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Measurements and fluxes of volatile chlorinated organic compounds (VOCl) from natural terrestrial sources

Measurement techniques and spatio-temporal variability of flux estimates

Teresia Svensson

SVENSK KÄRNBRÄNSLEHANTERING AB

SWEDISH NUCLEAR FUEL
AND WASTE MANAGEMENT CO

Box 3091, SE-169 03 Solna
Phone +46 8 459 84 00
skb.se

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Teresia Svensson, Linköpings Universitet

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This report concerns a study which was conducted for Svensk Kärnbränslehantering AB (SKB). The conclusions and viewpoints presented in the report are those of the author. SKB may draw modified conclusions, based on additional literature sources and/or expert opinions.

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Abstract

Volatile organic compounds (VOCs) and especially chlorinated VOCs (VOCl) are regarded as environmental risk substances in water bodies due to their toxic characteristics. Even in the atmosphere they highly impact atmospheric chemistry, e.g. degrading the ozone layer. Several studies have convincingly identified a number of natural VOCl sources thereby challenging the view of VOCl as only produced by humans. Yet, fundamental knowledge is still missing concerning the emission, distribution and the natural abundance of VOCl, especially regarding the high spatial and temporal variability of emissions from terrestrial sources. In the nuclear industry, Cl-36 is a dose-dominating radionuclide in some waste, and this adds to the need to better understand the processes, transport and fate of chlorine in the biosphere. In this report 38 studies on VOCl flux measurement estimates were reviewed to summarize the current knowledge on spatio-temporal variations of different VOCl and various measurement techniques.

Chloromethane is the most studied VOCl compound and chloroform, the second most studied. A few other studies have estimated fluxes of additional VOCl such as tetrachloromethane (CCl_4), methyl chloroform (CH_3CCl_3), tetrachloroethane ($\text{C}_2\text{H}_2\text{Cl}_4$), freons (CFCs), chloroethane ($\text{C}_2\text{H}_5\text{Cl}$), bromodichloromethane (CHBrCl_2). Studies were conducted in climates and terrestrial ecosystems ranging from arctic tundra to tropical rainforest but most studies focus on the temperate climate region. Wetlands and coastal systems dominate the studied ecosystems. Flux chambers are the most common method for investigation of the soil-atmosphere exchange of VOCl, but a few studies used soil gas profiles and one the Relaxed Eddy Accumulation (REA) technique. Methodological uncertainties are mainly related to sample contamination, few replicates, chamber design, and chamber deployment (the time of measurement) effects on the soil-atmosphere exchange itself. Despite the many challenges in measuring VOCl and estimating the fluxes, a substantial part of the chlorine in terrestrial ecosystems, and especially from wetlands and coastal areas, is emitted to the atmosphere as VOCl. In inland forested ecosystems, the release of Cl to the atmosphere could be as much as 0.1 g m^{-2} , which is 40 % of the wet deposition and there are studies that suggest that freshwater wetlands are much larger source of chlorine in the atmosphere than previously understood.

Sammanfattning

Flyktiga organiska föreningar (VOC) och i synnerhet klorerade VOCs (VOCl) betraktas som miljöfarliga ämnen i vattenmiljöer på grund av sina toxiska egenskaper, men även i atmosfären eftersom de har en stor inverkan på atmosfärskemin, t ex genom att påverka ozonskiktet. Ett antal studier har hittat flera naturliga källor för VOCl och därmed förändrat synen på VOCl som endast producerade av människor. Trots det så saknas kunskaperna fortfarande om utsläpp de naturliga flödena av VOCl, särskilt när det gäller variation i tid och rum från terrestra miljöer. I kärnkraftsindustrin är Cl-36 en dosdominerande radionuklid för en del avfallströmmar. Därför behövs en bättre förståelse för omsättningen av klor i ytnära ekosystem

Klormetan är den mest studerade av VOCl och den näst mest studerade är kloroform. Några andra studier har uppskattat flöde av andra VOCl som tetraklormetan (CCl_4), metylkloroform (CH_3CCl_3), tetrakloretan ($C_2H_2Cl_4$), freoner (CFC), klorethan (C_2H_5Cl), bromodiklormetan ($CHBrCl_2$). Studier genomfördes i klimat och markbaserade ekosystem som sträcker sig från arktisk tundra till tropisk regnskog, men de flesta studier fokuserar på tempererat klimatområde. Våtmarker och kustsystem är de studerade dominerande ekosystemen. Kammare är den vanligaste metoden för att uppskatta flöden av VOCl, men det finns också några studier med koncentrationsgradienter i markprofiler, och en form av mikrometeorologimetodik. De metodologiska osäkerheterna som diskuteras kretsar i första hand kring kontamination, få replikat, design av fältmätningar och fältmätningarnas påverkan på markprocesser och därmed indirekt på flödena. Trots de många utmaningarna för att mäta VOCl och uppskatta flödena är det klart att flödet av klor till atmosfären är ett viktigt flöde i klors biogeo-kemiska cykel i terrestra ekosystem. Skogsekosystem kan avge så mycket som 0.1 g m^{-2} , vilket är 40 % av våtdepositionen av klorid och det finns studier som tyder på att våtmarker är en långt mycket större källa till klor i atmosfären än man tidigare trott.

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1 Introduction

Chlorine-containing compounds have long been considered of industrial origin. During the last decades, environmental problems such as stratospheric ozone destruction, large-area contaminations e.g. by oil spilling, or harmful bi-products of drinking water chlorination have increased attention on these compounds. In addition to the mentioned environmental problems, there has also been an increasing focus and concern about radioactive waste containing Chlorine-36. In the intermediate level, radioactive waste, Chlorine-36 is one of the dose-dominant radionuclides. Its mobility and long half-life (300 000 years) combine to make it of potential concern for long-term management of radioactive waste. Research has shown that chlorine (Cl) in the environment is more active, i.e. taking part in biological processes, than previously thought (Bastviken et al. 2013). The natural formation of chlorinated organic compounds occurs in a range of ecosystems and organisms (Gribble 2015). During the past decades it became evident that there is ubiquitous and extensive natural chlorination and dechlorination of organic matter (i.e. formation and degradation of chlorinated organic matter) in terrestrial ecosystems. In fact, the levels of chlorinated soil organic matter (Cl_{org}) typically are as large as or even exceed the levels of chloride in most soils (Svensson et al. 2007, Redon et al. 2013) and the naturally formed compounds range from stable and refractory compounds to more mobile or even volatile compounds (Gribble 2010). These findings reveal that Cl takes part in many different processes within ecosystems which demands knowledge on the processes and fluxes of Cl in the environment to make more reliable risk assessment models (Bastviken et al. 2013). The same study concluded that it is evident that chloride dominates import and export from terrestrial ecosystems while organically bound Cl and biomass Cl can dominate the standing stock Cl within terrestrial ecosystems. This indicates that the emissions of total volatile organochlorines (VOCl) could be a significant Cl export pathway from the systems.

VOCl are regarded as environmentally hazardous trace gases for two primary reasons. Firstly, VOCl in various environmental compartments are toxic (e.g. chloroform and chloromethane) and biologically active (e.g. Dobrzynska et al. 2010, Hunkeler et al. 2012). Secondly, ozone in the polar stratosphere is catalyzed by chlorine radicals derived from volatile halocarbons such as chlorofluorocarbons (CFCs), chloromethane, tetrachloromethane and other chlorinated compounds (Montzka et al. 2011).

The natural emissions of chlorinated volatile organic compounds (VOCl) have received an increased interest since the early 1970s when it was discovered that natural sources seemed to dominate the occurrence of certain VOCl in the sea (Lovelock et al. 1973) and that chlorofluorocarbons were depleting the ozone layer (Molina and Rowland 1974). However, the scientific interest in terrestrial VOCl sources came later. High concentrations of VOCl in the atmospheric air over land were documented in the late 1990s (Khalil et al. 1999). Later studies have confirmed significant VOCl formation and release from terrestrial sources in general (Laternus et al. 2002), and from the forested ecosystems in particular (Dimmer et al. 2001, Rhew et al. 2010, Redeker and Kalin 2012). Despite the fact that the terrestrial exchange of VOCl is increasingly recognized, the terrestrial exchange of VOCl and regulation is not well understood which hampers the development of improved large-scale budgets for various VOCl compounds. Ambient air concentrations of VOCl are generally in the ppt-level range, which makes analysis of the compounds challenging. In addition, when estimating VOCl budgets, one must deal with the small-scale variability of the landscape and the large-scale flux extrapolations. No single technique spans the range in temporal and spatial scales required to produce a comprehensive VOCl balance.

The first study relating to terrestrial environments was published in Transactions of the British Mycological Society in 1971 (Hutchinson 1971), where the first evidence of natural formation was done by observations of enhanced concentrations of chloromethane in headspace of wood-rotting fungi (*Phellinus pomaceus*). Despite the relatively early discovery of the natural formation of VOCl, there was a long gap in studies until 1998 when Khalil and Rasmussen made the first estimates of VOCl fluxes. Since then, the published papers on terrestrial VOCl fluxes have been slowly increasing. Over the years there has been a focus on temporal and spatial screening to identify natural sources as well as to quantify natural variations. There are studies that have been focusing on spatial variation (Redeker et al. 2002, Pickering et al. 2013, Albers et al. 2011) which raised the awareness of natural variability and uncertainties in flux estimates. There are now also studies aiming at investigating regulation factors of fluxes (e.g. role of vegetation, soil properties) as isotopes are used to determine gross fluxes (gross production and gross consumption) (e.g. Rhew and Abel 2007, Redeker and Kalin 2012).

The present report contains a synthesis of the current knowledge on VOCI measurement challenges and VOCI soil-atmosphere flux estimates and the uncertainties embedded in the conducted investigations. The synthesis is based on 38 peer-reviewed articles that have estimated VOCI soil-atmosphere (area-estimated) fluxes based on field measurements from natural terrestrial ecosystems between 1970–2018. The majority of the studies were done in the temperate region (Figure 1-1). The search for studies was done in Scopus and the studies measured field and area estimated ($\text{ng g}^{-1} \text{h}^{-1}$) net-emissions were chosen.

The report focuses on the following questions:

- Which methods for measuring VOCI fluxes exist and what are their methodological uncertainties?
- In which environments and for what land-use types have VOCI flux estimates been made and are there potentially important natural sources that were excluded?
- What is the spatio-temporal variability of VOCI fluxes (e.g. where are VOCI fluxes highest) and how representative are flux estimates?
- Are VOCI fluxes related to environmental controls (climate, soil type, land-use, etc.)?

The sensitivity and reliability of the flux estimates over various temporal and spatial scales in light of natural variability are discussed. Current knowledge gaps are identified regarding why it is hard to measure VOCI fluxes, what weakness in methodology previous studies have showed and what needs to be done in the future.

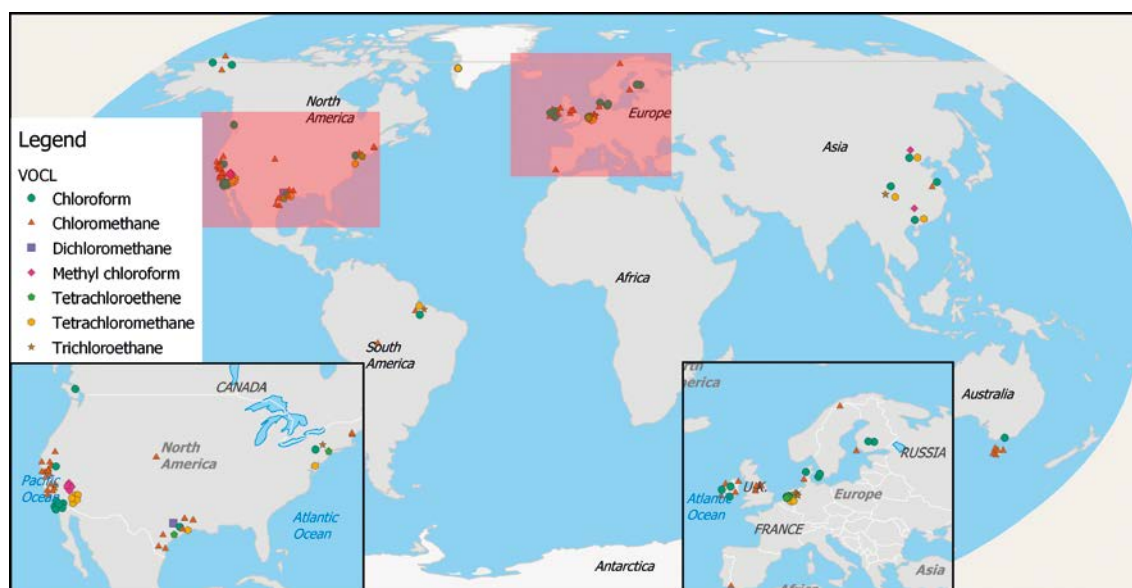


Figure 1-1. Sites with reported VOCI soil atmosphere fluxes from terrestrial ecosystems.

2 Measurement techniques

2.1 VOCl sampling methodology

Soil surface fluxes of trace gases are difficult to measure due to limitations in current techniques and methods. Upscaling of measurements is challenging due to a large spatial and temporal variability of sources and sinks. Measurements of trace gas fluxes at large spatial scales require the application of micro-meteorological measurement methods (interaction of the lower atmosphere with the surface) often in combination with simultaneous trace gas measurements. At local scale, a large number of simultaneous single chamber measurements (trace gases are trapped within an enclosure and emissions are estimated from the net change over time) and/or soil gradient methods (emissions are estimated from soil gradient gas concentrations and gas diffusion parameters in soil are needed). Non-intrusive soil emission and flux measurement techniques are common for other trace gases such as carbon dioxide and methane but at present are uncommon for VOCl. First the published literature on VOCl flux techniques will be described followed by a description of key analytical challenges.

2.2 Field measurements

Soil fluxes of trace gases have been estimated for several years, especially for greenhouse gases such as CO₂ and N₂. There are a couple of ways to measure soil-atmosphere fluxes. The most common method consists of a simple setup whereby a chamber (enclosure) placed at the soil surface captures gases. The gas concentrations are monitored, and net-flux is calculated as the change in concentrations over time.

There are two types of chambers; open (also called steady-state) and closed (also called transient or non-steady-state). For closed systems, air is circulated from a chamber to a gas analyser or an adsorbent and then returned to the chamber or air sample withdrawal from the chamber to with a canister. The flux is estimated from the rate of trace gas concentration increase inside a chamber that has been deployed on the soil surface for a short period of time. For open systems, fresh ambient air is pumped through a chamber, maintaining the ambient air concentration. The flux from the open chamber is calculated using the air flow rate and the difference in trace gas concentrations between the air entering and leaving the chamber after the air in the chamber headspace has reached a steady state. The advantage of dynamic chambers (with flow-through systems) over static chambers is that there is little chance that the chamber concentrations will be influenced by the concentration build-up in the chamber.

For VOCl measurements, only static chambers have been used at present. Dynamic chambers require continuous measurements of VOCl and these techniques still contain a number of significant limitations. Infrared Photo Acoustic Spectroscopy (PAS) is currently the only available method for continuous monitoring of VOCl. However, the detection limit is above ambient concentrations, which makes PAS not yet suitable for VOCl flux measurements.

2.2.1 Closed chamber methodology

In the closed-static chamber method, the chamber is closed and the gas concentration is allowed to increase or decrease depending on net flux. Samples are withdrawn from the inside of the chamber (chamber headspace) to estimate the concentration change per area and over time. VOCl can be sampled by pumping air through an absorbent, which acts as a chemical trap for air inside the chamber, or by whole-air sampling into e.g. steel canisters or tedlar-bags. After the chamber is closed for an assigned time period, the trapped sample or the whole-air sample is removed and the total amount of the target gas found in the sample is measured in the laboratory. The amount of VOCl divided by the soil surface area covered by the chamber and the time during which the chamber was closed, is assumed to be the rate of gas emission from the soil (e.g. Rhew et al. 2001).

While the closed-static chamber method is mostly manually operated with subsequent sampling and transport of samples for analysis at a gas chromatograph, it is a common method for analysis of trace gases such as CO₂ in situ in an automated system with a closed loop. The trace gas concentration

change is measured simultaneously as the headspace concentration changes inside the chamber. At the time of writing, no on-line analysis system has been established to measure VOCs. However, in some chambers, the VOC concentration is determined by sampling air on adsorbents from the chamber headspace through a closed sample loop (Valtananen et al. 2009). This principle is very similar to that of a closed-dynamic chamber.

The most common chamber method is the closed-static chamber method. The static chamber is used because of its higher sensitivity (can detect lower fluxes) as the VOC concentration is built up over time. However, the major disadvantage of the static chamber method is that the concentrations build up in the chamber headspace which can reduce the soil-gas concentration gradient and, thus, potentially bias flux estimates. There are discussions of the soil gradient change issue in the literature of e.g. N₂O (Rochette 2011, Venterea 2009), but no discussion of this in the literature on VOCs.

Chamber design

Several designs of flux chambers with variations in their geometry, material and sample collection technique have been proposed to collect ambient air or soil air samples. Generally, the sample design aims to minimize any interference with the production, consumption and transport of VOCs which control their soil-atmosphere exchange.

One-component chamber systems (also called “fast box” or “push in”) (Sutton et al. 2007, Rochette 2011) seal the soil surface from the surrounding air by one step. Because of their ease of use and relatively low cost compared to two/multi-component chambers, the one-component chamber system is useful for analysing spatial patterns of fluxes (Sutton et al. 2007). One-component chambers can suffer from possible measurement errors from physical soil disturbances or due to insufficient sealing. A few studies used the one-component chamber (Haselmann et al. 2000a, Moore et al. 2005, Manley et al. 2006, Albers et al. 2011) making use of both the on-surface method (chamber on top of the soil surface) and in soil method (soil chamber hammered into the ground). All of these studies indicated uncertainties with these methods regarding gas diffusion and general reliability of the flux estimate. The concerns included the physical disturbance of the soil surface (right before sampling) and the possible measurement error when trying to get a proper seal (permitting no gas diffusion on the side) on the soil surface.

Most of the published VOC flux studies used the two-component chamber design with a chamber base (a “permanent” collar in the ground) and a lid to seal the chamber base. Potential measurement errors of the chamber base installation in soil due to physical soil disturbances are commonly assumed to be negligible after a certain period of time has passed after the installation. For instance Rhew et al. (2008b) took measurements as soon as 1–2 days after chamber installation and assumed this was sufficient. Most VOC studies, however, neither report the time of insertion of the chamber collar relative to the onset of measurements nor the depth of the chamber collar. If some time has elapsed after installation, in addition to preventing soil disturbance, the chamber base also has the advantage of allowing repeated measurements to characterize temporal variations. The disadvantages of using collars are that fine-textured soils may shrink when drying and cracks may appear around the inside wall of the collar. Additionally, if the collars are inserted deeply into the soil, they will prevent or limit the growth of roots in the soil under the chamber. This could possibly result in biased measurement because of effects on the rhizosphere and, potentially, a modified soil water regime.

Studies are needed to investigate the proposed problems related to chamber installation with both portable and permanently installed chambers. There is also need to assess the effects of different chamber designs on flux and concentration estimates. Potential effects of collar insertion are not discussed in the investigated papers as with for instance CO₂ fluxes (Wang et al. 2005, Heinemeyer et al. 2011). However, we know from the literature that for instance chloromethane could be emitted from ectomycorrhizal fungi, which is a symbiosis between an extracellular fungal and a plant via its roots (Redeker et al. 2004), and there is reason to believe that collar insertion perturbs the rhizosphere and thereby affects flux measurements.

Since VOCs are usually found at very low ambient levels it is essential to assess the potential influence of sample contamination through leakage from or adsorption on chamber materials on flux estimates. Chamber materials used by the examined VOC studies, included both metal and plastics but only a few studies explored the potential effects of the chamber material on their results. For instance, Cox et al. (2004) observed an interaction of methyl halides with the chamber material Perspex (acrylic glass) where a significant release from the chamber material was found. A theo-

retical calculation led to a chamber release of $74 \text{ ng m}^{-2} \text{ h}^{-1}$ for chloromethane and of $0.5 \text{ ng m}^{-2} \text{ h}^{-1}$ for chloroform. Rhew and Abel (2007) observed a small (< 10 times the average flux) release of $80 \pm 22 \text{ ng m}^{-2} \text{ h}^{-1}$ for chloromethane for their polycarbonate (Lexan) chamber which they primarily attributed to the silicon sealant used in the chamber lid.

Geometry and size of the chambers used for measuring VOCl fluxes vary considerably. Chamber volumes range from 3 to 850 L and the soil surface area covered by the chambers varies from 0.02 m^2 (Valtanen et al. 2009) to 1 m^2 . The largest chambers are most often found when measuring in wet ecosystems such as wetlands and coastal salt marshes. Potential implications of chamber geometry for flux estimates were not further discussed in the reviewed literature apart from chamber height. The common height, usually less than 20 cm, could restrict the height of plants within the chamber (Varner et al. 1999, Rhew et al. 2008b). It is generally recommended to minimize the chamber volume to detect a concentration change at finer temporal resolution while keeping the volume sufficiently large to reduce the risk that the natural soil-gas concentration gradient is affected by a measurement induced build-up of VOCl inside the chamber (Davidson et al. 2002). Studies on other trace gases have reported so called “edge effects” of *small* collars because the insertion of a collar leads to compaction of the soil in the chamber, which is in turn likely to affect gas exchange ratios (Butterbach-Bahl et al. 2011). The relative error in flux estimates associated with a poor chamber seal, caused e.g. by roots or stones, increases with a decreasing chamber diameter since the flux is proportional to the source area while the risk of gas leaks is proportional to the perimeter (Butterbach-Bahl et al. 2011, Healy et al. 1996).

The selection of the chamber size appears to be related to the study design. If the aim is to do transect studies (gradient studies) to assess the range of variation of VOCl fluxes and to identify potential controlling variables, small chambers are preferable, but not as small as it will affect the reliability of the fluxes and possible vegetation influences. Rochette and Eriksen-Hamel (2008) used a chamber area/perimeter ratio to evaluate the effect of chamber size on the accuracy of N_2O flux measurements, but no such information exists for VOCl flux measurements.

If gas concentrations in the chamber headspace change after placing a chamber over a soil surface then the initial concentration gradient within the soil profile will also change (Davidson et al. 2002). As concentrations in the chamber increase, the diffusion gradient from soil decreases and the flux is likely to decline. This may lead to an underestimation of the flux. Therefore, many of the published studies have installed a venting tube connecting the chamber headspace to the atmosphere. If this is done correctly, there will be no contamination of the ambient air into the chamber air. Out of the published articles, a few have used (i.e. mentioned in the paper) a venting tube (Rhew et al. 2000, Cox et al. 2004). However, there is no discussion of the possible uncertainties of using a venting tube.

The errors discussed regarding chamber deployment time mostly concern chamber temperature (Butterbach-Bahl et al. 2011). Chamber temperatures can change considerably during the course of a day which is related to the time taken for deployment. The extent of temperature change partly depends on the chamber material (aluminium, acrylic glass). The majority of reviewed studies made use of transparent chamber materials and some of these measured the headspace temperature at the end of measurement period (e.g. Rhew et al. 2010; Khan et al. 2011). Dimmer et al. (2001) observed an increase of $+5$ and up to $+15$ °C in the chamber during the deployment time though the ambient temperature change was not reported. The large change in chamber temperature led to a relatively smaller change, increase by $+0.2$ °C, in soil temperature, which probably does not influence soil gas exchange. Transparent chambers are commonly used by studies focussing on plant activity related VOCl emissions (Yokouchi et al. 2002) and on chloromethane fluxes from wetlands (Varner et al. 1999). Rochette and Eriksen-Hamel (2008) suggests insulating chambers from temperature related effects by using shaded, opaque or reflective materials. In some cases, ice water was flushed on a coil inside the chambers during measurements to cool them (Rhew et al. 2008a, Redeker et al. 2003). Rhew et al. (2008b) found that transparent chambers without cooling had significant higher chloromethane and tetrachloromethane emissions in ecosystems in California compared to transparent chambers that were cooled. Emissions measured in dark chambers were not significantly different compared to emissions measured in cooled transparent chambers. To keep track of possible temperature-induced effects on VOCl fluxes, headspace air temperature and soil temperature should be monitored, and chamber deployment time should be kept as short as possible. If there are reasons to believe that the VOCl gas exchange is related to processes controlled by radiation (such as vegetation activity), transparent chamber materials should be used in combination with a temperature control system.

To calculate the flux from the temporal change in gas concentrations in the chamber headspace, a range of assumptions are taken depending on the flux estimation strategy. A monotonic increase in chamber headspace concentration is a widely taken assumption for trace gases. It is additionally assumed that the rate of change is constant over relatively short periods. Some studies however reported non-linear concentration changes resulting in an underestimation of the flux (Healy et al. 1996). However, an optimal deployment period needs to be investigated for each compound testing the assumption that the headspace concentration varies linearly over short time periods to ensure that linear regression can be used to estimate fluxes (Pickering et al. 2013).

Closed chambers, often chosen for their low cost, well defined footprint, and operational simplicity, have proven helpful for process-level VOCl studies and analyses of soil fluxes (e.g. Rhew et al. 2008b). However, their low sampling frequency (semi-weekly to semi-monthly in most long-term studies) is not sufficient to reliably assess the occurrence and magnitude of events and too labour intensive for studying VOCl temporal variability. In addition, chambers typically represent an area $< 1 \text{ m}^2$, again making the method laborious for attempts to cover large surfaces. In contrast, micrometeorological methods applied to trace gases can be used to estimate gas exchange over a larger surface area, and to capture higher temporal variability. Micrometeorological methods yield fluxes that are spatially integrated over large areas ($> 100 \text{ m}^2$), and continuous sampling is possible (Denmead and Raupach 1993). Micrometeorological techniques do not interfere with the soil or disturb the flux of the gas. However, there are special constraints for the development of VOCl gas detection caused by the low ambient concentrations (Pickering et al. 2013). A single previous publication mentioned the application of a micrometeorological system; a REA system, to VOCl fluxes from a boreal fen (Haapanala et al. 2006) but did not succeed in detecting any VOCl fluxes, probably due to not reaching the necessary detection levels with on-line real-time analysers.

Sampling

A homogenous gas concentration inside the chamber is needed for representative sampling. For this reason, several studies on VOCl enhanced air mixing inside chambers with ventilation fans. For some trace gases that are measured in small chambers, the air mixing induced by the internal air flow in the chamber is regarded as sufficient. In larger chambers, which contain a lot of vegetation, however, the use of a fan is often considered necessary (Livingston and Hutchinson 1995).

The time for chamber headspace sampling varies from 10 to 120 min (Albers et al. 2011, Hardacre et al. 2009). Longer sampling times increase the risk of measurement errors caused by temporal changes in temperature, gas concentrations and gradients.

Fluxes are measured by determining the rate of change of trace gas concentration in the chamber headspace. The change rate is mathematically derived by fitting linear regression models to observed time series of headspace gas concentrations (Levy et al. 2011). In most cases, VOCl concentrations are determined by physically removing a gas sample from the chamber headspace for analysis in the laboratory (e.g. Albers et al. 2011). It should be noted that each time a headspace gas sample is removed from the chamber, air outside the chamber flows into the chamber through a vent tube. This results in a dilution of the analyte in the chamber headspace. The error associated with this dilution effect depends on both the sample volume withdrawn and chamber size. In a few of the VOCl studies the air was flushed through an adsorbent where the VOCls are adsorbed and the VOCl-free air was returned to the chamber in a closed-loop (Valtanen et al. 2009).

2.2.2 Soil-air gradient and micrometeorological methods

The soil gradient method is based on Fick's first law of diffusion. In general, the theory is that VOCl compounds move from a high concentration area to the low concentration area. Thus, VOCl flux can be calculated based on concentration measurements at multiple soil depths. A major disadvantage of the soil-air gradient method is related to the soil air concentration measurement and soil depths. The measurements need to be done at a resolution to enable capture of the soil gradient. The calculation of soil-surface fluxes on the basis of soil gas concentrations also requires the measurement or estimation of soil porosity and the gas diffusion coefficient (Haselmann et al. 2000a).

Micrometeorological methods do not interfere with the soil and can potentially cover larger surface areas with high precision. The advantage of micrometeorological methods is that the total ecosystem

gas flux is measured. There is only one paper that reported a micrometeorological application to VOCl. A micrometeorological method used for other volatile organic compounds (VOCs), referred to as the Relaxed Eddy Accumulation (REA), was undertaken where the concentration of compounds was accumulated and sampled in the updraft and downdraft of air. The flux was estimated as the difference between the two samples sampled on adsorbents instead of on-line instrumentation (Haapanala et al. 2006). However, the fluxes of VOCl were unfortunately below detection limit.

2.2.3 VOCl sample analysis

Most challenges related with estimating VOCl fluxes concern reliable sampling at low concentrations. The concentrations of VOCl are in the lower ppt range. This means they are much lower than for other gases emitted from soils, for example carbon dioxide that exists at levels of several ppms. Actually, the precision and analytical detection limits are nowadays low, and this is not the largest challenge (Dobrzynska et al. 2010). The methodological challenge is indeed 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 are additional difficulties related to sampling methodology in the field (capturing the VOCl soil-atmosphere exchange) and estimation of VOCl fluxes (calculating the flux from the observed soil-atmosphere exchange).

There are a number of papers that have determined VOCl in air samples including a number of preparation steps and analytical methods (Ramírez et al. 2010, Dewulf et al. 2006, Demeestere et al. 2007, Dobrzynska et al. 2010). There is a risk of both loss of analytes and contamination during sampling, storage, and analysis of VOCl. That is because the concentrations of VOCl in the air are so low and special sample treatment needs to be done. Sample pre-concentration is needed to be able to detect the compounds of interest. There are two pre-concentration methods commonly used; use of adsorbents or cryogenic concentration. With adsorbents, the VOCl in air are adsorbed onto a sorbent column followed by thermal desorption with subsequent analysis using gas chromatography (GC) (Hoekstra et al. 2001, Valtanen et al. 2009) or the air sample is concentrated in a cryogenic sample loop followed by GC analysis (Rhew et al. 2010). The use of adsorbents has advantages as the pre-concentration is done already in the field and is less laborious than sampling whole-air samples. The adsorption and desorption efficiency of the adsorbents are not always 100 % and could vary for different compounds, which can be problematic especially when dealing with samples of low concentrations. There is also a risk of loss of the adsorbed sample during storage. Cryogenic trapping, on the other hand, has the disadvantages of being sensitive to moisture condensation in the trap. Whole-air sampling in canisters has been successfully performed by many researchers (Rhew et al. 2010, Redeker et al. 2003) which means that the pre-concentration step is done at the laboratory prior to the fieldwork (Wang and Austin 2006). The disadvantages of using canisters is that they take larger space than adsorbents while transporting to the laboratory. Overall, most studies used canister sampling despite the disadvantages in transportation from remote field stations. A more recent technique, including easy and fast sample preparation, is known as solid phase microextraction (SPME) and has been found useful for the determination of volatiles in air (Dobrzynska et al. 2010). This technique is based on the absorption of VOCl onto 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. Only one study examined in this report used SPME (Yassaa et al. 2009).

All of the methods listed above made use of GC with various detection methods. The two methods that provide the lowest detection limits are halide-specific detectors (e.g. electron capture detector; ECD) and mass spectrometers (MS). The advantage of halide specific detectors is they are not only very sensitive but are also specific for halide compounds. Therefore, their inability to detect and quantify non-halogen compounds can also be a disadvantage if these are also of interest in a particular study. Mass spectrometers, on the other hand, provide additional confirmation of the presence of a compound through its ionization pattern. It is therefore desirable when a variety of compounds need to be identified and quantified. When undertaking both methods, it is crucial that the samples are not contaminated or that the air sample interacts with the container material or is transformed during storage. Surprisingly, few studies have reported the uncertainties in sample collection and the eventual effects of storage on the samples and results (Pickering et al. 2013).

3 Origin and distribution of natural VOCs in terrestrial ecosystems

3.1 Natural formation processes

3.1.1 Chloromethane (CH₃Cl, methyl chloride)

The simplest volatile organochlorine compound is chloromethane, also called methyl chloride (CH₃Cl). Chloromethane is the most studied VOC that is known to be naturally produced in terrestrial environments. Since the beginning of the 70s, it has been shown that chloromethane is produced by a large variety of organisms other than fungi (Watling and Harper 1998, Moore et al. 2005), such as potato tubers, tropical plants such as tropical ferns (Yokouchi et al. 2002, Yokouchi et al. 2000, Saito et al. 2013, Saito et al. 2008, Saini et al. 1995), rice plants (Redeker and Cicerone 2004), salt tolerant plants (halophytic plants) (Derendorp et al. 2012) and fungi leaf cutter ants (Mead et al. 2008).

Hutchinson published the first observations of natural formation of chloromethane in 1971 after observing an enrichment of chloromethane of incubated fungi. More evidence of natural formation of chloromethane among many types of fungi was added throughout the years (Harper 1985, Watling and Harper 1998, White 1982). For instance, White (1982) labelled fungal growth substrate and found isotope labelled chloromethane in the headspace above cultures. Harper conclusively demonstrated that common wood rotting fungi were extremely efficient in methylating chloride even with rather low chloride concentrations (Harper 1985).

The best-known biochemical process behind chloromethane formation is methylation of chloride (see the review by Urhahn and Ballschmiter 1998). After the first reports on natural formation of chloromethane by organisms in 1971 (Hutchinson 1971), the first report on chloromethane synthesis was done by Wuosmaa and Hager (1990). They detected methyl transferase activity in white rot fungi (*Phellinus promaceu*) and ice plants (*Mesembryanthemum crystallium*) and found that enzyme activity is necessary for chloromethane formation. The methylation was suggested to originate from the S-adenosyl-L-methionine (SAM) methyl transferase in wood-rot fungi. This was confirmed by Ni and Hager (1999) as they isolated the methyl transferase enzyme and investigated the correlation between methyl transferase and the release of methyl chloride in in vivo experiments. It has been suggested that methyl transferase is part of the plant regulation of cell concentrations of chloride as the enzyme is regarded as a salt tolerant enzyme where activity remains high at high chloride concentrations (Ni and Hager 1999). There are a number of papers discussing salt-tolerant plants and bacteria and their biosynthetic ways of dealing with the excess of chloride and the possible result of chloromethane emissions (e.g. Ni and Hager 1999).

In the beginning of the 00s, it was found that chloromethane is formed by abiotic processes in plant and soil systems through chemical reactions (Hamilton et al. 2003, Yassaa et al. 2009, Wishkerman et al. 2008, Keppler et al. 2000). Keppler et al. (2000) suggested an abiotic pathway of oxidation–reduction reactions in an organic rich medium. The mechanism involves the oxidation of organic matter at the expense of a cation, notably Fe³⁺, a halide ion being methylated in the process. Another abiotic formation process revolves around degradation of plant material (Derendorp et al. 2012). It has been suggested that chloromethane can be formed through a reaction between pectin methoxyl groups and chloride ions (in leaf litter) (Hamilton et al. 2003). Both lignin and pectin from the plant contain methoxyl groups. Hamilton et al. (2003) observed both significant release of chloromethane from i) senescent leaves and dead plant material at temperatures of 30–50 degrees, and ii) heating of leaves and wood material up to 225 to 350 degrees. In both cases, the release was higher at higher temperatures. At only ambient temperature, pectin methoxyl groups are able to react with chloride ions. The formation of larger organohalogenes has been demonstrated by Myneni (2002). A study Redeker and Kalin (2012) suggested that the major pathway for chloromethane formation in Irish temperate forest soils is due to biotic formation as the abiotic formation was estimated to about 10 % of the biological formation rate.

Chloromethane has several sources in terrestrial ecosystems and natural formation seems to be abundant. For instance, in forests, the major focus of studies has been on fungi and a few studies on soil and the plants and plant litter. The top-soil layer of forest soils is suggested to be one of the key parts of forest ecosystems where chloromethane is produced as it is where chloromethane forming organisms,

such as wood-rot fungi and ectomycorrhizal fungi, reside (Watling and Harper 1998, Redeker et al. 2004, Redeker and Kalin 2012). In addition, it has been shown that litter also plays an important role as an emitter of methyl chloride (Hamilton et al. 2003, Blei and Heal 2011). However, in measurements over a seasonal period, the litter more often showed an uptake of chloromethane than a release, which suggests bi-directional fluxes. Plants are also known to show capacity to produce chloromethane (Saini et al. 1995), however the source strength are difficult to evaluate due to a limited number of studies (Yokouchi et al. 2002, Saito et al. 2008).

Studies at a larger scale include detection of elevated concentrations of chloromethane at events of biomass burning (Lobert et al. 1999) and volcanic eruptions suggesting that chloromethanes are formed abiotically at high temperatures. This was also confirmed in studies on plant material by Hamilton et al. (2003) and Derendorp et al. (2012).

3.1.2 Trichloromethane (CHCl₃, chloroform)

Chloroform formation is widespread in terrestrial environments. The conducted studies show that chloroform is emitted from soils, termite mounds, tropical soil-plant systems, forests, leaf litter and wetlands (Hoekstra et al. 1998b, Laturnus et al. 1995, Khalil et al. 1990, Hellen et al. 2006, Albers et al. 2010, Cox et al. 2004, Haselmann et al. 2000a). It also appears that chloroform is formed during biomass burning, but its relative source to the global burden is small (Rudolph et al. 1995, Andreae et al. 1996).

The second most studied VOC is chloroform. In contrast to the laboratory-based chloromethane studies, natural chloroform formation was discovered through the detection of elevated concentrations of chloroform in the field (Frank et al. 1989, Hoekstra et al. 1998a). The early observations were later confirmed, and today it is well established that chloroform is formed naturally in terrestrial environments (Hoekstra et al. 2001, Svensson et al. 2007, Laturnus et al. 2000). The studies on natural chloroform formation have been conducted in the field but also in laboratory experiments on formation by specific fungi (Hoekstra et al. 1998b, Haselmann et al. 2000a).

It is well established that chloroform is naturally formed, but the formation processes and underlying biochemical mechanisms are still under debate (Breider and Albers 2015). There is evidence that chloroform is formed as a by-product when extra-enzymatically formed reactive chlorine reacts with complex organic compounds (Hoekstra et al. 1998a, Breider and Albers 2015). The proposed process is thus biotically induced through exo-enzymatic chlorination of complex molecules, followed by chemically-driven reactions where a tri-chlorinated end-carbon is decoupled from larger molecules through hydrolyses. It is well known that a large number of soil organisms are able to produce enzymes that are able to catalyze the formation of reactive chlorine (Bengtson et al. 2009, Bengtson et al. 2013). It remains to be shown, however, if this process is the cause of chloroform formation in the field (Breider and Albers 2015). An abiotic pathway of chloroform formation has been suggested by oxidation of organic matter by iron (III) and hydrogen peroxide in the presence of chloride (Huber et al. 2009).

3.1.3 Tetrachloromethane (CCl₄, carbon tetrachloride)

Tetrachloromethane natural formation in nature is debated. Tetrachloromethane has been found at low levels in forest soils (Wang et al. 2007, Doležalová et al. 2011, Haselmann et al. 2000a). Haselmann et al. (2000a) detected tetrachloromethane in soil air, but the concentrations were very similar to the ambient air and therefore they did not consider soil as a source, which was confirmed in their laboratory experiments (Haselmann et al. 2000a, b). Happell et al. (2014) also found an uptake in soil. Based on current studies there is no accepted theory on natural production in soil as the concentrations are very low (Laturnus et al. 2005). It is suggested that the observed emission is due to an equilibrium with atmospheric concentrations of anthropogenic origin. Other suggested sources are sediments (Laturnus et al. 2005), black shales and volcanos (Isidorov 1990) and, potentially, biomass burning (Rudolph et al. 1995), and terrestrial plants (Gribble 2010). Isidorov and Jdanova (2002) found a release of tetrachloromethane from leaves and leaf litter from deciduous trees such as oak, aspen, poplar.

3.1.4 Methyl chloroform (CH₃CCl₃, 1,1,1-trichloroethane)

Terrestrial ecosystems and biomass burning have long been discussed as sources of methyl chloroform (Laternus et al. 2005). Methyl chloroform has been detected in soil, but the formation processes have not been confirmed. There have been observations of a terrestrial uptake in aerobic soils (Happell and Roche 2003).

3.1.5 Additional VOCs

There are few studies on the natural formation of additional VOCs (Keppler et al. 2002, Keppler et al. 2006). Chloroethyne and chloroethene were found to be emitted from deciduous forest, peatland, coastal salt marshes. Biomass burning are a source of dichloromethane, but not for the other VOCs to a much lower degree (Rudolph et al. 1995). Hoekstra et al. (2001) reported net emissions of tetrachloroethane, however there are no additional studies reporting net emissions (Appendix 5). Chloroethane was shown to have a net emission (Redeker et al. 2003), but there have been no additional studies of this VOC (Appendix 6). It has been conclusively shown that dichloromethane is produced by macroalgae in oceans (Keene et al. 1999), but it is still debated whether it is produced in terrestrial environments. Trajectory analyses of air-concentrations suggest that dichloromethane is emitted from near-coastal wetlands (Cox et al. 2004). However, the trajectory analysis by Cox et al. (2003) did not conclusively show that dichloromethane has a terrestrial source as the data cannot distinguish between urban and coastal sources and/or the coastal sources. There is also evidence suggesting that dichloromethane is formed during biomass burning and during volcanic eruptions (Lobert et al. 1999, Simmonds et al. 2006, Rudolph et al. 1995, Jordan et al. 2000).

Emissions of dichloromethane have been observed in native Tussock grass, soil with leaf litter under melaleuca scrub canopies, perennial ryegrass improved pasture, and soil with leaf litter under a mixed native forest canopies in Tasmania, Australia (Cox et al. 2004) (Appendix 7). Dichloromethane was also observed in rice paddies in Texas, USA but the emissions were not statistically confirmed (Redeker et al. 2003).

Khalil and Rasmussen (2000) found net uptake of CFCs in various soils (Appendix 8). A net emission was reported at one site in a rain forest in Brazil and at one site in Greenland. There are no reports on natural formation processes on CFCs and no evidence of emissions of methyl chloroform by biomass burning (Rudolph et al. 1995).

3.2 Fluxes of natural VOCs across climates and ecosystems

3.2.1 Chloromethane (CH₃Cl, methyl chloride)

Of the investigated 38 studies, 26 analysed chloromethane fluxes. Emissions of chloromethane were observed in all climate regions and the fluxes varied significantly (Figure 3-1, Appendix 1). Both emission and uptake were observed although large variations were shown at individual sites (Dimmer et al. 2001, Khan et al. 2013, Cox et al. 2004). Most studies were performed in wetlands including both freshwater wetlands and salt marshes in the temperate region. Among the studied sites, most wetlands showed a net emission of chloromethane (Dimmer et al. 2001, Varner et al. 1999b). Arctic tundra, on the other hand, showed both a large net uptake and a net emission (Teh et al. 2009). Grasslands varied significantly and have not been shown to be a clear net emission source. The single study from a temperate forest showed a significant net emission (Redeker and Kalin 2012). Besides the variation of chloromethane fluxes among different sites, there were also many sites showing both net emission and net uptake (e.g. Wang et al. 2006, Rhew and Abel 2007).

3.2.2 Chloroform (CHCl₃, chloroform)

The first measurements of chloroform concentrations in soil air suggested 4–36 times concentrations compared to ambient air (Frank et al. 1989). The observed pattern was also observed in a study in the Netherlands where Hoekstra et al. (2001) found higher concentrations of chloroform in soil air (25 ng L⁻¹) than in ambient air (< 0.1 ng L⁻¹). A study of sandy soils in a coniferous forest in Denmark suggested a considerable spatial variation with reported concentrations that spanned from below 5 ppbv to above 400 ppbv in samples less than 10 m apart (Albers et al. 2011).

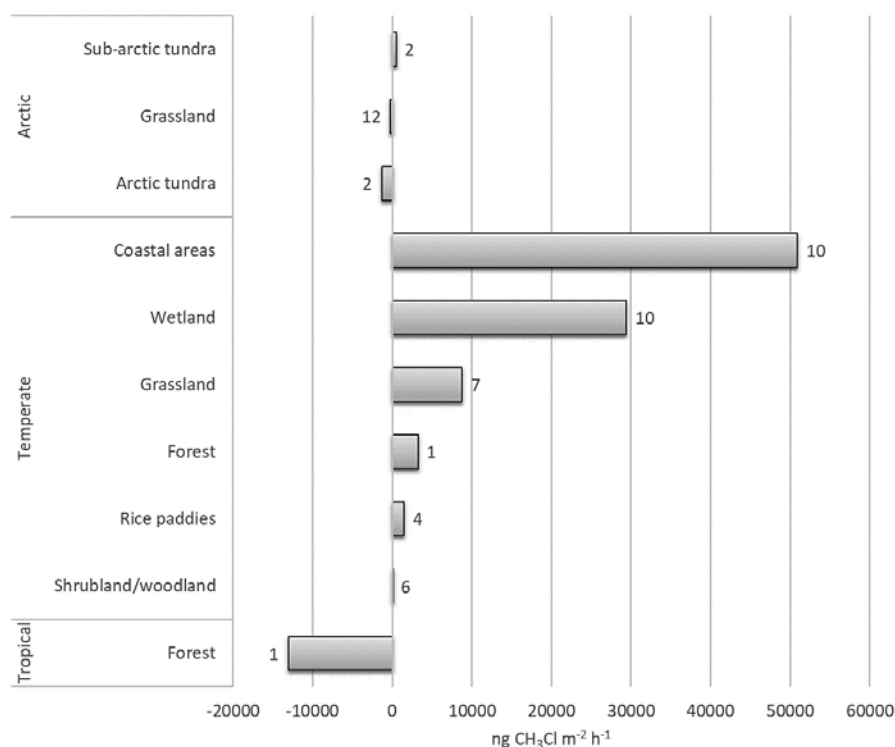


Figure 3-1. Reported average chloromethane fluxes from terrestrial ecosystems for each reported site. Numbers on each bar represent the number of studies (locations) included in the estimated average. For more information see Appendix 1.

In two studies that focussed on the vertical distribution in a soil profile (Albers et al. 2010, 2008, Hoekstra et al. 2001, Haselmann et al. 2000a), among all the investigated sites in the coniferous forest soils, the chloroform concentrations increased down to 0.5–1 m soil depth. Haselmann et al. (2000a) found the highest concentrations in the litter layer and at the B-horizon (40 cm depth). Laternus et al. (2000) and Hoekstra et al. (2001) found a similar depth variation with increasing concentrations to approximately 40 cm and then decreasing concentrations down to a soil depth of 8 m. Albers et al. (2010) also found similar patterns at four forest soil profiles down to 4–6 m soil depth. The same group also found that the vertical profiles can shift among seasons, with more pronounced vertical variation during summer than during winter.

Of the 38 selected studies, 17 estimated chloroform fluxes (Figure 3-2). Most of the studies were conducted in temperate regions (23 °C–66 °C) where emissions were found in forest, wetland, shrubland, grassland, coastal ecosystems and agricultural areas. The highest emissions in temperate climate regions were measured in a forested bog in Ireland and a coastal salt marsh in China (Dimmer et al. 2001, Wang et al. 2007), but the variation is large. Dimmer et al. (2001) reported a large variation in conifer forest bog at 4 km distance with an average of 251 ng m⁻² h⁻¹ at one site and 1451 ng m⁻² h⁻¹ at the other site. Albers et al. (2010) reported a variation that was even higher with an average of 276 ng m⁻² h⁻¹ at the low emission spot and 2676 ng m⁻² h⁻¹ at the high emission spot. Wetlands and forests seems to show very high fluxes (Dimmer et al. 2001, Varner et al. 1999, Hardacre et al. 2009), although Hellén et al. (2006) found no emissions in a boreal fen in Finland. Hoekstra et al. (2001) investigated fluxes from forest soils and sand dunes in the Netherlands but reported emissions were in the lower range compared to the other investigated ecosystems. Some studies reported uptake of chloroform ranging from less than 20 ng m⁻² h⁻¹ to more than 30 000 ng m⁻² h⁻¹ (Pickering et al. 2013, Rhew et al. 2008a, Khan et al. 2011, Wang et al. 2007). There are a few studies from the arctic areas and almost all studied sites showed chloroform emissions. The Alaskan tundra emitted chloroform up to over 1 200 ng m⁻² h⁻¹ with a mean flux of 236 ng m⁻² h⁻¹ (Rhew et al. 2008b). Khalil and Rasmussen (2000) performed two measurements on Greenland and found no emissions at a grass site and as high as 1458 ng m⁻² h⁻¹ from a mossy site. There are some studies from forest soils and all of the investigated studies showed emissions of chloroform, except for one study at a clear-cut site that observed an uptake (Pickering et al. 2013). One of the studies showed emissions of both chloroform and chloromethane (Dimmer et al. 2001).

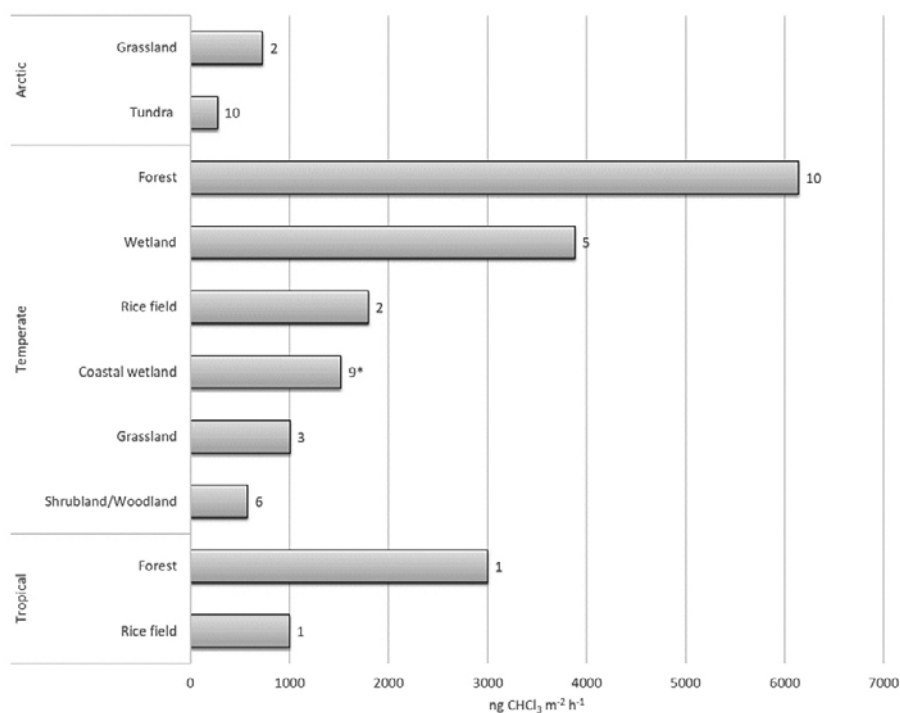


Figure 3-2. Reported average chloroform fluxes from terrestrial ecosystems for each site reported. Numbers on each bar represent the number of studies (locations) included in the estimated average. For more information see Appendix 2.

Most flux estimates were based on a few measurements varying both in time and space. The replicates on a spatial scale are less than 20 and most of the measurements at the sites were done with less than three replicates. The number of sampling occasions to observe diurnal, seasonal variations are mostly less than 10. For chloroform, Dimmer et al. (2001) studied the diurnal variation and it seemed to be more evident for chloromethane than for chloroform and for a wetland site than in a coniferous forest. For chloroform, there was no obvious diurnal variation (Dimmer et al. 2001). On a seasonal scale, Albers et al. (2011) found higher fluxes during summer (June) than during winter (March).

Hellén et al. (2006) measured chloroform fluxes for forest soil under snow cover, but did not find any fluxes. However, at another site, Helmig (2009) observed increasing snow pack chloroform concentrations closer to the soil surface. The estimated emissions are though at a lower range than of all the published studies, with an average of 22 (2–42) ng h⁻¹ m⁻².

3.2.3 Tetrachloromethane (CCl₄, carbon tetrachloride)

There is scattered information about tetrachloromethane soil fluxes (Figure 3-3). Five studies reported emissions of tetrachloromethane. Khalil and Rasmussen (2000) observed a net emission in rice fields but not in other agricultural areas. Hoekstra et al. (2001) found net emissions of tetrachloromethane at two sites of dunes of Wassenaar in the Netherlands. The emissions found by Hoekstra et al. at a sandy site were in the same range as found at a salt marsh site by Rhew et al. (2008b). However, the reports on tetrachloromethane formation are few and quite uncertain as the emissions are relatively low and the soil air concentrations are close to the observed ambient air concentrations. As such, it is discussed whether the fluxes might be a result of release of previously adsorbed compounds. For instance, Wang et al. (2006) found very low fluxes, both negative and positive, from salt marshes in Jiangsu Province, China, with an unusually high ambient air concentration. Khalil and Rasmussen (2000) also found low and varying fluxes from agricultural areas without detecting any corresponding ambient air concentrations.

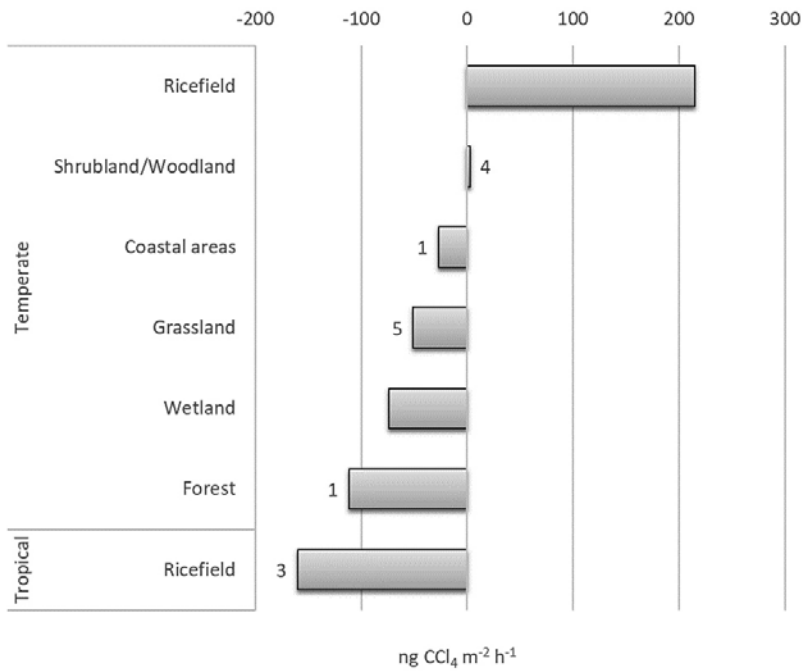


Figure 3-3. Reported average tetrachloromethane fluxes from terrestrial ecosystems for each reported site. Numbers on each bar represent the number of studies (locations) included in the estimated average. For more information see Appendix 3.

3.2.4 Methyl chloroform (CH₃CCl₃, 1,1,1-trichloroethane)

There are a few studies reporting emissions of methyl chloroform (Figure 3-4) and both net emission and net uptake have been observed in salt marshes, shrublands, rice fields and forests (Rhew et al. 2008a, Hoekstra et al. 2001, Khalil et al. 1998, Wang et al. 2007, Khalil and Rasmussen 2000).

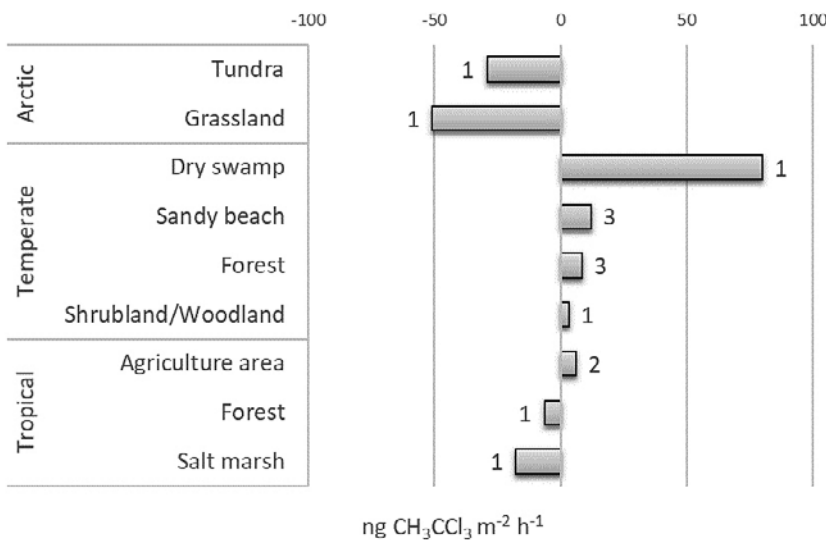


Figure 3-4. Reported average methyl chloroform fluxes from terrestrial ecosystems for each reported site. Numbers on each bar represent the number of studies (locations) included in the estimated average. For more information see Appendix 4.

3.2.5 Estimated total Cl emission

VOCl emissions have been noted as potentially important processes in the Cl cycling in soil. Graedel and Keene (1996) connected VOCl fluxes and global Cl cycling for the first time. This was followed by Wintertons (2000) thorough review on the Cl cycle. In soil, the VOCl flux has been described as the least well-understood part of the Cl cycle (Öberg 1998). Prior studies on VOCl have focused on the emissions of the specific VOCl and not the emissions of total Cl from terrestrial ecosystems. There has been one attempt to estimate the total Cl volatilization, based on secondary data, in a budget of a forested ecosystem (Öberg et al. 2005). Based on that study, it was concluded that volatilization of total Cl, in a temperate forest, was significantly contributing to Cl losses from the soil. The estimated loss by volatilization, approximately $100 \text{ mg Cl m}^{-2} \text{ yr}^{-1}$, was estimated to be similar to the loss of Cl through the leaching of organic Cl from top-soil to deeper soil, $200 \text{ mg Cl m}^{-2} \text{ yr}^{-1}$. An estimate was also calculated based on a laboratory study, using ^{36}Cl as a tracer to investigate chlorination processes in soil. It stated that approximately $200 \text{ mg Cl m}^{-2} \text{ yr}^{-1}$ was emitted from forest soil (Bastviken et al. 2009). That could be compared to the wet deposition of chloride in the same area, which is $400 \text{ mg Cl m}^{-2} \text{ yr}^{-1}$. In that perspective VOCl are without doubt important for the Cl cycling in soils. However, the estimates from the laboratory study should be treated with caution as they might overestimate the emissions due to an acceleration of the release processes caused by the room temperature soil incubations.

It is evident from the reviewed papers that Cl can be emitted from terrestrial ecosystems and especially chloromethane and chloroform from particular ecosystems. For chloromethane, coastal areas and wetlands dominate in number of conducted studies and they contain the highest reported emissions reaching as large as $600 \text{ mg Cl m}^{-2} \text{ yr}^{-1}$ (Figure 3-5). For chloroform, forests and wetlands have the highest number of studies and also the highest reported emissions (Figure 3-6). Among all the reviewed studies, the net emission varies significantly. The highest net emission that has been observed was chloromethane measured in coastal areas, which reached as high as almost $50\,000 \text{ mg Cl m}^{-2} \text{ yr}^{-1}$. Coastal ecosystems and wetlands have the highest recorded emissions of Cl for many VOCl, but also other ecosystems are important for the Cl fluxes such as wetlands. Very high global fluxes, $740\text{--}1\,100 \text{ Gg y}^{-1}$ was estimated for freshwater wetlands although the authors stress the uncertainties partly associated with the strong association to vegetation *Calluna vulgaris* as well as in uncertainties in global land cover area estimates (Hardacre and Heal 2013). Much lower estimates of the relative contribution of chloromethane from temperate salt marshes were $< 1\%$ global chloromethane budget (Blei et al. 2010).

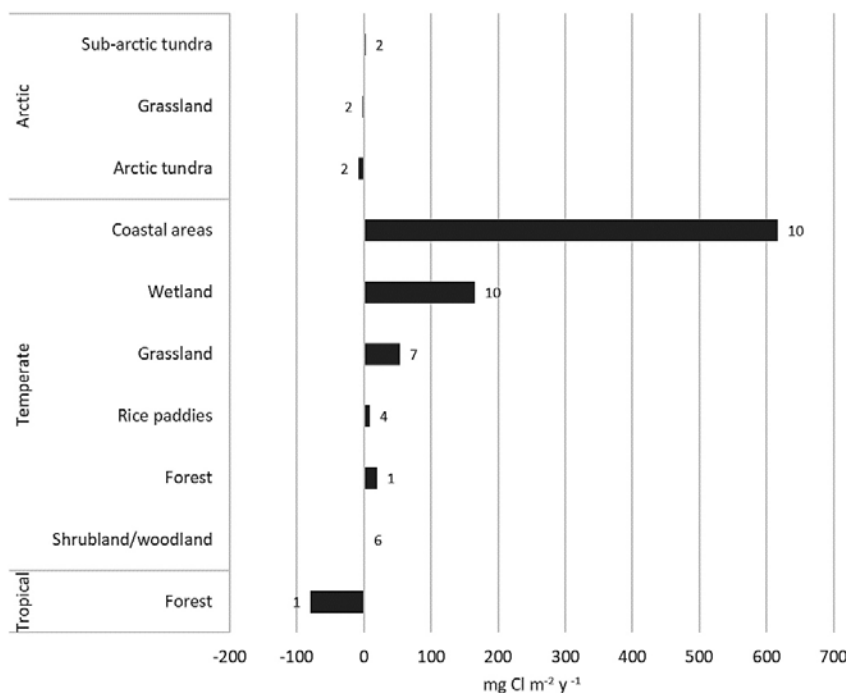


Figure 3-5. Estimated mean Cl ($\text{mg Cl m}^{-2} \text{ yr}^{-1}$) fluxes originating from chloromethane from the various reported ecosystems.

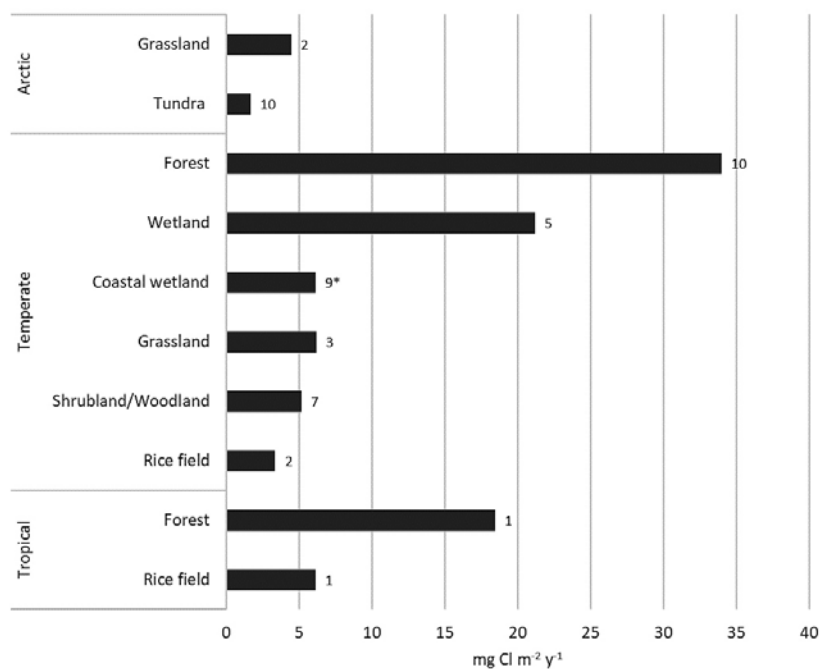


Figure 3-6. Estimated mean Cl (mg Cl m⁻² y⁻¹) fluxes originating from chloroform from the various reported ecosystems.

3.3 Environmental controls

VOCl soil fluxes are a result of the interactions between physical soil factors and biological processes responsible for the production and consumption of VOCl. Production and consumption of VOCl in soils are believed to be a result of both biotic and abiotic processes (Breider and Albers 2015, Laturus et al. 2005), but the size of the fluxes between the soil and the atmosphere also depend on physical soil factors. Soil temperature and soil water content are the most commonly studied factors, which could directly affect their production or consumption in soils. Soil porosity or air-filled spaces in soil and soil water content, are physical factors that could change the gas transport thereby influence how VOCl can diffuse and move in soils. The current knowledge on the interactions between the controlling physical factors and the biological processes responsible for VOCl production and consumption in soils will be described in this section.

Research has been conducted during the past ten years to quantify VOCl emission rates from terrestrial sources and it has been demonstrated that gas emission rates from some areas most likely have a diurnal pattern (Rhew et al. 2000, Rhew et al. 2002, Valtanen et al. 2009, Albers et al. 2011, Hardacre et al. 2009). Daytime fluxes of chloromethane and chloroform were much higher than the night time fluxes in a coastal salt marsh (Dimmer et al. 2001), but no significant pattern was found in a coniferous forest soil. This is consistent with a diurnal study of chloromethane in a sub-arctic mire (Hardacre et al. 2009) and a study at a coastal meadow (Valtanen et al. 2009). The common belief is that VOCl formation takes place in shallow soils, so changes in soil surface temperature could influence the fluxes. When analysing the fluxes from wetlands or partly flooded areas, temperature effects become an issue as the measurements are often done with transparent chambers to let the photosynthetically active radiation through the chamber walls for the plants. Dimmer et al. (2001), Hardacre et al. (2009) and Valtanen et al. (2009) all used transparent chambers. Dimmer et al. (2001) discussed the temperature increase inside the chambers and relation to soil surface temperature and argued that the increase in soil surface temperature was negligible and therefore not influencing the fluxes. Chloromethane fluxes often show positive correlation with air temperature and photosynthetically active radiation (Saito et al. 2008, Varner et al. 1999b, Dimmer et al. 2001, Manley et al. 2007). For chloroform fluxes, soil moisture and air temperature do not show any correlation, when the chambers were vented to retain the air temperature (Rhew et al. 2008a). However, it seems that if the inside chamber temperature increased, the chloroform fluxes also increased (Rhew et al. 2008a). Even if the fluxes of VOCl compounds were studied in different climate regions, it is hard to predict the climate influence as the variation on a smaller scale exceeded the variation on the climate region scale. The VOCl fluxes have been measured

during a selected part of the year, and therefore it is hard to discuss any seasonal variation. Albers et al. (2011) studied chloroform fluxes from the forest floor during both summer and winter and found on average lower emissions during winter. Hellén et al. (2006) could not observe any fluxes at a forested site with snow cover. Helmig et al. (2009) observed an efflux of chloroform from snow pack while but snow appeared to act as a sink for chloromethane.

VOCl fluxes are not only suggested to be dependent on temperature, but also on soil moisture. Rhew et al. (2010) tested chloromethane fluxes in woodland soils under laboratory conditions and found that medium soil moisture showed the highest fluxes. Chloroform fluxes in tundra also showed variations with changing soil moisture. The highest fluxes were shown in moist soils (> 70 %) with no standing water (Rhew et al. 2010). It is likely that temperature has an effect when the soils are both wet and dry (Rhew and Abel 2007). Hardacre et al. (2009) on the other hand did not find any differences in chloromethane fluxes between wet and dry sites. There are too few studies on the how hydrology affects microbial and chemical processes and/or the mass transfer in the soils.

Chloride concentration in soils has been suggested to influence abiotic and biotic VOCl formation (Cox et al. 2004, Keppler et al. 2000). Cox et al. (2004) suggested that the rather high emissions found at sites with Eucalyptus were an effect of the plants' high chloride content. There are also suggestions of a vegetative transport of VOCl (Wang et al. 2006).

Of the currently published papers, the majority has focused on how variable the emissions are on only a few locations with few "replicates" (site measurements). In general, assessment of spatial variability addresses some specific questions. How variable is the emission in question? What proportion of the total variation observed can be accounted for spatial factors? Can we predict the pattern in space? At what scale or scales is the pattern, if present, expressed? To rigorously address questions linking variation of other variables to the soil emission heterogeneity, a well-designed study and accordingly robust statistical tools are needed. The uncertainties discussed by study authors mostly focus on underlying causes to the large temporal and spatial variation of fluxes, such as chamber design and problems with e.g. i) increasing temperatures for transparent chambers without climate control (Rhew et al. 2008a) and how to distinguish between plant and soil emissions (Redeker et al. 2000, Hardacre et al. 2009), ii) short measurement periods (only measurement during end of growing season) (Varner et al. 1999), iii) uncertainties in global extrapolation of fluxes due to several assumptions, which are in themselves uncertain (Rhew et al. 2000), iv) detection limits too high to reveal an uptake for some VOCl (Khalil and Rasmussen 2000), and v) the natural variation in itself which sometimes it hard to draw conclusions about spatial or seasonal patterns (Albers et al. 2011). It is without doubt that the belowground compartment of soil is heterogeneous. The heterogeneity of soil is imposed by e.g. belowground parent material or vegetation, water and nutrients rarely homogeneously distributed in soils. Nevertheless, while the spatial heterogeneity is well recognized, the scale of trace gas emissions in general, to what extent they are emitted and what is the ecological role, are poorly understood. VOCl will likely have a complex spatial pattern for several reasons. With a number of organisms known to produce gases on a small scale, and the knowledge of the complex Cl biogeochemical cycling at a larger geographical scale (Winterton 2000, Gribble 2015). Our understanding of the scale of variability in space is in most cases on a qualitative level. The published studies to date do not offer generalizations about patterns or controls/drivers or consequences. This could be due to a lack of appropriate quantitative tools.

4 Concluding remarks

Studies have convincingly identified a number of natural VOCl sources and challenged the view of VOCl as being solely produced by humans.

From the reviewed studies, it can be concluded that the most common methods for measuring VOCl soil air fluxes are enclosure-based methods. In the reviewed literature, the challenges mentioned mainly revolve around; i) how to make accurate sampling at low concentrations (ppt-level), ii) possible contamination from equipment, iii) chamber material interference of biological processes, iv) study design to capture spatio-temporal variation many samples, v) the biogeophysical factors that influence VOCl processes and vi) sampling design to minimize the effects of measurements. There is no study that discusses the possible complexity (e.g. non-linear model) of going from the single concentration measurements during chamber deployment to flux estimations. The choice of the flux method is often a compromise between accuracy, applicability and cost. However, there are very few studies that discuss and highlight how many samples are needed to be able to produce reliable data in the study design.

Concentrations of chlorinated volatiles have been observed in many terrestrial ecosystems such as tropical forests, grasslands, deciduous forests, taiga and tundra as well as from agricultural land such as rice fields. The majority of studies have been performed in the northern hemisphere. Seven different volatile chlorinated organic compounds were studied in terrestrial ecosystems, where the most frequently studied compounds are chloromethane (CH_3Cl) and chloroform (CHCl_3), of which CH_3Cl is the most frequently studied. The VOCl compounds more rarely studied are; CCl_4 (tetrachloroethane), $\text{C}_2\text{H}_3\text{Cl}$ (VC, chloroethylene), CH_2Cl_2 (dichloromethane), CH_3CCl_3 (methyl chloroform), $\text{C}_2\text{H}_5\text{Cl}$ (trichloroethane).

Temporal and spatial quantification of sources and sinks of VOCl is a considerable scientific challenge. Our ability to predict VOCl flux remains limited because of multiple controlling mechanisms that interact over different temporal and spatial scales. The reviewed papers point at several challenges of VOCl flux estimations, not related to the method itself but rather to the studied ecosystem; i.e. i) trace gases can have several sources, ii) the gases could be produced and/or consumed simultaneously in the soil, iii) the reactions are dependent on several environmental factors such as soil temperature and soil moisture, iv) the more local environmental factors are in turn dependent on different “ecological” drivers such as climate and soil properties.

Cl is without doubt emitted from terrestrial ecosystems to the atmosphere and especially the VOCl chloromethane and chloroform. Coastal areas and wetlands had the highest chloromethane emissions and forests and wetlands was dominated by chloroform emissions and fluxes can sometimes in the same order as wet and dry deposition of Cl. Quantifying this efflux and understanding the factors that underlie the temporal and spatial variation in its magnitude are fundamental to our understanding of the behaviour of Cl and its fate in the environment.

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Appendix 1

Table A1-1. Reported chloromethane fluxes from terrestrial ecosystems for each site reported. Reported uptake fluxes in a soils are reported as negative (–).

Ecosystem	Lat Long	Environment and location	Mean ng m ⁻² h ⁻¹	Min ng m ⁻² h ⁻¹	Max ng m ⁻² h ⁻¹	No sampling locations	Season/Month of sampling	Reference
Arctic climate region (66°N to the north pole)								
Tundra	68°N, 18°E	Subarctic, Sweden	550	–1 250	2 350	15	June–September	(Hardacre et al. 2009)
	68°N, 18°E	Subarctic, Sweden	400	–1 200	2 000	6	June–September	(Hardacre et al. 2009)
	71°N, 157°W	Arctic, Alaska	–934	–1 174	–694	16	July	(Teh et al. 2009)
	68°N, 149°W	Arctic, Alaska	–1 626	–2 024	–1 229	20	August	(Teh et al. 2009)
Grassland	68°N, 116°E	Mossy, Greenland	–333			2	July	(Khalil and Rasmussen 2000)
	68°N, 116°E	Grass, Greenland	–167			2	July	(Khalil and Rasmussen 2000)
Temperate climate region (23°N–66°)								
Forest	54°N, 5°W	Beech/pine forest, Ireland	3 242	3 154	3 329	5	January–December	(Redeker and Kalin 2012)
Shrubland/ woodland	32°N, 117°W	Scripps coastal reserve, California		–526	2 314	14	January–December	(Rhew et al. 2001)
	32°N, 117°W	Elliot Chaparral Reserve, California		–905	3 703	7	January–December	(Rhew et al. 2001)
	33°N, 116°W	Boyd Deep Canyon Reserve, California		–206	168	8	January–December	(Rhew et al. 2001)
	41°N, 117°W	Sub eucalypt canopy, Tasmania	–182	–1 100	1 300	1	January–December	(Cox et al. 2004)
	41°N, 117°W	Sub Melaleuca canopy, Tasmania	–1 000	–1 700	–120	1	January–December	(Cox et al. 2004)
	38°N, 120°W	Oak-savanna woodland, California	–926	–1 170	–682	3	January, February, July	(Rhew et al. 2010)
Agricultural areas	29°N, 95°W	Rice paddy, Texas	1 200	–580	2 600	24	Growing season	(Redeker et al. 2003)
	39°N, 122°W	Rice paddy, California		1 250	1 667	2	Growing season	(Redeker et al. 2000)
	38°N, 121°W	Rice paddy, California		–28	3 976	3	Growing season, June–October	(Khan et al. 2011)
Grassland	41°N, 117°W	Tussock grass, Tasmania	–510	–1 700	310	1	January–December	(Cox et al. 2004)
	41°N, 117°W	Pasture, Tasmania	–510	–1 100	–13	1	January–December	(Cox et al. 2004)
	60°N, 21°E	Coastal meadow, Finland		63	865	4	July	(Valtanen et al. 2009)
	40°N, 104°W	Shortgrass rangeland, Colorado	–399	–714	–85	8	May	(Teh et al. 2008)
	38°N, 121°W	Annual grassland, California		–980	88 568		April, July	(Rhew and Abel 2007)
	37°N, 122°W	Annual grassland, California		–1 298	156		April, July	(Rhew and Abel 2007)
	38°N, 121°W	Peatland pasture, California	18 934	–5 891	43 758	3	January–December	(Khan et al. 2013)

Ecosystem	Lat Long	Environment and location	Mean ng m ⁻² h ⁻¹	Min ng m ⁻² h ⁻¹	Max ng m ⁻² h ⁻¹	No sampling locations	Season/Month of sampling	Reference
Wetland	53°N, 9°W	Forested bog, Ireland	5947	0	16 655	1	September	(Dimmer et al. 2001)
	53°N, 9°W	Forested bog, Ireland	1 758	1 667	1 849	1	September	(Dimmer et al. 2001)
	53°N, 9°W	Inland marsh, Ireland	2 089	1 221	3 116	1	September	(Dimmer et al. 2001)
	53°N, 9°W	Blanket bog, Ireland		34	1 187	5	September	(Dimmer et al. 2001)
	43°N, 71°W	Poor fen, New Hampshire	1 104	513	1 696		End of growing season	(Varner et al. 1999)
	43°N, 71°W	Rich fen, New Hampshire	387	513	1 696		End of growing season	(Varner et al. 1999)
	55°N, 3°W	Blanket peat bog, Scotland		-380	13 700	4	January–December	(Hardacre and Heal 2013)
	55°N, 2°W	Semi-natural, constructed wetland, Scotland		-380	1 070	5	January–December	(Hardacre and Heal 2013)
	55°N, 3°W	Raised peat bog, Scotland		1 000	550 000	8	January–December	(Hardacre and Heal 2013)
	55°N, 8°W	<i>Phragmites australis</i> wetland, Scotland		-980	9 870	4	January–December	(Hardacre and Heal 2013)
Coastal system	55°N, 8°E	Seagrass meadow, Germany		62	5 206		August–September	(Weinberg et al. 2013)
	37°N, 7°W	Seagrass subtropical lagoon, Portugal	788	-2 489	3 736		August–September	(Weinberg et al. 2015)
	53°N, 9°W	Coastal marsh	377	23	548	1	September	(Dimmer et al. 2001)
	41°N, 117°W	Coastal wetland	300	-34	760	1	January–December	(Cox et al. 2004)
	32°N, 117°W	Coastal salt marsh, California		427	294 525	5	February, June, October, November	(Rhew et al. 2000)
	32°N, 117°W	Coastal salt marsh, California		72	336 600	5	April, August, December	(Rhew et al. 2000)
	56°N, 2°W	Salt marsh, Scotland		-1 610	6 440	8	January–December	(Blei et al. 2010)
	54°N, 3°W	Salt marsh, Scotland		-2 380	42 300	11	January–December	(Blei et al. 2010)
	37°N, 122°W	Salt marsh, California		463	31 556	6	February, April, June	(Rhew et al. 2010)
27°N, 97°W	Salt marsh, Texas		-282	1 285 391	24	April–November	(Rhew et al. 2014)	
Tropical region (23°S to 23°N)								
Forest	2°S, 50°W	Rain forest, Brazil	-13 000				May/June	(Khalil and Rasmussen 2000)

Appendix 2

Table A2-1. Reported chloroform fluxes from terrestrial ecosystems for each site reported. Reported uptake fluxes in a soils are reported as negative (–).

Ecosystem	Lat Long	Environment and location	Mean ng m ⁻² h ⁻¹	Min ng m ⁻² h ⁻¹	Max ng m ⁻² h ⁻¹	No sampling locations	Season/Month of sampling	Reference
Arctic climate region (66°N to the north pole)								
Tundra	71°N, 157°W	Arctic tundra, Alaska	236	7	1283	20	July	(Rhew et al. 2008b)
	68°N, 149°W	Arctic tundra, Alaska	180	0	587	16	August	(Rhew et al. 2008b)
	68°N, 19°E	Subarctic, dry pine forest, Abisko		42	2850	5	January–December	(Johnsen et al. 2016)
	68°N, 18°E	Subarctic, birch forest, Abisko		12	577	5	January–December	(Johnsen et al. 2016)
	68°N, 18°E	Subarctic, Sphagnum bog, Abisko		8	130	5	January–December	(Johnsen et al. 2016)
	61°N, 45°W	Arctic, dry prostrate dwarf-shrub tundra, Greenland		15	36	5	January–December	(Johnsen et al. 2016)
	61°N, 45°W	Arctic, moist erect dwarf-shrub tundra, Greenland		15	87	5	January–December	(Johnsen et al. 2016)
	67°N, 50°W	Arctic, non-tussock sedge wetland, Greenland		52	522	5	January–December	(Johnsen et al. 2016)
	67°N, 50°W	Arctic, moist prostrate dwarf-shrub tundra, Greenland		21	76	5	January–December	(Johnsen et al. 2016)
67°N, 50°W	Arctic, dry prostrate dwarf-shrub tundra, Greenland		18	176	5	January–December	(Johnsen et al. 2016)	
Grassland	68°N, 116°E	Mossy, Greenland	729			1	July	(Khalil and Rasmussen 2000)
Temperate climate region (23°N-66°)								
Forest	56°N, 8°E	Spruce forest, Denmark		16	1998	77	May, October	(Albers et al. 2011)
	56°N, 8°E	Mixed coniferous forest, Denmark		40	2676	61	February, November	(Albers et al. 2011)
	61°N, 24°E	Coniferous forest, Finland		100	800	8	April–October	(Hellén et al. 2006)
	52°N, 5°E	Douglas forest, The Netherlands	110	49	120	8		(Hoekstra et al. 2001)
	55°N, 11°E	Beech/spruce forest, Denmark		3	160	1		(Haselmann et al. 2000a)
	52°N, 5°E	Beech forest, The Netherlands	17	8	73	4		(Hoekstra et al. 2001)
	52°N, 4°E	Pine forest, The Netherlands	10	1	19	4		(Hoekstra et al. 2001)
	38°S, 146°E	Boola Boola National Forest, Australia	52000			1	April–November	(Khalil and Rasmussen 2000)
	49°N, 125°W	Clear-cut coniferous forest, British Columbia		–130	620	89	May	(Pickering et al. 2013)

Ecosystem	Lat Long	Environment and location	Mean ng m ⁻² h ⁻¹	Min ng m ⁻² h ⁻¹	Max ng m ⁻² h ⁻¹	No sampling locations	Season/Month of sampling	Reference
Shrubland/ Woodland	41°N, 117°W	Sub eucalypt canopy, Tasmania	3000	1600	5000	1	January–December	(Cox et al. 2004)
	41°N, 117°W	Sub Melaleuca canopy, Tasmania	320	160	950	1	January–December	(Cox et al. 2004)
	33°N, 116°W	Shrubland, California	33	–15	154	41		(Rhew et al. 2008a)
	69°N, 53°W	Subarctic, lichen-graminoid heath, Greenland		13	40	5	January–December	(Johnsen et al. 2016)
	69°N, 53°W	Subarctic, birch/willow shrubland, Greenland		15	36	5	January–December	(Johnsen et al. 2016)
	69°N, 53°W	Subarctic, wet birch shrubland, Greenland		15	87	5	January–December	(Johnsen et al. 2016)
Agricultural areas	38°N, 121°W	Rice paddy, California		–16	2204	3	Growing season, June–October	(Khan et al. 2011)
	40°N, 116°E	Rice paddy, Beijing		600	4400			(Khalil et al. 1998)
Grassland	41°N, 144°E	Tussock grass, Tasmania	1800	46	4800	1	January–December	(Cox et al. 2004)
	41°N, 144°E	Pasture, Tasmania	1200	72	2100	1	January–December	(Cox et al. 2004)
	52°N, 4°E	Grass, The Netherlands	14	12	16	1		(Hoekstra et al. 2001)
Wetland	53°N, 9°W	Forested bog	251	126	400	1	September	(Dimmer et al. 2001)
	53°N, 9°W	Forested bog	16678	10605	22751	1	September	(Dimmer et al. 2001)
	53°N, 9°W	Inland marsh	822	582	1301	1	September	(Dimmer et al. 2001)
	53°N, 9°W	Blanket bog, Ireland		45	3242	2	September	(Dimmer et al. 2001)
	52°N, 4°W	Dry swamp, The Netherlands	12	3	48	1		(Hoekstra et al. 2001)
Coastal area	52°N, 4°E	Sand, The Netherlands	13	1	21	1		(Hoekstra et al. 2001)
	32°N, 117°W	Salt marsh, California	73	–5	413	32	January–December	(Rhew et al. 2008a)
	32°N, 117°W	Sandy beach with kelp	12423			1	January–December	(Rhew et al. 2008b)
	32°N, 117°W	Sandy beach without kelp	90			1	January–December	(Rhew et al. 2008b)
	53°N, 9°W	Coastal marsh	388	171	502	1	September	(Dimmer et al. 2001)
	33°N, 120°E	Coastal salt marsh, Jiangsu province	–3696	–38052	21090			(Wang et al. 2007)
	41°N, 117°W	Coastal wetland, Tasmania	73	15	270	1	January–December	(Cox et al. 2004)
	33°N, 79°W	Coastal wetland, Freshwater wetland, South Carolina	440				January, April, June, July, September	(Wang et al. 2016)
	33°N, 79°W	Coastal wetland, Oligohalome wetland, South Carolina	151				January, April, June, July, September	(Wang et al. 2016)
33°N, 79°W	Coastal wetland, Mesohaline wetland, South Carolina	20				January, April, June, July, September	(Wang et al. 2016)	
Tropical region (23°S to 23°N)								
Forest	2°S, 50°W	Ducke forest, Brazil	3000			2	May, July	(Khalil and Rasmussen 2000)
Agricultural areas	23°N, 113°E	Rice paddy, Guangzhu	1000					(Khalil et al. 1998)

Appendix 3

Table A3-1. Reported tetrachloromethane fluxes from terrestrial ecosystems for each site reported. Reported uptake fluxes in a soils are reported as negative (–).

	Lat Long	Environment and location	Mean ng m ⁻² h ⁻¹	Min ng m ⁻² h ⁻¹	Max ng m ⁻² h ⁻¹	No sampling locations	Season/ Month of sampling	Reference
Arctic climate region (66°N to the north pole)								
Temperate climate region (23°N-66°)								
Forest	52°N, 5°E	Douglas forest, The Netherlands	-220	-250	-93	8		(Hoekstra et al. 2001)
	52°N, 5°E	Beech forest, The Netherlands	-54	-160	-19	1		(Hoekstra et al. 2001)
	52°N, 5°E	Pine forest, The Netherlands	-60	-190	53	4		(Hoekstra et al. 2001)
Shrubland/ Woodland	33°N, 116°W	Shrubland, California	3	-0,7	11	41		(Rhew et al. 2008a)
Agricultural area	30°S, 104°E	Canola moist	-21			1	April	(Khalil and Rasmussen 2000)
	30°S, 104°E	Several plowed crops	-4			1	April	(Khalil and Rasmussen 2000)
	30°S, 104°E	Several plowed crops	8			1	April	(Khalil and Rasmussen 2000)
	40°N, 116°E	Rice paddy, Beijing		250	1500			(Khalil et al. 1998)
Grass	52°N, 4°E	Grass, The Netherlands	-51	-90	-12	9		(Hoekstra et al. 2001)
Wetland	52°N, 4°E	Dry swamp, The Netherlands	-74	-93	-37	1		(Hoekstra et al. 2001)
Coastal area	52°N, 4°E	Sand, The Netherlands	4	-74	130	1		(Hoekstra et al. 2001)
	32°N, 117°W	Salt marsh, California	8	-11	31	32	January–December	(Rhew et al. 2008a)
	33°N, 120°W	Salt marsh, China		-686	218			(Wang et al. 2007)
	32°N, 117°W	Sandy beach with kelp	87	85	88	1	January–December	(Rhew et al. 2008b)
	32°N, 117°W	Sandy beach without kelp	0			1	January–December	(Rhew et al. 2008b)
Tropical region (23°S to 23°N)								
Forest	2°S, 50°W	Ducke forest, Brazil	-17			2	May, July	(Khalil and Rasmussen 2000)
Agricultural area	23°N, 113°E	Rice paddy, Guangzhu	-160					(Khalil et al. 1998)
	23°N, 113°E	Rice paddy, Beijing	-160					(Khalil et al. 1998)

Appendix 4

Table A4-1. Reported methyl chloroform (trichloroethane) fluxes from terrestrial ecosystems for each site reported. Reported uptake fluxes in a soils are reported as negative (-).

Ecosystem	Lat Long	Environment and location	Mean ng m ⁻² h ⁻¹	Min ng m ⁻² h ⁻¹	Max ng m ⁻² h ⁻¹	No sampling locations	Season/ Month of sampling	Reference
Arctic climate region (66°N to the north pole)								
Grassland	68°N, 116°E	Mossy, Greenland	-29			1	July	(Khalil and Rasmussen 2000)
	68°N, 116°E	Grass, Greenland	-51			1	July	(Khalil and Rasmussen 2000)
Temperate climate region (23°N-66°)								
Forest	52°N, 5°E	Douglas forest, The Netherlands	-29	-64	44	8		(Hoekstra et al. 2001)
	52°N, 5°E	Beech forest, The Netherlands	27	-28	100	1		(Hoekstra et al. 2001)
	52°N, 4°E	Pine forest, The Netherlands	28	1 170	53	4		(Hoekstra et al. 2001)
Shrubland/ Woodland	33°N, 116°W	Shrubland, California	4	-24	33	4		(Rhew et al. 2008a)
Agricultural areas	30°S, 104°E	Canola moist	-8			1	April	(Khalil and Rasmussen 2000)
	30°S, 104°E	Several plowed crops	26			1	April	(Khalil and Rasmussen 2000)
	30°S, 104°E	Several plowed crops	17			1	April	(Khalil and Rasmussen 2000)
Grassland	52°N, 4°E	Grass, The Netherlands	16	9	22	9		(Hoekstra et al. 2001)
Wetland	52°N, 4°E	Dry swamp, The Netherlands	80	-36	-170	1		(Hoekstra et al. 2001)
Coastal system	52°N, 4°E	Sand, The Netherlands	77	-20	160	1		(Hoekstra et al. 2001)
	32°N, 117°W	Salt marsh, California	1	-2	17	32	January–December	(Rhew et al. 2008a)
	33°N, 120°E	Salt marsh, Jiangu province		-178	43			(Wang et al. 2006)
	32°N, 117°W	Sandy beach with kelp	0			1	January–December	(Rhew et al. 2008b)
	32°N, 117°W	Sandy beach without kelp	0			1	January–December	(Rhew et al. 2008b)
Tropical region (23°S to 23°N)								
Forest	2°S, 50°W	Ducke forest, Brazil	-25			2	May, July	(Khalil and Rasmussen 2000)
	2°S, 50°W	Ducke forest, Brazil	13			2	May, July	(Khalil and Rasmussen 2000)

Appendix 5

Table A5-1. Reported tetrachloroethane fluxes from terrestrial ecosystems for each site reported. Reported uptake fluxes in a soils are reported as negative (-).

Ecosystem	Lat Long	Environment and location	Mean ng m ⁻² h ⁻¹	Min ng m ⁻² h ⁻¹	Max ng m ⁻² h ⁻¹	No sampling locations	Season/ Month of sampling	Reference
Arctic climate region (66°N to the north pole)								
Temperate climate region (23°N-66°)								
Forest	52°N, 5°E	Douglas forest, The Netherlands	22	8	39	8		(Hoekstra et al. 2001)
	52°N, 5°E	Beech forest, The Netherlands	10	2	22	1		(Hoekstra et al. 2001)
	52°N, 4°E	Pine forest, The Netherlands	-6	-13	-2	4		(Hoekstra et al. 2001)
Grassland	52°N, 4°E	Grass, The Netherlands	11	5	17	1		(Hoekstra et al. 2001)
Wetland	52°N, 4°E	Dry swamp, The Netherlands	2	-6	16	1		(Hoekstra et al. 2001)
Coastal system	52°N, 4°E	Sand, The Netherlands	-11	-15	-5	1		(Hoekstra et al. 2001)
Tropical region (23°S to 23°N)								

Appendix 6

Table A6-1. Reported chloroethane fluxes from terrestrial ecosystems for each site reported. Reported uptake fluxes in a soils are reported as negative (-).

Ecosystem	Lat Long	Environment and location	Mean ng m ⁻² h ⁻¹	Min ng m ⁻² h ⁻¹	Max ng m ⁻² h ⁻¹	No sampling locations	Season/Month of sampling	Reference
Arctic climate region (66°N to the north pole)								
Temperate climate region (23°N-66°)								
Agricultural	29°N, 95°W	Rice paddy, Texas		20	560	24	Growing season	(Redeker et al. 2003)
Tropical region (23°S to 23°N)								

Appendix 7

Table A7-1. Reported dichloromethane fluxes from terrestrial ecosystems for each site reported. Reported uptake fluxes in a soils are reported as negative (-).

Ecosystem	Lat Long	Environment and location	Mean ng m ⁻² h ⁻¹	Min ng m ⁻² h ⁻¹	Max ng m ⁻² h ⁻¹	No sampling locations	Season/Month of sampling	Reference
Arctic climate region (66°N to the north pole)								
Temperate climate region (23°N-66°)								
Shrubland/ woodland	40°S, 144°E	Sub eucalypt canopy, Tasmania	-7	-29	29	1	January–December	(Cox et al. 2004)
	40°S, 144°E	Sub Melaleuca canopy, Tasmania	-37	-120	-18	1	January–December	(Cox et al. 2004)
Grassland	40°S, 144°E	Tussock grass, Tasmania	-7	-49	27	1	January–December	(Cox et al. 2004)
	40°S, 144°E	Pasture, Tasmania	-12	-30	15	1	January–December	(Cox et al. 2004)
Wetland	40°S, 144°E	Coastal wetland	16	-10	90	1	January–December	(Cox et al. 2004)
Tropical region (23°S to 23°N)								

Appendix 8

Table A8-1. Reported CFC fluxes from terrestrial ecosystems for each site reported. Reported uptake fluxes in a soils are reported as negative (-).

Ecosystem	Lat Long	Environment and location	Mean ng m ⁻² h ⁻¹	Min ng m ⁻² h ⁻¹	Max ng m ⁻² h ⁻¹	No sampling locations	Season/ Month of sampling	Reference
Arctic climate region (66°N to the north pole)								
Grassland	68°N, 58°W ^a	Mossy, Greenland	-4			2	July	(Khalil and Rasmussen 2000)
	68°N, 58°W ^b	Mossy, Greenland	38			2	July	(Khalil and Rasmussen 2000)
	68°N, 58°W ^b	Grass, Greenland	13			2	July	(Khalil and Rasmussen 2000)
	68°N, 58°W ^c	Grass, Greenland	-4			2	July	(Khalil and Rasmussen 2000)
Temperate climate region (23°N-66°)								
Wetland	30°S, 104°E ^a	Canola moist	-54			1	April	(Khalil and Rasmussen 2000)
	30°S, 104°E ^a	Several plowed crops	-25			1	April	(Khalil and Rasmussen 2000)
	30°S, 104°E ^a	Several plowed crops	-21			1	April	(Khalil and Rasmussen 2000)
	30°S, 104°E ^c	Canola moist	-50			1	April	(Khalil and Rasmussen 2000)
	30°S, 104°E ^c	Several plowed crops	-29			1	April	(Khalil and Rasmussen 2000)
	30°S, 104°E ^c	Several plowed crops	-8			1	April	(Khalil and Rasmussen 2000)
Tropical region (23°S to 23°N)								
Forest	2°S, 50°W ^a	Ducke forest, Brazil	4			2	May, July	(Khalil and Rasmussen 2000)
	2°S, 50°W ^a	Ducke forest, Brazil	-21			2	May, July	(Khalil and Rasmussen 2000)
	2°S, 50°W ^b	Ducke forest, Brazil	-129			2	May, July	(Khalil and Rasmussen 2000)
	2°S, 50°W ^c	Ducke forest, Brazil	-25			2	May, July	(Khalil and Rasmussen 2000)

a) CFC-11. b) CFC-12. c) CFC-113.

SKB is responsible for managing spent nuclear fuel and radioactive waste produced by the Swedish nuclear power plants such that man and the environment are protected in the near and distant future.

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