

Field based estimates are rare. Öberg et al. (2005) estimated the chlorination to be 2 kg ha⁻¹ yr⁻¹ from mass balance calculations while laboratory measurements in the same area yielded chlorination rates of 2–13 kg ha⁻¹ yr⁻¹ (corresponding to 50–300% of the wet deposition at this catchment; Bastviken et al. 2007, 2009).

Table 4-3 gives an overview of some published soil organic matter chlorination rates of relevance for field conditions. Available data indicates higher chlorination rates on a weight basis in litter compared to in deeper soil layers. Extensive chlorination has been shown upon litter degradation (Myneni 2002) and seasonal patterns have been suggested (Leri and Myneni 2010).

Dechlorination processes (transformation from Cl_{org} to Cl⁻ by either organic matter decomposition or by selective removal of Cl atoms from organic molecules) have been extensively studied in relation to organochlorine pollution and bioremediation (e.g. van Pée and Unversucht 2003). However, while well known for specific Cl_{org} compounds there are yet no known studies reporting directly measured dechlorination rates for bulk Cl_{org} in terrestrial environments. In spite of this, dechlorination is believed to be important and in mass balance calculations steady state conditions with similar chlorination and dechlorination rates are often assumed (Öberg et al. 2005). Based on indirect evidence a recent study suggested that the balance between chlorination and dechlorination is more important for soils Cl⁻ levels than Cl⁻ deposition (Gustavsson et al. 2012).

Migration across different depth zones can be important for internal Cl cycling in soils. Intensive chlorination has been observed in surface soil and litter layers, while Cl_{org} levels decrease with soil depth and the form of Cl⁻ dominating in the hydrological export from catchments is Cl⁻ (Figure 4-2). This has led to the suggestion that Cl_{org} is leached from surface soils and either absorbed (and preserved) or transformed to Cl⁻ in deeper soil layers (Figure 4-3) (Öberg and Sandén 2005, Rodstedth et al. 2003, Svensson et al. 2007b).

4.5 Ecosystem Cl budgets

There have been a few attempts to make ecosystem or catchment scale Cl budgets. The ecosystem budgets are typically based on concentration measurements in combination with information about carbon and water cycling that can support estimates of Cl transport and transformation. Figure 4-4 illustrate published budgets. While they all converge regarding the order of magnitudes, many potentially important reservoirs and fluxes remain unknown or uncertain because of lack of data.

Net ecosystem budgets of Cl⁻, i.e. comparison of atmospheric deposition and stream export are common because Cl⁻ is often covered in monitoring efforts. A recent summary of such data reveal that there is an imbalance in many catchments (Table 4-4) (Svensson et al. 2012). This is not surprising given the new knowledge of several processes that can retain Cl⁻ (plant uptake, formation of Cl_{org}) or release Cl⁻ (decay of biomass, dechlorination), and imbalances were most striking in areas with a wet Cl⁻ deposition below 6 kg ha⁻¹ yr⁻¹.

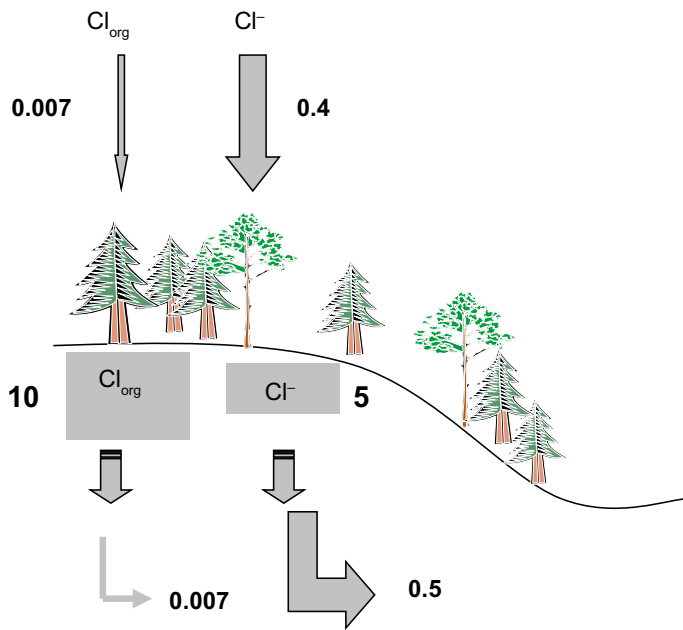


Figure 4-2. Major paths of Cl transport to and from the Stubbetorp catchment, near Norrköping, Sweden (Svensson et al. 2007b). Fluxes to and from the catchment are dominated by chloride (Cl⁻) while the standing Cl stock in soil is dominated by Cl_{org}. Reservoirs are in g m⁻² and fluxes represent g m⁻² yr⁻¹.

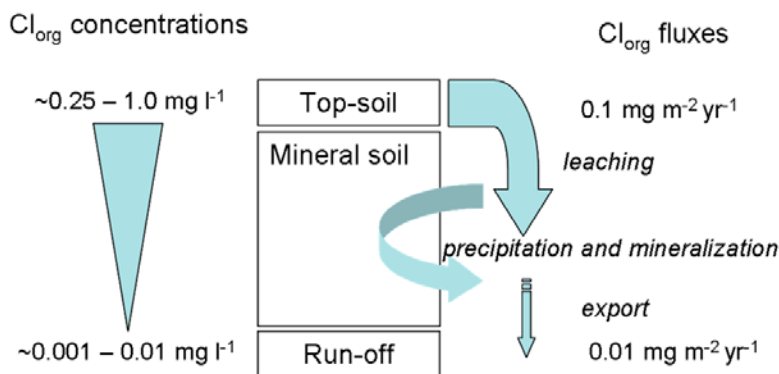


Figure 4-3. Estimated organic chlorine transport in soil. Concentration data and flux estimations for top-soil are based on data from Rodstedth et al. (2003) and Svensson et al. (2007b). Cl_{org} is leached from the top soil and gradually lost from the soil water by precipitation or adsorption to the solid phase or by organic matter degradation while the water moves downward through the soil column. Cl⁻ shows an opposite pattern with lower relative concentrations in surface soils and increasing concentrations downward partly due to the release of Cl⁻ from Cl_{org}. This model can explain why the water released from soils has higher concentrations of Cl⁻ than Cl_{org}, while Cl_{org} dominates in surface soils.

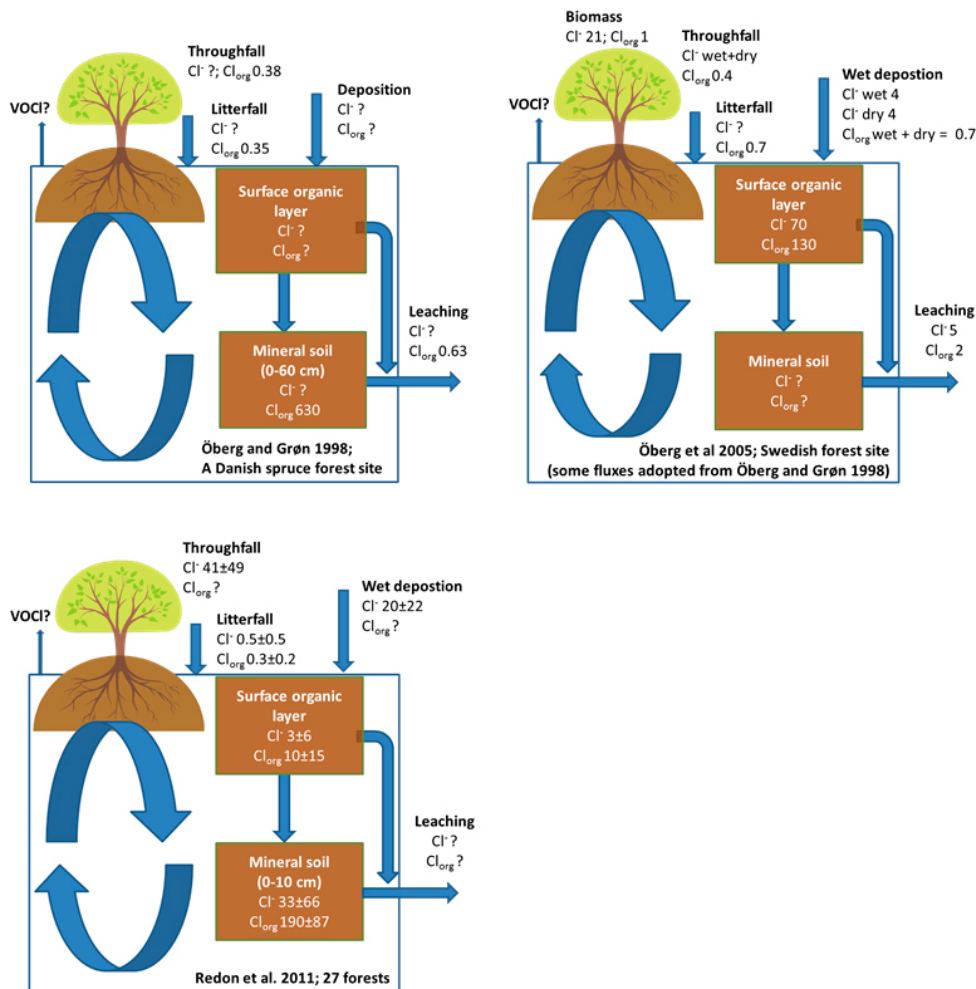


Figure 4-4. Examples of terrestrial Cl budgets. Units are kg ha^{-1} (reservoirs) and $\text{kg ha}^{-1} \text{yr}^{-1}$ (fluxes). Note that the budget by Öberg et al. 2005 is not independent from the budget by Öberg and Grøn (1998). Cl⁻ and Cl_{org} denotes chloride organochlorines, respectively, and VOCl is volatile organic chlorines e.g. chloroform.

A couple of laboratory lysimeter studies specifically addressed Cl⁻ balances by irrigating soil cores with artificial rain water having well known Cl⁻ concentrations and monitoring efflux from the cores (Rodstedth et al. 2003, Bastviken et al. 2006). Both these studies noted substantial imbalances indicating substantial Cl transformation in the soil, but the patterns were not clear (sometimes a net loss and sometimes a net accumulation) and could not be easily explained.

A field scale ³⁶Cl tracer study was performed by Nyberg et al. (1999) which injected ³⁶Cl⁻ in a small catchment. When injections were made in surface soils only 47% could be recovered over 30 days while 78% of simultaneously injected radioactive water (³H₂O) was recovered. Upon injection in deeper soils, the ³⁶Cl⁻ recovery was greater (83%), but still lower than for ³H₂O (98%). Clearly, Cl⁻ is preferentially retained in surface soil.

The Cl⁻ retention affects residence times of Cl in catchments and implies longer residence times than for water which previously were assumed to be reflected by Cl⁻ transport through soils. Few studies have addressed this issue yet, but estimates from one study of forest Cl cycling conclude that overall Cl residence times considering both Cl⁻ and Cl_{org} pools and fluxes were 5-fold higher than residence times considering only Cl⁻ and neglecting Cl_{org} formation (Redon et al. 2011).

As noticeable above, in all parts of Chapter 4, data have primarily been collected in forests and to some extent also pastures, agricultural land, and peat bogs. Unfortunately, wetlands, sediments and discharge areas where potential ³⁶Cl contaminants will leave underground aquifers are poorly studied; to our knowledge, no studies on Cl cycling including Cl_{org}, Cl uptake by organisms, food web transfer and loss by emission of VOCl from wetlands, streams, reservoirs or lakes have been published.

Table 4-4. Chloride (Cl⁻) balances of catchments. Negative numbers indicate loss of Cl⁻ from the catchment while positive numbers indicate accumulation in the catchment. Note that balances can be biased by underestimated dry deposition in some areas depending on the sampling methods.

Site and location	Forest type	Sampling years	Cl balance (input-output) (kg ha ⁻¹ y ⁻¹)	Cl balance % of input	Ref.
Aneboda, Sweden	Coniferous	9	-5.7	41	1
Bear Brook, ME, USA	Deciduous	3	-4.2	27	2
Birkenes, Norway	Coniferous	19	-19.2	57	3
Coweeta-14, NC, USA	Deciduous	4	0.6	9	4
Coweeta-18, NC, USA	Deciduous	12	-0.6	11	4
Coweeta-2, NC, USA	Deciduous	12	-1.1	22	4
Coweeta-27, NC, USA	Deciduous	12	0.2	2	4
Coweeta-32, NC, USA	Deciduous	4	-0.1	1	4
Coweeta-34, NC, USA	Deciduous	4	0.8	11	4
Coweeta-36, NC, USA	Deciduous	12	-3.7	60	4
Fernow forest, w-4, WV, USA	Deciduous	15	-1.5	71	5
Forellenbach, Germany	Coniferous	16	-3.8	83	3
Gammtratten, Sweden	Coniferous	6	-0.9	45	1
Gårdsjön, Sweden	Coniferous	10	2.7	3	6
Hietajärvi, Finland	Coniferous	15	-0.3	30	3
Hubbard Brook, w-3, USA	Deciduous	29	-1.1	35	7
Hubbard Brook, w-6, USA	Deciduous	33	-0.8	23	7
Kindlahöjden, Sweden	Coniferous	9	-0.3	3	1
Kosetice Observatory, Czech Republic	Coniferous	18	2.5	46	8
Lehstenbach, Germany	Coniferous	6	0.4	4	9
Llyn Brianne catchment C16, Great Britain	Heath/grass	2	-2.2	3	10
Lysina, Czech Republic	Coniferous	1	4.5	45	11
Maryland, HCWS, USA	Deciduous	1	-4.4	102	12
Panola Mountain, GA, USA	Deciduous	12	-3.1	111	13
Pluhuv Bor, Czech Republic	Coniferous	1	0.8	13	11
Plynlimon catchment Afon Cyff, Great Britain	Heath/grass	2	-5.3	4	10
Plynlimon catchment, Upper Hafren, Great Britain	Moorland	18	-5.8	4	16
Plynlimon catchment, Nant Tanllwyth, Great Britain	Coniferous	5	9.9	6	17
Saarejärve, Estonia	Coniferous	13	1.8	33	14
Steinkreuz, Germany	Deciduous	6	-0.1	1	9
Strengbach, France	Mixed coniferous/ deciduous	3	-0.2	1	15
Valkea-Kotinen, Finland	Coniferous	15	-1.7	121	3

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5. USDA Forest service (Mary Beth Adams, USDA Forest Service, personal communication, October 5, 2006).
6. (Hultberg and Grennfelt 1992).
7. Cary Institute of Ecosystem Science, 2007-October.
8. Czech Hydrometeorologica Institute, 2009-September.
9. (Matzner 2004).
10. (Reynolds et al. 1997).
11. (Kram et al. 1997).
12. (Castro and Morgan 2000).
13. (Peters et al. 2006).
14. The Estonian Environment Information Centre 2009-October.
15. (Probst et al. 1992).
16. (Neal et al. 2010; Colin Neal, Centre for Ecology and Hydrology, UK, personal communication, Spetember 2010).
17. (Neal et al. 2004; Colin Neal, Centre for Ecology and Hydrology, UK, personal communication, Spetember 2010).

5 Chlorine transformation processes

Recent results show that most of the soil chlorination is driven by enzymes and thereby organisms, but abiotic chlorination at significant rates seems also to have occurred (Bastviken et al. 2009). Other studies indicate that besides the dominating biotically driven Cl^- retention there is support for additional abiotic processes related to iron cycling in soils (Kepler et al. 2000, Fahimi et al. 2003). However, since the redox cycling of iron is usually a consequence of microbial activity, the proposed abiotic processes may be indirectly linked to biological processes. It is also clear that chlorination capacity is widespread among various groups of organisms including bacteria, fungi, algae, insects, mosses, and vascular plants (e.g. Clutterbuck et al. 1940, Hunter et al. 1987, de Jong and Field 1997, Öberg 2002).

The chlorination of organic matter can occur both inside and outside cells. The intracellular chlorination seems strictly regulated by enzymatic processes. Enzymes known to mediate the intracellular chlorination include enzyme groups named FADH_2 -dependent halogenases and perhydrolases (FADH_2 is a cofactor necessary for the enzyme function). The underlying process for the extracellular chlorination seems to be a formation of reactive chlorine (e.g. hypochlorous acid, HOCl), from reactions between hydrogen peroxide and Cl^- . The reactive Cl is a strong oxidant and reacts with surrounding organic matter which renders an unspecific chlorination of various organic compounds in the large and complex pool of soil organic matter (Hoekstra 1999, van Pée and Unversucht 2003). Even though the extracellular chlorination thereby is less rigorously controlled by enzymes, it still depends on enzymes such as heme and vanadium containing haloperoxidases for the production of reactive chlorine (van Pée 2001).

Given the rapid chlorination rates (i.e. the rapid Cl^- retention) in soil, the high abundance of organochlorines, and the widespread capacity among organisms to chlorinate organic material there should be a fundamental ecological explanation for the organic matter chlorination. Yet, it is still unknown why such processes occur in soil. Intracellular chlorination processes have been explained as ways of detoxification or are believed to represent production of compounds serving as chemical defense (e.g. antibiotics), hormones, or pheromones (Hoekstra 1999). However, direct verification of these hypotheses is limited. Extracellular chlorination represents a different process, although it is well documented that reactive chlorine species such as hypochlorous acid are potent bactericides used by phagocytes to kill invading microorganisms (e.g. Apel and Hirt 2004) and that many microorganisms and plants produce allomones, i.e. substances that deter or kill competing or pathogenic organisms. Hence, the ability to use reactive chlorine in the chemical warfare between competing microorganisms could provide a substantial advantage and become a general strategy. In support of this, one screening of genetic databases found that many of the identified haloperoxidases from terrestrial environments are originating from organisms that are associated with living plants or decomposing plant material (Bengtson et al. 2009). Hence, the ability to produce reactive chlorine could be especially common in environments that are known for antibiotic-mediated competition for resources (interference competition). Yet, the ability to produce haloperoxidases is also recorded, for example, for plant endosymbionts and parasites, and there is little or no empirical evidence that suggests that these organisms are antagonistic.

Another hypothesis relate to microbial processing of organic material representing their substrates. There is a general perception that chlorinated organic matter is less bioavailable than non-chlorinated organic compounds. However, chloroperoxidases, like many other oxidases, catalyse production of small reactive molecules (hypochlorous acid in the case of chloroperoxidase) that can break C-C bonds in complex and refractory organic compounds (Hoekstra 1999, van Pée and Unversucht 2003). Thereby, smaller and more bioavailable parts of the refractory compounds may be formed. In support of this it has been shown that exposure of lignin to reactive chlorine enhance its biodegradability (Johansson et al. 2000), and that fungal chloroperoxidase activity resulted in depolymerization and breakdown of synthetic lignin (Ortiz-Bermúdez et al. 2003). Similarly, biodegradation of chlorinated bleaching effluent lignin were greater than the degradation of corresponding chlorine-free lignin (Bergbauer and Eggert 1994). After dechlorination these compounds should be highly preferred as substrates by microorganisms. Hence, promoting formation of Cl_{org} could be a way of increasing the organic substrate supply for microorganisms.

A third potential reason for the chlorination could be connected to defense against oxygen radicals. Formation of reactive chlorine is related to consumption and thereby detoxification of reactive oxygen species including hydrogen peroxide and oxygen radicals. Therefore extracellular chloroperoxidase mediated formation of e.g. hypochlorous acid that can be prevented from entering the cell may form one line of defence against reactive oxygen species. Interestingly, and in support of this hypothesis, repeated oxidative stress exposure have been found to induce the expression of chloroperoxidase genes and increase the production of reactive chlorine in some algae and bacteria (Bengtson et al. 2013).

As explained above the first rate estimates of chlorination in soils are now available, and there are several hypotheses, all with some support, regarding the reasons for the chlorination. However, it is still not known how the chlorination is regulated and how environmental variables influence chlorination rates. Tests with different nitrogen levels have yielded ambiguous results (Rodstedth et al. 2003, Bastviken et al. 2006), and local variability seems large. A few studies have found that rates are slower under anoxic conditions (Bastviken et al. 2009), which is reasonable given that chlorination or organic matter is an oxidative process. This points at an indirect regulation of soil moisture, but apart from that the regulation of natural chlorination is still unclear. Chlorination rates in sediments and other environments (e.g. in plants) is yet unknown as well.

Recent findings indicate that chlorinated compounds can be used as terminal electron acceptors in microbial metabolism. Interestingly, the Gibbs free energy yield of this process is similar to the energy yield with nitrate as the electron acceptor, and thereby only slightly lower than the energy yield of oxic respiration (Smidt and de Vos 2004). Hence, chlorinated organic compounds can be very potent as electron acceptors. Dechlorination could therefore be the result of either degradation of the chlorinated organic matter or the microbial use of chlorinated organic molecules as electron acceptors (i.e. halorespiration) and there is a wide literature regarding dehalogenation processes in terms of biochemistry and related to specific compounds (e.g. Pries et al. 1994, Fetzner 1998, Dolfing 2000, Olivas et al. 2002, van Pée and Unversucht 2003, Smidt and de Vos 2004). However, the rates and regulation of dechlorination of bulk Cl_{org} in nature is still unknown.

6 Chlorine in organisms

6.1 General uptake by plants and microorganisms

Growing plants rapidly take up large amounts of Cl^- . The ratio of Cl^- concentrations in fresh plant tissue to concentrations per dry mass in the top 20 cm of soil ranged from 1.5 to 305 for common agricultural plants (Kashparov et al. 2007b). Similar ranges were found by Kashparov et al. (2007a; Table 6-1). This is in line with the high proportion of total catchment Cl found in biomass from the Forsmark area (60%, Tröjbom and Grolander 2010) and a Danish forest (10%, Öberg and Grøn 1998); both sites dominated by coniferous forest. Further, a Cl^- uptake grossly exceeding cellular needs by pine trees followed by rapid leaching, and thereby an extensive internal cycling through the biomass has been proposed (Van den Hoof and Thiry 2012).

Recent evidence also indicates that soil microorganisms rapidly take up Cl^- during growth phases. In the only known experiment studying this so far 20% of the ^{36}Cl added to experiment soil was incorporated into microbial biomass within 5 days (Bastviken et al. 2007). It was suggested that rapid microbial growth following as system disturbance (e.g. a rain event, leaf fall in autumn etc) could lead to rapid microbial uptake of Cl^- based on physiological need. It is unclear if this can affect Cl_{org} formation rates.

6.2 Cl compounds with potentially long residence time in biota

The purpose of this section is to identify possible mechanisms for ^{36}Cl to become “resident“ in biota. Today a large number of natural products containing organically bound halogens are known (Gribble 2003, 2010). In terrestrial vascular plants alone, a couple of hundred chlorinated compounds have been identified (Gribble 2010), but many of these are relatively short lived with a specific function, such as the chlorinated auxins, “death hormones“, that trigger senescence (Engvild 1986). For the purpose of this review we exclude such more or less ephemeral compounds as they do not undergo transfer through the food chain and likely have little effects on anything but their target organism. Of interest for this review are compounds that have characteristics that allow them to accumulate and have a long half-life in biota, and which may be transferred between organisms in the food chain. The reason for this interest is to identify possible compounds that might contribute to a prolonged exposure of organisms to radiation from ^{36}Cl . Thus, focus will be on pools of chlorine that may have a long half-life in organisms rather than chloride ions that in comparison undergo a fairly rapid turnover.

Halogenated natural products (Drechsel 1896) and enzymatic oxidation of halide ions (Chodat and Bach 1902) have been known for over a century. However, essentially due to analytical limitations the understanding of the role of halogenated natural products was limited until the middle of the 20th century. Thus, when environmental chemistry began as a discipline in its own right in the early 1960s following the publication of “Silent Spring“ (Carson 1962), many environmentalists were unaware of the occurrence of halogenated natural products (Mu et al. 1997), and there were much discussion about what possible unknown anthropogenic pollutants proliferated in the environment as only 5–10% of the extractable organically bound chlorine (EOCl) could be accounted for by known compounds (Bernes and Naylor 1998).

Table 6-1. Average concentration ratio (CR; concentrations in fresh plants divided with concentrations in dried soil in the upper 20 cm layer) of Cl^- in food compared to in surface soils on the area supporting the food production. Adopted from Kashparov et al. (2007a).

Food	CR
Leafy vegetables	28–71
Fruit vegetables	17–18
Root vegetables	8–98
Beans	16–20
Straw	149–237
Fruits	0.6–4
Milk and beef	48–57

The past two decades has seen the identification of an increased number of halogenated compounds that have structural similarities with the well-known persistent organic pollutants (POPs). POPs include the chlorinated pesticides and polychlorinated biphenyls and were the first compounds to become of interest to environmental chemists. Some of the compounds that have come under interest recently, specifically methoxylated polybrominated diphenyl ethers (MeO-PBDEs), occur at very high concentrations at high trophic levels (Mwevura et al. 2010, Alonso et al. 2012), and by analyzing the carbon isotopes it has been shown that they are natural products. A number of compounds that contain both chlorine and bromine have also been identified, and although less seems to be known about these than the MeO-PDBEs it is likely that they are natural products. A number of mixed brominated chlorinated bipyrroles and terpenoids have also been identified as likely persistent and bioaccumulating natural products (Tittlemier et al. 1999, Rosenfelder and Vetter 2012). It is generally believed that these brominated and mixed brominated chlorinated compounds are produced at low trophic levels in algae and sponges, and are used as allomones, e.g. to deter grazing animals (Gribble 2010). As is clearly shown by the very high concentrations of MeO-PBDEs that may occur in cetaceans (Mwevura et al. 2010, Alonso et al. 2012) these compounds undergo biomagnification and are persistent with a long half-life in biota. Although less is known about, e.g. mixed brominated chlorinated dibenzo-*p*-dioxins (Unger et al. 2009), bipyrroles, and terpenoids, these have such physical-chemical properties that they generally should undergo biomagnification. If such compounds are formed in the presence of ^{36}Cl , the turnover of ^{36}Cl in the organism will to some degree depend on the half-life of these compounds. Although these compounds may accumulate to high concentrations, especially in homeothermic organisms at high trophic levels, the major halogen is bromine with limited contribution of chlorine. Thus, these compounds may be of relatively little importance as pools of ^{36}Cl that will be persistent in biota. However, ongoing work on persistent halogenated natural products should be followed as new compounds in which chlorine plays a more central role may be found in unexpected environments.

Several types of halogenated carboxylic acids¹ are known as natural products (Dembitsky and Srebnik 2002). Most of these, however, are structurally complex, often containing reactive functional groups that shorten their half-lives. There are, however, some polyhalogenated homosequiterpene acids that potentially are persistent, but we have found no studies that investigate food chain transfer and accumulation actually takes place with these complex acids.

The one group of halogenated carboxylic acids that have been shown to have a long half-life and undergo food-chain transfer is the chlorinated fatty acids (CIFAs). These compounds become especially interesting as they do exert toxicity, but they are not generally recognized by biota as xenobiotics (Ewald 1998). CIFAs were identified as constituting the bulk of EOCl (up to 70% or even more) in environmental samples in the 1990s (Håkansson et al. 1991, Mu et al. 1997). To date the origin of CIFAs is not fully understood. There clearly are anthropogenic influences as EOCl concentrations are particularly high close to point sources. An important type of point source was identified as production of chlorine bleached pulp and paper (Håkansson et al. 1991). During chlorine bleaching direct chlorination of unsaturated FAs takes place, and CIFAs were identified in the effluent from bleaching facilities. Some reports also indicate that the CIFA-profile depends on the type of anthropogenic pollutants present (Vereskuns 1999). In spite of these caveats on the concentrations and profile, CIFAs are, as far as known today, ubiquitous and present also in areas where the concentrations of anthropogenic POPs are low. It is also noteworthy that away from point source of chlorinated organic material EOCl is relatively evenly distributed in the aquatic environment (Bernes and Naylor 1998). In view of this general distribution of EOCl, a *de novo* synthesis of CIFAs in organisms, also those that are not subject to any anthropogenic source of organically bound chlorine, is likely. However, although formation of CLFAs via chloroperoxidase action have been shown in some marine organisms (Mu et al. 1997), a general cause for the presence of CLFAs in organisms away from point sources appears not yet to have been identified. Food chain transfer and biomagnification of CIFAs has been shown in wild populations of fish (Mu et al. 2004), and in laboratory experiments from chironomids (midges) to fish (Björn 1999).

¹ Some authors, e.g. Dembitsky and Srebnik (2002), call even very complex molecules “fatty acids” as long as they contain a carboxylic functional group. We prefer to reserve the term “fatty acids” to such carboxylic acids that actually may occur in lipids.

In contrast to traditional POPs, CIFAs do not primarily accumulate in fatty tissues, but are incorporated in membrane lipids. Thus the concentrations of CIFAs relative other fatty acids (FAs) are higher in muscle tissues than in depot fat, at least in mammals (Björn 1999, Åkesson Nilsson 2004). To date there is no information of any specific role of CIFAs in membrane lipids, but the three-dimensional structure of CIFAs is, at least in some cases, very similar to unsaturated FAs; e.g. *threo*-9,10-dichlorooctadecanoic acid (*threo*-9,10-dichlorostearic acid) has a three-dimensional structure similar to *cis*-9-octadecenoic acid (oleic acid), which has a double bond between carbons 9 and 10. Thus, CIFAs may fill similar functions as unsaturated FAs in membrane lipids. However, there are also reports suggesting that a high proportion of CIFAs in the membranes causes membrane leakage (Gunilla Åkesson Nilsson, personal communication).

CIFAs are metabolized via β -oxidation, but the metabolic process seems to stop at chlorinated myristic acid (tetradecanoic acid) (Mu et al. 1997). Indeed, dichloromyristic acid accumulates in some systems after addition of longer chained CIFAs (Mu et al. 1997). This accumulation of dichloromyristic acid is not fully understood, but seemingly the enzymes responsible for β -oxidation are sterically hindered by the presence of the chlorine atoms. A further implication of this is that CIFAs may be more recalcitrant in biota than other FAs. Thus, incorporation of ^{36}Cl into FAs may lead to longer exposure time to radiation than would otherwise be expected, but the present lack of data prevents quantification of this effect.

Of special interest for a discussion on human exposure to radiation from ^{36}Cl is that dichloromyristic acid accumulates also in human systems (Gustafsson-Svärd et al. 2001) and there is a possibility of *de-novo* synthesis of CIFAs in inflammatory processes (Åkesson Nilsson 2004). The results as yet are preliminary, but the wider implication is that if an individual that for some reason has an ongoing inflammatory process is exposed to ^{36}Cl , this radioisotope could be incorporated into compounds that are recalcitrant in the organism. Further, preliminary experiments have indicated that CIFAs may be particularly prone to accumulate in the myelin sheath of nervous tissue (Kylin, unpublished), why targeted damage to the nervous system cannot be excluded.

7 Techniques for studying Cl in the environment

This section will first describe various analysis techniques that can be used to study Cl in the environments. This is followed by a discussion regarding sampling and preservation. Thereafter examples of approaches to study Cl related processes are provided. Finally key aspects of Cl monitoring in ecosystems will be addressed.

7.1 Ion chromatography

Cl⁻ in water samples can be determined by e.g. ion chromatography or ion-selective electrodes. Ion chromatography with chemical suppression (such as MIC-2, Metrohm), according to standard procedure for determination of Cl⁻ of water with low contamination (ISO 10304-1:1992) is frequently used. In short, water samples are filtered (0.15 µm filter, Metrohm) and separated on an anion column and detected with a conductivity meter.

7.2 AOX

Water samples are typically analyzed for Cl_{org} as AOX (adsorbable organic halogen; ISO 9562:2004). In short, the organic compounds in the water sample is adsorbed on activated carbon, and washed with an acidified nitrate solution to remove remaining chloride. Thereafter the sample is combusted at 1,000°C in an oxygen atmosphere and the formed halides is titrated with silver ions with microcoulometric titration with an AOX instrument (e.g. ECS3000, Euroglas). This AOX method measures the sum of chlorine, bromide, and iodine but does not distinguish between the different halogens. Since Cl 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 Cl dominates in the samples. Therefore, Cl_{org} is used as the sum of organically bound chlorine and if other halides are present in considerable amounts, the AOX method will overestimate the Cl_{org} in the samples. There were previous concerns that chloride might interfere with the AOX measurements and thereby overestimate the Cl_{org}, but such interference is not significant unless there are high Cl⁻ concentrations such as in brackish waters (Asplund et al. 1994). Further tests of how to perform AOX analyses in high Cl⁻ samples may be necessary.

The AOX method has been adapted for other types of bulk Cl_{org} analyses including extractable organic halogens (EOX) and volatile organic halogens (VOX). Apart from the pretreatments the combustion and coulometric detection is similar. Two other adaptations of the AOX method is described in the below section.

7.3 TOX and TX

The concentration of Cl_{org} (TOX) in solid samples is now frequently 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 dry sieved and milled soil sample is washed with an acidic nitrate solution to remove remaining chloride. The residual soil is combusted and TOX is detected according to the procedure for AOX analysis described above. A recent suggestion, based on results that significant amounts of Cl⁻ can be trapped inside microbial cells in soils (Bastviken et al. 2007), is to also have a sonication step before the final washing, but if the milling is done thoroughly this may disrupt most cells using the original approach. The total amount of chlorine (TX) can be determined by adding sieved and milled soil to a small crucible followed by direct combustion in the AOX instrument. Cl⁻ can then be calculated as TX minus TOX and this represents an alternative method of determining chloride in soil rather than measuring Cl⁻ in water soil leachate (Johansson et al. 2001). There is a risk of overestimation of chloride by using “TX minus TOX” because TX analyzes not only Cl_{org} and porewater chloride but possibly also mineral chloride and this has to be considered when deciding methods. Additional methods that has been used for studies of Cl_{org}, although requiring much more

expensive equipment, are X-ray absorption spectroscopy (XAS: e.g. Reina et al. 2004) and neutron activation (Xu et al. 2004). Redon et al. (2013) cross checked Cl_{org} analyses of mineral soil samples by neutron activation and by the TOX method and found no significant differences (unpublished data), but additional cross comparisons of several techniques for different types of samples would be beneficial.

7.4 VOCl

There are several difficulties in estimating VOCl including low ambient air concentrations, and sampling and storage without contamination. The concentrations of VOCl are in the lower ppt range, compared to carbon dioxide (CO_2), which is found in hundreds of ppm levels in the atmosphere. Despite the low concentrations, there are now instruments capable of analyzing VOCl in ppq-levels (Dobrzyńska et al. 2010). Therefore, the analytical challenges for VOCl detection are now more related to sample collection (enabling a reliable and large enough sample amount for detection) and storage of samples (without loss or contamination of the compounds of interest) than to the analytical detection in the laboratory. For measuring VOCl soil-atmosphere exchange there will also be additional difficulties such as related to sampling methodology in the field (capturing the VOCl soil-atmosphere exchange) and estimating the VOCl fluxes (calculating the flux from the observed soil-atmosphere exchange).

There are some recent papers presenting analytical methods and sample preparation for determining VOCl in air samples (e.g. Dobrzyńska et al. 2010, Ramirez et al. 2010, Dewulf and Van Langenhove 2006, Demeestere et al. 2007). As with all trace gases, it is essential to take precautions during sampling, storage, and analysis to avoid loss of analytes. Despite high-precision instruments, the concentrations of VOCl in the air are so low that sample pre-concentration is typically needed to be able to detect the compounds of interest. Methods commonly used for the determination of VOCl concentrations in air are based on either adsorption onto a sorbent column followed by thermal desorption with subsequent analysis using gas chromatography (GC) (e.g. Valtanen et al. 2009, Hoekstra et al. 2001) or on cryogenic concentration of VOCl directly from a sampled volume of air followed by GC (e.g. Rhew et al. 2008). The disadvantages of the sorption tubes are that sorption and desorption efficiencies may not be 100%, which may limit the detection limit for samples at low concentrations. In addition, storage of sorbent tubes before desorption and analysis can result in losses of e.g. chloroform. Determination of VOCl using methods based on cryogenic trapping can be influenced by moisture condensation in the trap. The other way of sampling VOCl in air is to use canisters. This has been successfully done by many researchers (e.g. Redeker et al. 2003). Evacuated canisters used to collect air samples in the field for transport to the laboratory must be carefully cleaned to avoid contamination of the sample. Since canister sampling is not a pre-concentration technique, it requires a subsequent sorbent and/or cryogenic concentration stage in the laboratory (Wang and Austin 2006). The more recent technique, solid phase microextraction (SPME) has been shown to be useful for the determination of volatiles in air (Dobrzyńska et al. 2010). This technique is based upon the absorption of chloroform into a polymer coated on a silica fiber. Following equilibration of the fiber with the atmosphere, the volatile is released via thermal desorption in the injection port of a gas chromatograph. Sample preparation is very easy and fast with this technique although sample collection conditions and thermal desorption conditions must be carefully controlled for the best precision. The canisters are difficult to use if a large amount of samples is needed, due to canisters' large volume and limited space available for storage and transportation. In the reviewed papers there seems to be almost equal numbers using sorbents or canister techniques. There is only one study that has used SPME (Yassaa et al. 2009).

7.5 XSD and AED to identify Cl compounds in complex matrices

An interesting technique to identify chlorinated organic compounds in a complex matrix is the halogen selective detector (XSD) for GC (Åkesson Nilsson et al. 2001, Åkesson Nilsson 2004). The selectivity of this detector is much higher than other GC detectors why unknown compounds containing halogens can be identified in a complex matrix. The XSD can be used either to select chromatographic peaks that should be identified with high-resolution spectrometric techniques, or

to monitor for known compounds in complex matrices that would otherwise require more expensive and laborious methods, e.g. GC-high resolution mass spectrometry (MS). Thus, the sample throughput can be increased.

GC coupled to an atomic emission detector (AED), in which a microwave induced plasma is used to excite the elements, has also been used to identify halogenated compounds in the environment (Flodin et al. 1997a, Hjelm et al. 1996, Laniewski et al. 1998, 1999), including to select peaks for characterization with MS (Flodin et al. 1997b, Johansson et al. 1994). The AED will give information about which type of halogen atom the individual peak contains, and it is also possible to identify other non-carbon elements in the compounds. In contrast, the XSD will only give information that the peak contains an unspecified halogen. The AED is, however, more expensive and complex to operate, with a lower sample throughput as potential consequence. With some very complex mixtures it may also be less selective than the XSD.

7.6 ICP

Several techniques for the simultaneous determination of multiple elements have been built around the inductively coupled plasma (ICP). Traditionally, the ICP has been used to excite the elements for atomic emission spectroscopy (AES), also called optical emission spectroscopy (OES). However, until recently ICP-AES instruments have not been well suited for the determination of halogens; the low emission wavelengths of the halogens have not been compatible with the instrument configuration and the limits of detection have not compared favourably with other techniques (Strellis et al. 1996, Teledyne Leeman Labs 2013). Recently, developments of instrument configurations and detectors have made it possible to efficiently include the halogens in multi-element determinations by ICP-AES (Teledyne Leeman Labs 2013, Naozuka et al. 2003, Oliveira et al. 2012), and the number of scientific publications using this technique is growing.

Coupling the ICP with MS (ICP-MS) provides a powerful technique to not only determine the elements, but individual stable isotopes (Barnes and Straub 2010, Pereira Barbosa et al. 2013). During the 2000s applications in which ICP-MS has been coupled to chromatography that allows characterization of the elemental and isotopic composition of individual compounds (González-Gago et al. 2007, Kretschy et al. 2012) have become increasingly common. It is also possible to couple ICP-MS with, e.g. laser ablation to determine the elemental and isotopic composition of very small targets areas (Fietzke et al. 2008, Seo et al. 2011).

7.7 Stable chlorine isotopes

Isotopes of an element participate in the same chemical reactions but react at slightly different rates due to their difference in mass. This difference in reaction rates between the isotopes are referred to as isotopic fractionation and usually result in discrimination against the heavier isotope in the reactions. This fractionation can differ widely between different reactions e.g. depending on what enzymes catalyze the reaction. Therefore comparisons of stable isotope ratios before and after reactions can be very useful for identifying roles and contributions of different processes in elemental cycles. This approach is extensively used for light elements where the relative mass difference between stable isotopes is large, such as H, C and N. The mass difference between stable Cl isotopes is smaller but the Cl stable isotope ratio, e.g. ^{37}Cl proportion of the total Cl expressed as

$$\delta^{37}\text{Cl} (\text{‰}) = (R_{\text{sample}}/R_{\text{reference}} - 1) \cdot 1000$$

where R is the abundance ratio of $^{37}\text{Cl}/^{35}\text{Cl}$ in the sample and reference material, respectively, have recently shown promising for separating natural and anthropogenic sources of some chlorinated compounds (Holmstrand et al. 2010). In addition there are indications that chlorination catalyzed by chloroperoxidases fractionate strongly with reaction products having $\delta^{37}\text{Cl}$ values of -12‰ (Aeppli et al. 2013, Reddy et al. 2002), while Cl_{org} in fish and polar bear fat have $\delta^{37}\text{Cl}$ values closer to reference values (-1 to -3‰ : Wassenaar and Koehler 2004).

This field is in its early phase and analyses are demanding in terms of sample preparation (Cincinelli et al. 2012). Most efforts have targeted individual compounds (Aeppli et al. 2010). One approach described for bulk Cl is based on the following steps (Wassenaar and Koehler 2004):

1. Separation of Cl^- and Cl_{org} (by e.g. extraction or adsorption techniques).
2. Cl_{org} samples are converted to Cl^- by combustion.
3. The Cl^- is precipitated to AgCl .
4. AgCl is converted to methyl chloride (CH_3Cl) by reaction with iodomethane.
5. The CH_3Cl is injected in a multicollector continuous-flow isotope ratio mass spectrometry system (CF-IRMS).

Other approaches outlined in Cincinelli et al. (2012) include various GC-MS, GC-IRMS (gas chromatography isotope ratio mass spectrometry) and TIMS (thermal ionization mass spectrometry) techniques ensuring that sample sizes and mass resolution are large enough. ICP-based techniques have also been proposed (Fietzke et al. 2008).

7.8 Sample preparation and preservation

The procedures for sample preparation and possible preservation differ widely depending on the specific analysis of interest. While e.g. sampling and sample handling for measuring VOCl or specific Cl_{org} compounds is highly demanding due to e.g. low concentrations, the sample procedures for bulk Cl samples are easier and straight-forward. To completely cover all these aspects is beyond the scope of this work, and we will here just highlight a few aspects related to sampling and preservation.

Regarding bulk Cl analyses, there is increasing awareness that organic and inorganic Cl pools are both large and behave very differently in the environment, and should therefore preferably be separated in the analyses. Many of the analyses are specific in their detection, e.g. ion chromatography detects only Cl^- and not Cl_{org} while AOX only detect adsorbable Cl_{org} . However, when making pretreatments for bulk analysis such as TOX, TX or ICP, details may be important. For example if fresh soil is extracted with water (at low pH and with nitrate to facilitate ion exchange to liberate Cl^-), it is likely that the soil will not release the Cl^- present in microbial cells (Bastviken et al. 2007). To fully extract most of the Cl^- it is therefore better to dry, freeze, and/or sonicate the soil to break up microbial cells before the extraction.

In terms of preservation, this again strictly depends on the analyses. For the high concentration Cl pools (Cl^- and bulk Cl_{org}) it has become common practice to freeze liquid samples and dry solid phase samples which are often milled prior to analysis. However, effects of drying or freeze-thaw cycles on analysis results have seemingly not been systematically evaluated.

7.9 Process rate studies

Studying process rates are important for mass balance studies to determine turnover rates and residence times. Further, to allow predictive modeling knowledge about how critical processes and their rates are regulated or influenced by environmental variables is often critical. A number of fundamental approaches for process studies have been used for Cl as outlined below.

A classical way to study processes such as chlorination, dechlorination, Cl uptake or release, has been to monitor changes in concentrations over time in a confined sample or system. This approach applied to leaf litter bags was behind breakthrough findings such as simultaneous loss and gain of Cl^- and Cl_{org} , respectively in decaying litter (Myneni 2002), and for studies of the fates of Cl in soil cores (Rodstedth et al. 2003, Bastviken et al. 2006). This approach depends on concentration changes that are large enough to be detected during the time frames in focus and if net changes are of interest.

For processes near steady state, or that occur slowly, other approaches have to be used. This applies for example to soil organic matter chlorination and dechlorination, which can occur simultaneously possibly resulting in a small or slow net change in spite of highly active and relatively rapid processes. In such cases tracer studies become an important tool. In the case of Cl, radiotracer experiments with ^{36}Cl provide a highly sensitive way to measure gross transformation rates. This approach was used to confirm soil organic matter chlorination and determine rates by adding $^{36}\text{Cl}^-$ to soils and measure the formation of $^{36}\text{Cl}_{\text{org}}$ (Bastviken et al. 2007, Gustavsson et al. 2012) as well as for studying the temperature sensitivity of soil organic chlorination (Bastviken et al. 2009).

At the ecosystem scale, mass balance modelling by combining concentration measurements with material fluxes in the ecosystem is the most common way to estimate Cl cycling. It is powerful in its logical simplicity and provides good overviews of fluxes and stocks. Ideally, to support predictive modelling and study influence of environmental variables such modelling should also have a time dimension based on regular repeated measurements, and preferable possibilities to make sub-scale experimental treatments, although this is rarely possible because of resource constraints. To date, there seems to be no such mass balance studies with repeated sampling of both Cl^- and Cl_{org} pools, which severely limits the possibilities of predictive modelling.

8 Future challenges

The research about natural Cl cycling is still in its infancy, especially in the light of recent findings of the importance of the Cl_{org} pool in the terrestrial environment. Therefore several fundamental questions remain. Some of these are discussed below based on the interest to understand transport, uptake and/or exposure, and residence times of ^{36}Cl in terrestrial and aquatic ecosystems. For all these questions it is clear that Cl^- and Cl_{org} pools can be expected to behave very different, e.g. in terms of solubility, bioavailability, residence times. Therefore inorganic and organic Cl pools have to be considered separately in order to understand and model the dynamics of Cl in landscapes over time.

8.1 What is the spatio-temporal variability of Cl^- and Cl_{org} distribution in landscapes?

This is a very fundamental question and includes inputs, standing stocks and outputs from various types of landscape units. Previous studies, generally non-repeated snapshot measurements, have revealed differences between soil types, as well as local variations within sample plots (Johansson et al. 2003a, b). Currently, there are no systematic assessments of the temporal variability at different spatial scales. Such measurements are a key asset for all further studies including; i) the design of sampling programs, ii) validate data comparability from different locations or collected at different times, and iii) accurately assessing data uncertainty in models. It is important that seasonal patterns are considered to test for data comparability across seasons. Although seemingly simple and basic, such studies are fundamental for building appropriate environmental models.

8.2 Which conditions and processes control Cl^- and Cl_{org} levels and transport?

The regulation of Cl^- and Cl_{org} levels are key topics for long term modelling with ambitions to include varying environmental conditions. Fundamental environmental variables such as water content, organic matter content, primary productivity, dominating vegetation, nutrient levels, temperature, etc could have large impacts on the relative distribution of Cl^- and Cl_{org} , in turn affecting bioavailability, transport pathways and residence times in ecosystems. In addition, a better understanding of why so many organisms perform chlorination of organic matter would greatly facilitate modelling of chlorination rates, i.e. what is the adaptational value of biological chlorination?

Dechlorination rates, i.e. release of organically bound Cl from the organic matter, of bulk soil Cl_{org} is at present unknown. This means that we do not know if the Cl_{org} we observe in soils represent primarily a dynamic pool that is turned over rapidly or if the measured soil Cl_{org} pool largely consists of very stable compounds that have slowly accumulated. Therefore, rates and regulation of dechlorination are important to understand and predict the fate of Cl_{org} . **Persistence versus lability** of the Cl_{org} is a related question that determines **bioavailability** and **residence times**. From a modelling point of view an interesting question is if Cl_{org} can be modelled as average organic matter. The indications of increasing Cl:C ratio with material age indicates that this is not the case, but data is very limited at this point.

In terms of transport, circumstantial evidence presented above highlight that the **emissions of VOCl** from various landscape compartments needs to be better quantified. Several measurements of individual compounds exist, but new techniques now make studies on the total VOCl emissions possible. Circumstantial evidence as outlined above indicates that total VOCl emissions could be a substantial part of the export of chlorine from terrestrial ecosystems, but this remains to be confirmed with additional measurements.

Most of the questions regarding the regulation of Cl^- and Cl_{org} levels and transport are hitherto not addressed and will require experimental assessments. However, other approaches can also provide valuable information. For example better understanding of chemical composition and structure of Cl_{org} would greatly facilitate interpretations regarding how chlorination and dechlorination can occur from a chemical perspective, what enzymes are likely to be involved and thereby under what conditions various processes may occur.

8.3 Cl cycling in inland waters

Soil and ground water discharge areas, e.g. wetlands, streams and lakes, are likely recipients of sub-surface sources of ^{36}Cl in humid climate zones. At present, while Cl^- measurements are common in aquatic monitoring, there is, to our knowledge, no data regarding Cl cycling of the separate Cl^- and Cl_{org} pools.

8.4 How to model Cl cycling in terrestrial environments?

As explained above, Cl cycling models need information about both Cl^- and Cl_{org} . The presently available data for both Cl^- and Cl_{org} is typically based on single measurement campaign “snap-shot” information from a limited number of environments. These data support static mass balance models only, models that are restricted by a number of assumptions, including the steady-state assumption, or that Cl_{org} behaves as organic matter. Further, model uncertainty is difficult to assess given the poor knowledge concerning spatial and temporal variability. Also, the unexpected indications that large parts of the total catchment Cl can be found in biomass show that many of our previous beliefs guiding our model assumptions need to be re-evaluated.

Thus, without data covering the temporal dimension for both Cl^- and Cl_{org} separately along with relevant environmental variables in sediment, water, soil and biomass pools, and without information of how major processes (e.g. chlorination and dechlorination) is regulated, long-term dynamic models have to be based on educated guesswork.

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