Biogeochemistry **60:** 121–139, 2002.

Terrestrial natural sources of trichloromethane (chloroform, $CHCl_3$) – An overview

FRANK LATURNUS[1]*, KIM F. HASELMANN[2], THOMAS BORCH[3] & CHRISTIAN GRØN[4]
[1]*Environmental Science Programme, Department of Thematic Studies, Linköpings Universitet, Campus Norrköping, 60174 Norrköping, Sweden;* [2]*Department of Chemistry, University of Southern Denmark, 5230 Odense, Denmark;* [3]*Center for Biofilm Engineering, Montana State University, Bozeman MT 59717-3980, U.S.A.;* [4]*Eurofins A/S, 2970 Hørsholm, Denmark (*author for correspondence, e-mail: frank.laturnus@ituf.liu.se)*

Key words: atmospheric input, chloroform, forest soil, natural formation, natural terrestrial sources, volatile chlorinated compounds

Abstract. The widespread use of volatile chlorinated compounds like chloroform, trichloroethene and tetrachloroethene in industrialized societies causes a large annual release of these compounds into the environment. Due to their role as a source for halogen radicals involved in various catalytic atmospheric reaction cycles, including the regulation of the stratospheric and tropospheric ozone layers, these compounds also constitute a risk for drinking water resources as they can be transported to the groundwater from contaminated field sites or even from atmospheric deposition. Therefore, identification and investigation of sources and sinks of volatile chlorinated compounds are of particular interest. Chloroform, a major contributor to natural gaseous chlorine, was found to be emitted by several anthropogenic and natural sources including the oceans and terrestrial areas. The origin of chloroform in the terrestrial environment can be anthropogenic point sources, atmospheric deposition, release by vegetation and production directly in the soil. The calculated annual biogenic global chloroform emission is 700 Gg, and marine and terrestrial environments are nearly equal contributors. The estimated emissions from anthropogenic sources account for less than 10% of the estimated total emissions from all sources. Among terrestrial sources, forests have recently been identified as contributing to the release of chloroform into the environment. With the data available, annual emissions of chloroform to the atmosphere from forest sites were calculated and compared to other natural sources. At present knowledge, forests are only a minor source in the total biogenic flux of chloroform, contributing less than 1% to the annual global atmospheric input. However, it should be noted that data are available for Northern temperate forests only. The large tropical forest areas may provide a yet unknown input of chloroform.

Introduction

In 1987, a resolution called the Montreal Protocol declared that all industrial nations will stop the use of chlorocarbons- and chlorofluorocarbons (CFCs) by 1996. This agreement was the result of a cooperative effort between researchers and politicians in reaction to the threat of a disappearing stratospheric ozone layer that is largely responsible for the Earth's surface protection against harmful solar UV-radiation. This major ecological problem is caused by the use and industrial release of CFCs into the atmosphere (UNEP report 1987; Prather & Watson 1990; UNEP report 1998). Beside CFCs, other reactive chlorine-containing compounds released to the atmosphere include methyl chloride, dichloromethane, chloroform, trichloroethane, trichloroethene and tetrachloroethene. Although their influence on stratospheric photochemistry may be less important when compared to CFCs, they do have a major influence on tropospheric photochemistry. These volatile chlorinated compounds are widely used in industrialized societies as solvents, fuel components, as intermediates in the chemical industry, and they are added to many manufactured products, including paints, adhesives, gasoline, and plastic (Collins et al. 2002). The major anthropogenic sources of these compounds are fossil-fuel combustion, incineration, and industrial releases primarily due to pulp and paper manufacturing and water treatment (Keene et al. 1999; Aucott et al. 1999). As a result of this widespread use, volatile chlorocarbons can be globally found throughout atmospheric, surface, and subsurface locations. Anthropogenic emission and evaporation of these compounds from sources like automobiles, combustion of coal, industries, or commercial activities not involved in manufacturing, such as refueling stations and dry-cleaning operations are also present in the atmosphere (Collins et al. 2002). Additionally, point sources such as leaking underground storage tanks, process sewer lines, septic tanks, landfills, waste-disposal pits and detention basins lead to an introduction into the environment, where they can be detected in ground water and in the marine environment (Baehr et al. 1999; Squillace et al. 1999; Dewulf et al. 1998). While the industrial regions of Europe, North America and Japan are the largest sites of anthropogenic emissions, there are also significant sources in the developing nations of Asia. In contrast, anthropogenic emissions within the Southern hemisphere are much smaller and more widely dispersed (Collins et al. 2002). These large inter-hemispheric differences reflect the significant contribution of anthropogenic emissions to ambient concentrations in the Northern hemisphere.

Besides industrial sources of chlorinated compounds, natural sources may contribute significantly to the chlorocarbons in the environment. The oceans have been found to be a major source for naturally-produced volatile halogenated compounds (Lovelock et al. 1975; Singh et al. 1983; Cicerone et al. 1988), where macroalgae (Goodwin et al. 1997; Laturnus 2001) and probably phytoplankton (Moore et al. 1995) release these compounds. Although the majority of volatile halocarbons produced by marine organisms contain bromine and iodine, chlorinated compounds have also been identified. Nightingale et al. (1995) found the release of chloroform by temperate macroalgae to be an average of 0.07 nmol per gram of wet tissue per day (range 0.0005–0.25 nmol [g wet tissue]$^{-1}$ day^{-1}), and Scarratt and Moore (1999) reported a release rate of 370 nmol chloroform [g chlorophyll a]$^{-1}$ day^{-1}(range 130–780 nmol chloroform [g chlorophyll a]$^{-1}$ day^{-1}) from microalgae. The terrestrial ecosystem may also be an important source for volatile halocarbons thereby contributing to the global halogen budget and cycle.

The present paper provides an overview on chloroform released by terrestrial sources. Chloroform is a major contributor to natural gaseous chlorine, especially in the lower atmosphere (Khalil et al. 1998). Since chloroform has been identified as a carcinogen and is present in enclosed environments and in drinking water it may be a cause for concern when high concentrations are discovered (Golden et al. 1997; Fawell 2000). Many volatile chlorinated compounds detected in the terrestrial environment are of industrial origin alone due to atmospheric pollution and contamination of ground water and soil (Laturnus et al. 2000; Collins et al. 2002). However, the global anthropogenic flux of chloroform into the atmosphere is much too low to account for observed global background concentrations. Therefore, it is clear that natural sources also exist and must make major contributions to the total global sources (Aucott et al. 1999; Winterton 2000). While chloroform alone may play a minor role in the global chlorine cycle, it may be worth considering more seriously when taken together with other naturally-produced chlorocarbons (Khalil & Rasmussen 1999).

Analytical methods

The analytical methodology for the detection of volatile halocarbons in the environment is now well-developed and allows ultra-sensitive and reliable measurements even in remote areas like the Polar Regions. The quantitative and qualitative analyses of volatile halogenated hydrocarbons in the present review were achieved by high resolution gas chromatography (HRGC) and with detection methods such as electron capture detection (ECD), microwave-induced plasma atomic emission spectrometry (MIP-AES), ion-trap mass spectrometry (ITMS), membrane inlet mass spectrometry (MIMS), and the use of isotope labeled compounds. The analyses of different sample matrices for volatile organohalogens were performed by purge-and-trap/headspace/thermodesorption units coupled to a gas chromatograph and various analytical detector systems (Slaets et al. 1999; Laturnus et al. 1999; Khalil & Rasmussen 1999; Laturnus et al. 2000; Urhahn & Ballschmiter 2000; Murphy et al. 2000; Hoekstra et al. 2001).

Terrestrial sources

The terrestrial part of the Earth, although covering only 29% of the planet's surface, may be an important additional source for volatile halocarbons. Similar to the marine environment, where at present only two sources of chloroform have been identified (macro and microalgae), terrestrial natural sources for chloroform are still poorly investigated. Khalil et al. (1998) found besides methane, nitrous oxide and other trace gases, a positive flux of chloroform liberated into the atmosphere during the investigation of rice fields. The authors measured fluxes in the range of 120 to 800 nmol chloroform m^{-2} day^{-1}. Dimmer et al. (2001) discovered that peatland ecosystems are also important sources of low molecular weight halocarbons. The authors recorded a flux of chloroform and of methyl halides from Irish peatland ecosystems at globally significant amounts.

Another recently described terrestrial source for chloroform is the burning of vegetation (Lobert et al. 1999). Estimated annual global emissions from biomass burning are 2 Gg chloroform, mainly emitted by savanna fires (38% of the global emission) and wood and charcoal burning (24% of the global emission) with 64% released in the Northern Hemisphere (equator split). Biomass burning is a major source for many atmospheric trace constituents, and about 90% of today's biomass burning appears to be induced by humans. Only a minor fraction is considered to be entirely natural, caused for example by volcanic eruptions and lightning. Therefore, describing biomass burning as a natural source for chloroform must be done carefully. Although very little quantitative information is available about the long-term trend of biomass burning, several thousand years ago, global emissions by biomass burning were dominated by natural events and the contribution of anthropogenic burning was small. With the exponential growth of the human population in developing countries, biomass burning is now viewed as an anthropogenic source of trace compounds into the atmosphere (Lobert et al. 1999). However, biomass burning appears to be a minor source of chloroform on a global scale with an annual release of less than 1% of known sources.

Khalil et al. (1990a) reported the formation and release of chloroform from biogas pits often used in Asia. In China up to 10 million biogas generators are estimated to be in use. Typically biogas generators are concrete cylindrical cisterns with a volume of 4 to 10 m^3 where human waste, pig manure, rice straw, and other organic farmyard wastes are fermented in saturated sludges. The anaerobic processes in the pits produce biogas, which is mostly methane, CO_2 and small quantities of other gases. Khalil et al. (1990a) found an average flux of chloroform of 400 nmol day^{-1} per pit. Although the fermentation and formation processes in a biogas generator are natural, the majority of all biogas pits are man-made. Therefore, biogas pits may be considered a 'quasi' natural source for chloroform. On a global scale the emission rates of chloroform from biogas generators are too small to contribute significantly to the global cycles of this gas (Khalil et al. 1990a).

Termites are probably a truely natural source for chloroform. Khalil and co-workers (1990b) found positive fluxes of chloroform from six different species studied. The concentrations of chloroform inside the termite mounds were a thousand times greater than ambient levels. The chloroform release from mounds showed a seasonal dependence with significant lower emissions during the winter. The estimated flux of chloroform from termite mounds has been calculated to 0.002 pmol cm^{-2} sec^{-1} (Khalil et al. 1990b).

Volcanism may also be a significant natural source of chloroform because the chloroform concentrations detected in volcanic gases (up to 40 nmol L^{-1}) are around 1.5 to 2 orders of magnitude higher than those above the oceans (Isidorov 1990; Jordan et al. 2000). The chloroform detected in volcanic gases is of a non-biogenic origin. During eruptions, a pressure differential of hundreds of atmospheres leads to a rapid removal of chloroform from the reaction zone inside the volcano thus ensuring stability. The volcanic ash-gaseous plumes and clouds probably serve as gigantic chemical reactors in which chloroform and other organic compounds are synthesized from simple gases. However, biogenic processes cannot be excluded (Isidorov 1990).

The Earth's crust contains organic gases in the free state, sorbed by the rocks, in sediments, granite and basalt layers, and dissolved in water. A part of these gases reaches the Earth's surface along deep fractures and cracks and can diffuse into the atmosphere (Isidorov 1990). Investigations in tectonically active regions showed, for example, an increase in local methane concentrations compared to the usual background concentrations. Isidorov (1990) reported that gases emitted from the Earth's crust can contain chloroform in concentrations of 17 to 25 μmol m^{-3}. However, estimations of the significance as a natural source is hardly possible as studies on Earth's crust as a source for organic compounds are still scarce.

MacLeod and deTroconis (1982) detected up to 1.7 nmol chloroform kg^{-1} in Sapodilla fruits, Gil and MacLeod (1980) found trace concentrations of chloroform in cruciferaes, and Isidorov et al. (1985) showed the emission of chloroform by living samples of Northern white cedar. Also, Gribble (1996) reported that chloroform has been detected in deciduous mosses, drill wells, mine gas and minerals, lemon, orange, barley, and mushrooms. However, since no further studies on the formation and possible emission of chloroform by these plants were performed, estimation of their global significance as sources of chloroform cannot be evaluated.

Forest soil

To investigate forest soils as a possible terrestrial source of chloroform, measurements of top soil air and ambient air concentrations ($C_{soil}/C_{ambient}$) were performed (Frank et al. 1989; Frank & Frank 1990; Haselmann et al. 2000a; Laturnus et al. 2000, Hoekstra et al. 2001). These studies reported chloroform values for soil air in the range of 3.4–100 pmol L^{-1} and in atmospheric air between 0.8–4.2 pmol L^{-1}, resulting in relative concentration ratios of top soil air and ambient air of 4:1–36:1 with average values around 10:1. Spruce forests showed the highest relative ratios compared to deciduous forests, grasslands and peat moorland. Since the ambient air values are uniform (relative standard deviations (RSD) are less than 50%), the ratio variations were due to differences in soil air chloroform levels. Other volatile C_1- and C_2- chlorinated compounds showed a different behavior compared to chloroform. Their relative ratios of soil air to ambient air concentrations were close to unity with only slight variations between sample sites (low RSD). Looking at the spatial depth variations of chloroform, a maximum concentration has been observed in the top organic rich soil layer by Hoekstra et al. (1998b) and Haselmann et al. (2000a). The depth variations were studied more extensively by Laturnus et al. (2000), where concentrations were measured down to the ground water table. For chloroform, the results showed an increase in the first half meter and then a decrease towards the ground water table, whereas no change for other chlorinated C_1- and C_2-compounds were observed. As no point sources of chloroform contamination were reported for the sampling areas, an upward diffusion of chloroform from contaminated ground water towards the topsoil can be excluded. Furthermore, release studies of the top layer of forest soil showed increasing chloroform concentrations within a defined time window, while the concentrations of other volatile chlorocarbons investigated remained fairly constant (Haselmann et al. 2000a). The results indicate a biogenic formation of chloroform in the upper layers of the soil and identified forest soil as a possible source for naturally-produced chloroform in the environment (Laturnus et al. 2000).

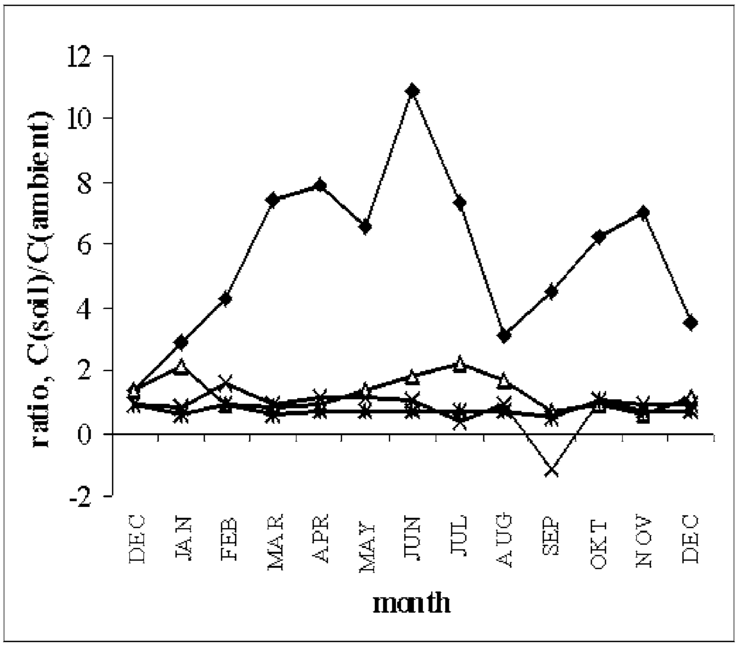

Figure 1. The ratio of top soil air to ambient air concentrations of chloroform (♦), tetrachloromethane (∗), 1,1,1-trichloroethane (×) and tetrachloroethene (Δ) monthly measured in a spruce forest during a one-year-sampling period (Haselmann et al. 2002).

The formation and emission of chloroform by forest soil and the observed large variations seen between sampling areas lead to the question of whether a seasonal variation exists. This may be expected if the production is biologically catalyzed. Recently, a year-round study in a spruce forest was conducted by Haselmann et al. (2002). Soil air and ambient air concentrations of chloroform and other chlorinated C_1- and C_2-compounds were monitored monthly throughout a one-year period. Chloroform showed increasing concentrations in spring and autumn, and lower concentrations in late summer and winter. In Figure 1, relative concentrations in top soil air *vs.* ambient air is plotted for the monitoring period. Chloroform exhibited a distinct annual variation with a high soil air to ambient air ratio throughout the period, thus differing from the other chlorinated compounds investigated. This pattern of seasonal chloroform concentration variation resembles the one assumed for the biological activity in forest soils, reaching highest values in warm and humid periods and lower activity in dry and/or cold periods. Studies done by Haselmann et al. (2000b) showed a reduced release of chloroform from dry soil compared to soil with a higher humidity. Therefore, it is suggested that the observed

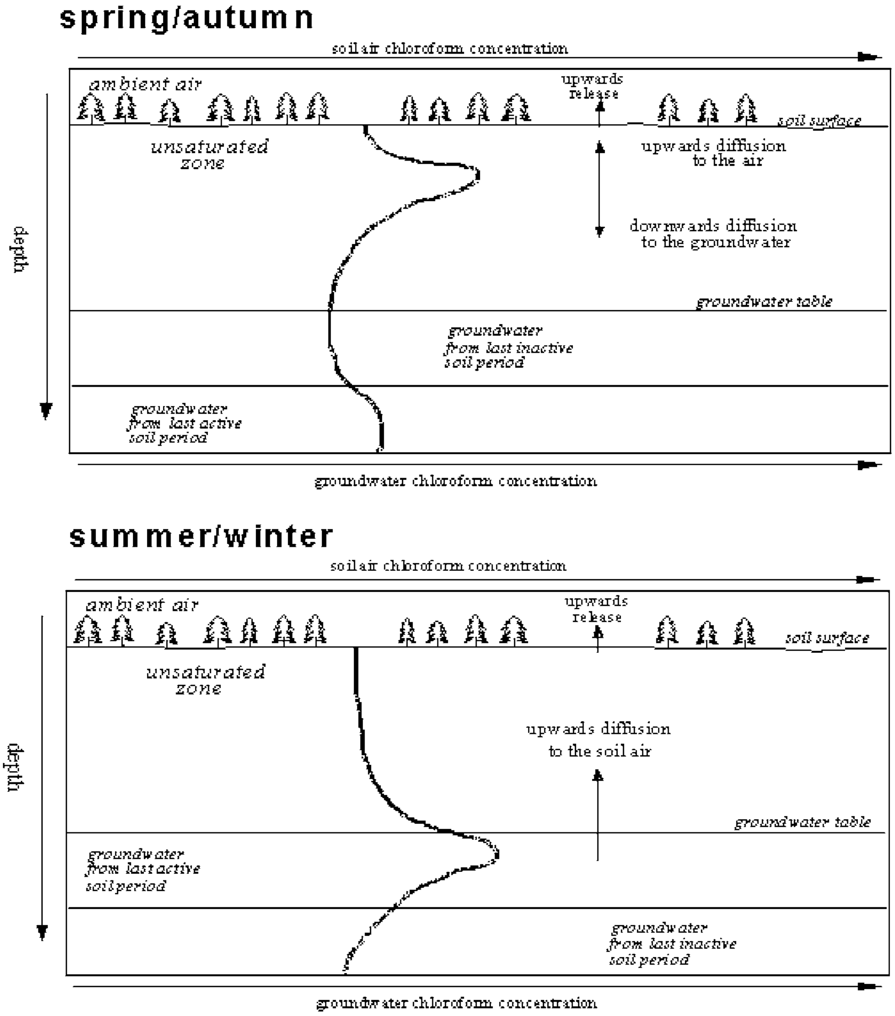

Figure 2. Chloroform concentration profiles suggested for periods with soil production and the ground water as a sink (spring/autumn) and for no or reduced soil production and the ground water as a source (summer/winter) (Laturnus et al. 2000).

chloroform concentration profiles reflect production in the soil in a microbiologically active period (late spring and early autumn), diffusive loss to the atmosphere, and downward diffusion toward a sink in the ground water (Figure 2). The production is expected in the upper 1 m of the soil due to its high organic matter content and a comparatively high microbial activity. A peak chloroform concentration was observed in the deeper part of the productive zone due to the free diffusion of chloroform produced close to the surface (Laturnus et al. 2000). The concentration profile in a microbiologically inactive period (winter and summer) exhibits a steep gradient caused by upward diffusion from the ground water source to the atmosphere (Figure 2).

However, besides the biogenic formation of chloroform, abiotic mechanisms may also be possible. Frank et al. (1989) hypothesizes that chloroform may be found by decarboxylation of trichloroacetic acid, and laboratory studies of the addition of trichloroacetic acid to an organic rich forest soil showed an increase of the release of chloroform (Haselmann et al. 2000b). Another mechanism leading to the formation of chloroform may be the transformation of tetrachloromethane in iron-reducing environments by abiotic (mineral-mediated) or sulfate reducing reactions (McCormick & Adriaens 2000; Devlin & Mueller 1999). Recently, Keppler et al. (2000) reported the formation of volatile organohalogens during oxidation of organic matter by an electron acceptor such as iron (III). These reactions do not require sunlight or microbial mediation, and may also be valid for the formation of chloroform.

Naturally-produced chloroform can be released into the atmosphere and can also affect the ground water. Studies of ground water in a pristine aquifer free of point sources of soil and ground water contamination and remote from industrial areas, showed concentrations of chloroform up to 14 nmol L^{-1} (Laturnus et al. 2000). These levels are still below the present regulatory limits for drinking water (Federal Register 1998; Mills et al. 1998). However, they are close to a probable future regulatory level, and are within a risk level generally considered of public concern. Therefore, natural sources of chloroform have to be included when discussing contamination of ground water.

Dynamic formation and degradation of chloroform in forest soil

Hoekstra et al. (1998b) demonstrated the production of chloroform from inorganic chloride and suggested chlorination of soil organic matter as a possible source of chloroform in the soil. This chlorination process is most likely due to biological activity occurring in the top soil layers, since it has been shown that fungi are capable of producing chloroform from inorganic chloride (Hoekstra et al. 1998a). Some organisms contain haloperoxidases, an enzyme group which can catalyze the incorporation of inorganic halides into organic molecules (Neidleman & Geigert 1986). High halogenating activities have been found in the upper soil layers probably due to the presence of these haloperoxidases (Asplund et al. 1993; Laturnus et al. 1995). Laboratory experiments showed that in the presence of haloperoxidases, inorganic halides and hydrogen peroxide, organohalogens like chloroform were formed from organic material like humic substances (Walter & Ballschmiter 1992; Hoekstra et al. 1995). The halogenation can take place inside the organisms or by haloperoxidases released into soil as a result of excretion or death of the organisms (Laturnus et al. 1995). In addition to enzymatic formation, chloroform generation has been suggested to be formed by decarboxylation of trichloroacetic acid detected in soil and conifer needles or by chlorination of humic acids followed by decomposition to chloroform (Frank et al. 1989, 1992).

Forest soil was found to be a source for atmospheric and ground water chloroform. However, it may also be a sink for chloroform through soil degradation processes. Chloroform, a recalcitrant chemical, shows no ability to degrade aerobically, and is not biodegradable under denitrifying conditions (Bouwer & McCarty 1983; T. Borch et al. pers. communication). However, degradation under anaerobic conditions are quite efficient (Gupta et al. 1996a, b). The majority of biodegradation studies with chlorinated aliphatics have been conducted in batch, column and field experiments under saturated conditions with sufficient concentrations of organics to ensure reducing conditions. Only a few studies investigated the degradation kinetics of chloroform. Also, knowledge regarding the biodegradation of chlorinated aliphatics in unsaturated soils is very limited. T. Borch et al. (pers. communication) found no biodegradation of chloroform in an unsaturated organic farming soil under denitrifying conditions in contrast to a rapid degradation of compounds like tetrachloromethane. However, results indicated that 60% of the chloroform was biodegraded within 42 days in a similar experiment conducted in unsaturated anaerobic sludge. In both experiments, no abiotic degradation was observed for chloroform. In general, abiotic and biotic degradation of chloroform requires more time compared to tetrachloromethane and other chlorinated compounds with a higher degree of substrate halogenation, probably due to a lower relative standard potential of the less chlorinated compounds (Vogel et al. 1987).

The abiotic dechlorination of chlorinated aliphatics is often significantly slower in soil and ground water systems under natural conditions compared to the biotic degradation occurring in these environments. However, the importance of abiotic degradation should not be neglected due to the long residence times of chlorinated aliphatics in the environment. Abiotic degradation of chloroform with zero valent iron has been reported by Gillham and O'Hannesin (1994) and Roberts et al. (1996) and with 'green rust' by Erbs et al. (1999). Recently, Andrews and Novak (2001) reported degradation of chloroform at higher rates with increasing concentration of divalent iron and

Table 1. Detected release rates and calculated annual emissions of chloroform from forest soil. Ranges are in brackets

method	release rate [nmol m^{-2} day^{-1}]	emission[a] [Gg yr^{-1}]	reference
concentration gradient	6.7 (0.8–34)	4.9 (0.4–24)	Haselmann et al. 2000a
concentration gradient	24.3	10	Hoekstra et al. 2001
direct soil measurements	0.8	0.5	Haselmann et al. 2000a
laboratory incubation	100	75	Haselmann et al. 2000b
laboratory incubation[b]	159	118	Hoekstra et al. 1998b
direct flux measurements	67 (34–109)	50 (24–81)	Khalil & Rasmussen 2000

[a] emissions calculated from the release rates using an area of Northern temperate forest of 1.7×10^7 km^2.
[b] soil incubated with pure cultures of the fungi *Caldariomyces fumago*.

increasing pH. This might account for some of the enhanced degradation capacity observed in the presence of zero valent iron since the oxidation of zero valent iron results in increased levels of divalent iron and a higher pH. At present, no calculations have been performed to estimate the global biotic removal of chloroform in forest soil.

Global significance

To evaluate forest soils as a source of atmospheric chloroform, the data obtained from the field investigations were used to assess the emission rates of chloroform. An emission of 6.7 nmol m^{-2} day^{-1} was calculated by Haselmann et al. (2000a) with a range from 0.5 to 32 nmol m^{-2} day^{-1} corresponding to the lowest and highest release rates found in the soil of a sampling area. Extrapolation to Northern temperate forests, assuming constant emission with season, climate, forest age and soil type, leads to an annual emission of 4.9 Gg chloroform (range 0.4 to 24 Gg), which is in the same range as emissions reported by other authors (Table 1). Compared to the estimated annual chloroform emission of 700 Gg from all known natural sources, Northern temperate forests are apparently only a minor source (Table 2). However, the contributions of subtropical and tropical forests are yet unknown and may change the significance of forests as natural sources of chloroform in the environment.

Table 2. Biogenic and anthropogenic sources and sinks of chloroform

	annual average emission [Gg]	range [Gg]	reference
source – biogenic			
macroalgae[a]	0.84	0.009–3.1	Nightingale et al. 1995
microalgae[b]	23	7.9–49	Scarratt & Moore 1999
oceanic flux[c]	340		Khalil et al. 1999
forests[d]	4.9	0.4–24	Haselmann et al. 2000
soil[e]	200	100–400	Khalil et al. 1999
termites	100	10–100	Khalil et al. 1990b
rice fields[f]	23	7.7–50	Khalil et al. 1998
peatland ecosystems	4.7	0.1–150	Dimmer et al. 2001
source – anthropogenic			
pulp & paper manufacturing	34	25–43	Aucott et al. 1999
water treatment	22	7.9–35	Aucott et al. 1999
biomass burning	2		Lobert et al. 1999
biogas pits	0.000015	0.000006–0.00002	Khalil et al. 1990a
others	15	9–20	Aucott et al. 1999
sink			
chemical reactions with OH radicals	560		Keene et al. 1999
transport to stratosphere	2		Keene et al. 1999

[a] calculated with estimated global macroalgae biomass of 2.8 × 10^{14} g (Carpenter & Liss 2000).

[b] calculated with estimated global microalgae biomass of 1.44 × 10^{12} g chlorophyll *a* (calculated from data presented by Behrenfeld et al. 2001).

[c] oceanic flux minus emissions from micro and macroalgae.

[d] for Northern temperate forests.

[e] global land area excluding polar areas.

[f] calculated with estimated global rice field area of 1.45 × 10^{12} m^2 (Redeker et al. 2000).

In the past, it was thought that atmospheric chloroform was primarily from anthropogenic sources. A comparison of the annual emissions of chloroform from known anthropogenic and natural sources indicates that biogenic sources dominate the global annual chloroform input (Table 2, Figure 3). Of the estimated annual global released amounts of 700 Gg chloroform only 9.5% originate from anthropogenic sources. Although anthropogenic sources of chloroform are relatively insignificant at a global level compared to natural sources, it should be noted that industrial or other releases of chloroform, may have severe local or regional impacts when concentrated at specific point sources.

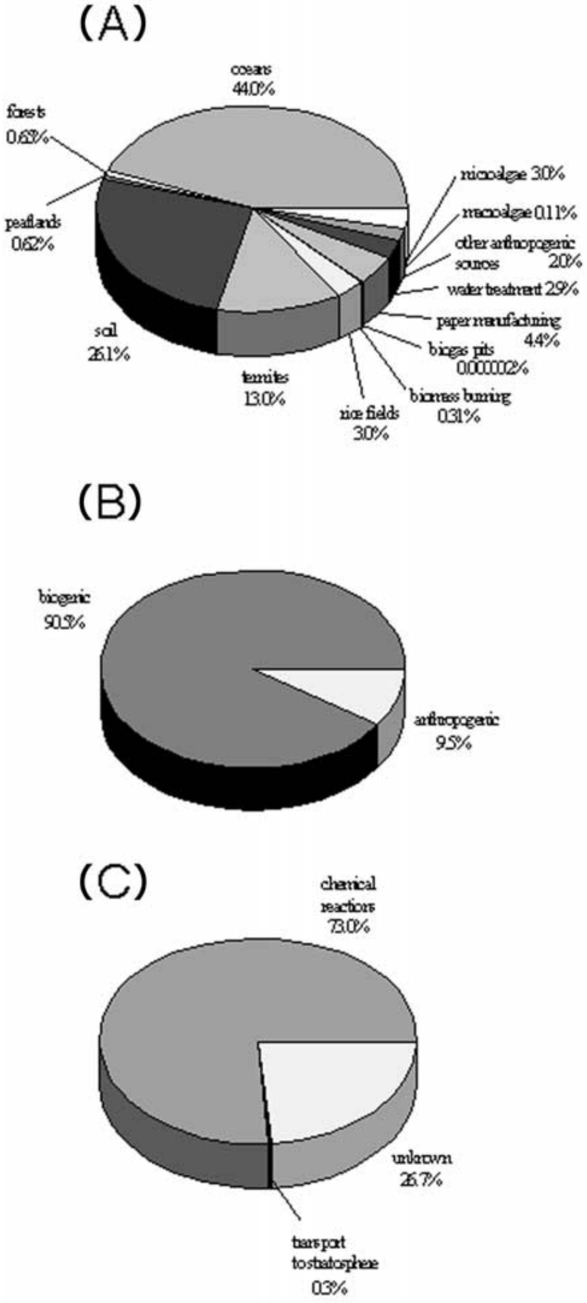

Figure 3. Percentage distribution of the annual global emissions of chloroform by anthropogenic and biogenic sources. (A) Biogenic and anthropogenic sources. (B) Comparison biogenic to anthropogenic chloroform input into the environment. (C) Sinks of chloroform in the atmosphere compared to estimated total atmospheric input.

Among the biogenic sources the oceans and the lands appear to be almost equal sources of chloroform emission. Although the terrestrial environment is only 29% of Earth's surface, it is an important contributor to the occurrence of chloroform in the environment. This is supported by looking at the observed interhemispheric differences in chloroform concentrations. The concentration distributions suggest substantially larger source strengths in the Northern Hemisphere, which contains only about 40% of the Earth's oceans (Keene et al. 1999).

The oceans have been estimated to account for about half of the annual emission of chloroform into the atmosphere. However, only two sources have been found to release chloroform inside the oceans: macroalgae and microalgae (Figure 3). The annual contribution from macroalgae to the global emission of chloroform is negligible. The contribution from microalgae is approximately 3% of the total atmospheric chloroform input, assuming that the results obtained in laboratory studies can be applied to the field. However, macro and microalgae contribute only 7% to the estimated annual emission of chloroform from the oceans. Apparently, there are other yet unknown sources inside the oceans responsible for the occurrence of chloroform. Possible sources can be volcanism, tectonic activities, cold vents, and other marine organisms.

A constant release of chloroform into the atmosphere and a removal occurs at the same time. The major sink for chloroform is reaction with hydroxyl radicals in the troposphere (Figure 3) resulting in an estimated atmospheric lifetime of about 0.5 years (Aucott et al. 1999). A small part of the total chloroform can be transported into the stratosphere and for example participate in the catalytical ozone destruction. In addition to these atmospheric processes, the oceans, soils, and other terrestrial ecosystems could be involved in removing chloroform from the atmosphere. A dualism may occur: ecosystems acting as a source in some locations and as a sink in other regions, or even as a source in some seasons and as a sink in another. The magnitude of these sinks is likely to be much smaller than the reaction with tropospheric hydroxyl radicals (Khalil et al. 1999). However, they may be the reason for the calculated imbalance between globally integrated emissions and tropospheric sinks (Figure 3).

Conclusion

Evaluation of global sources of chloroform shows that the influence of natural sources on the atmospheric release of chloroform is more significant than anthropogenic sources and dominates its tropospheric cycle. The estimated emissions from anthropogenic sources account for less than 10% of the estimated combined total emissions from all sources. Of the calculated annual biogenic global chloroform emission of 700 Gg, the marine and the terrestrial environments are nearly equally responsible. At present knowledge, forests are only a minor source in the total biogenic flux of chloroform, contributing less than 1% to the annual global atmospheric input. However, it should be noted that data are available for Northern temperate forests only. The large tropical forest areas may provide a yet unknown input of chloroform. The calculated emissions of chloroform from known biogenic and anthropogenic sources show a slight imbalance to the calculated losses due to reaction with hydroxy radicals and stratospheric destruction. However, the uncertainties in the source and budget calculations are so large that it is difficult to say whether the budget is or is not imbalanced by the known sources and the estimated emission rates (Khalil & Rasmussen 1999).

Acknowledgements

FL gratefully acknowledge financial support by EuroChlor, Belgium, for the presentation of parts of the manuscript at the AGU autumn meeting 2000, San Francisco, U.S.A. TB acknowledge support by Grant No. DAAD19-99-1-0092 from the United States Department of Defense, Army Research Office. The authors are grateful to Mark Shirtliff for comments and language corrections on the manuscript.

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