

Review Articles

Natural Formation and Degradation of Chloroacetic Acids and Volatile Organochlorines in Forest Soil

Challenges to Understanding

Frank Laturus^{1*}, Isabelle Fahimi², Milan Gryndler³, Anton Hartmann⁴, Mathew R. Heal⁵, Miroslav Matucha⁶, Heinz Friedrich Schöler², Reiner Schroll⁴ and Teresia Svensson¹

¹The Swedish Institute for Climate Science and Policy Research, ITUF, Linköpings universitet, 601 74 Norrköping, Sweden

²Institute of Environmental Geochemistry, University of Heidelberg, Im Neuenheimer Feld 236, 69120 Heidelberg, Germany

³Institute of Microbiology, Czech Academy of Sciences, Videnska 1083, CZ 142 20, Prague 4, Czech Republic

⁴Institute of Soil Ecology, GSF-National Research Centre for Environment and Health, Ingolstädter Landstrasse 1, 85758 Neuherberg, Germany

⁵School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK

⁶Institute of Experimental Botany, Czech Academy of Sciences, Videnska 1083, CZ 142 20, Prague 4, Czech Republic

* Corresponding author (frank.laturus@ituf.liu.se)

DOI: <http://dx.doi.org/10.1065/espr2005.06.262>

Abstract

Goal, Scope and Background. The anthropogenic environmental emissions of chloroacetic acids and volatile organochlorines have been under scrutiny in recent years because the two compound groups are suspected to contribute to forest dieback and stratospheric ozone destruction, respectively. The two organochlorine groups are linked because the atmospheric photochemical oxidation of some volatile organochlorine compounds is one source of phytotoxic chloroacetic acids in the environment. Moreover, both groups are produced in higher amounts by natural chlorination of organic matter, e.g. by soil microorganisms, marine macroalgae and salt lake bacteria, and show similar metabolism pathways. Elucidating the origin and fate of these organohalogen is necessary to implement actions to counteract environmental problems caused by these compounds.

Main Features. While the anthropogenic sources of chloroacetic acids and volatile organochlorines are relatively well-known and within human control, knowledge of relevant natural processes is scarce and fragmented. This article reviews current knowledge on natural formation and degradation processes of chloroacetic acids and volatile organochlorines in forest soils, with particular emphasis on processes in the rhizosphere, and discusses future studies necessary to understand the role of forest soils in the formation and degradation of these compounds.

Results and Discussion. Reviewing the present knowledge of the natural formation and degradation processes of chloroacetic acids and volatile organochlorines in forest soil has revealed gaps in knowledge regarding the actual mechanisms behind these processes. In particular, there remains insufficient quantification of reliable budgets and rates of formation and degradation of chloroacetic acids and volatile organochlorines in forest soil (both biotic and abiotic processes) to evaluate the strength of forest ecosystems regarding the emission and uptake of chloroacetic acids and volatile organochlorines, both on a regional scale and on a global scale.

Conclusion. It is concluded that the overall role of forest soil as a source and/or sink for chloroacetic acids and volatile organochlorines is still unclear; the available laboratory and field data reveal only bits of the puzzle. Detailed knowledge of the natural degradation and formation processes in forest soil is important to evaluate the strength of forest ecosystems for the emission and uptake of chloroacetic acids and volatile organochlorines, both on a regional scale and on a global scale.

Recommendation and Perspective. As the natural formation and degradation processes of chloroacetic acids and volatile organochlorines in forest soil can be influenced by human activities, evaluation of the extent of this influence will help to identify what future actions are needed to reduce human influences and thus prevent further damage to the environment and to human health caused by these compounds.

Keywords: Chloroacetic acids; degradation; forest decline; forest soil; human impact; natural formation; ozone destruction; volatile organochlorines

Introduction

Chlorine-containing compounds have for a long time been considered to be of industrial origin only, with the presumption that production and emission of these compounds could easily be controlled and regulated in the event that they caused a threat for life on Earth. In the last decades, environmental problems such as stratospheric ozone destruction, large-area contaminations e.g. by oil spilling, or food contamination by pesticide application, have shifted chlorine-containing compounds of anthropogenic origin into the focus of human society. As a consequence, organochlorine compounds have been greatly investigated and are now under considerable scrutiny. However, alongside findings that chlorinated organohalogen are responsible for severe environmental damage it was discovered that a large variety of chlorine-containing compounds are also produced naturally

(Asplund et al. 1993, Müller et al. 1996). Forest ecosystems, for example, have been found to be an important natural source for organohalogenes (Khalil et al. 1999, Keppler et al. 2000, Laturus et al. 2002, Öberg 2003). However, information about the participation of natural processes in environmental issues is still scarce, and nothing is known so far about how the natural production of chlorine-containing substances is affected by human-induced environmental pollution or climate changes.

Among chloroacetic acids (CAA), trichloroacetic acids (TCAA) is known as a herbicide used to control weeds in brassicas and similar crops, first introduced in the late 1940s (see Lewis et al. 2004). Today its use is discontinued due to regulatory pressure and because new herbicides more effective at lower concentrations are now available (McCulloch 2002). In addition to industrial production as herbicides or generated as drinking water disinfection byproducts, other anthropogenic sources of CAA are formation during photochemical degradation of certain volatile organochlorines (VOCl), and during paper production (Juuti et al. 1993). As CAA are highly soluble in water they prefer to accumulate in the hydrosphere (McCulloch 2002). Thus, most of the CAA formed in the atmosphere are rapidly washed-out and accumulate in soil water, groundwater, river and lake water. The concentrations determined in waters vary from $<10\text{--}7100\text{ ng L}^{-1}$ (Berg et al. 2000). Owing to the hydrophilic character of CAA, chronic human exposure to these chemicals can occur. The toxicity of CAA with respect to their LD_{50} values is $\text{DCAA} > \text{TCAA} > \text{MCAA}$ (Bhat et al. 1991) (where TCAA, DCAA and MCAA refer to tri-, di- and monochloroacetic acid, respectively).

Volatile organochlorines (VOCl) have been under scrutiny since the mid-1980s when the discovery was made that certain chlorine-containing volatile organic compounds are participating in the destruction of stratospheric ozone (e.g. Krüger et al. 1987). As a result of the severe loss of ozone every year in the stratosphere over the Polar Regions – a loss popularly known as 'the ozone hole' – politicians of major industrial nations reacted and agreed on controlling and banning the production and use of certain chlorine-containing compounds, such as chlorofluorocarbons (CFCs), bromochloromethane (CH_2BrCl) and tetrachloromethane (CCl_4), which were found to have a large effect in stratospheric ozone destruction (UNEP 1987, Wellburn 1994). Alongside compounds already defined as ozone-depleting-substances, several other reactive chlorine-containing compounds are released into the atmosphere from anthropogenic sources (Keene et al. 1999).

These chlorine-containing substances are widely used as solvents, fuel components, as intermediates in the chemical industry, and as additives to many manufactured products, including paints, adhesives, gasoline, and plastic (Collins et al. 2002). As a result of this widespread use VOCl are found worldwide. Their major anthropogenic sources to the atmosphere are fossil-fuel combustion, incineration, industrial release (primarily pulp and paper manufacturing and water treatment) and biomass burning (Keene et al. 1999). Additionally, point sources such as leaking underground storage

tanks, process sewer lines, septic tanks, landfilling, waste disposal pits and detention basins have led to an introduction of VOCl into groundwater and into the marine environment (Baehr et al. 1999, Dewulf et al. 1998, Krysell and Nightingale 1994, Squillace et al. 1999). Although some VOCl are not yet formally referred to as ozone-depleting substances, they undoubtedly could contribute to stratospheric ozone destruction. The question is: to what extent? The answer requires knowledge of the relevance and size of both anthropogenic emission and natural emissions.

The aim of the review is to provide an overview on the available knowledge on the natural formation and degradation of CAA and VOCl in forest soils. The two compound groups are related to each other via the fact that CAA can be derived from the atmospheric photooxidation of some VOCl. For example, airborne trichloroethene and tetrachloroethene either of anthropogenic or natural origin can be photochemically metabolised into the phytotoxic compound trichloroacetic acid (Weissflog et al. 2004a). Processes especially occurring in the soil and in the rhizosphere are emphasised as being of importance for both the production and degradation of organohalogen compounds. An overview on these processes is given in Fig. 1. However, it should be noted that data available on these soil processes are still scarce leading to only a vague picture of what happens in soil. Thus, the second part of the review highlights the gaps in the current knowledge of natural processes in forest soils. Future studies are proposed to fill the gaps and to understand the possible influence of human activities on these natural processes.

1 Present knowledge on Natural Processes

1.1 Chloroacetic acids (CAA)

1.1.1 Concentrations

Concern over CAA in soil is dominated by the concentration and behaviour of trichloroacetic acid (TCAA). Environmental TCAA is particularly linked with conifer forests because it has been observed to accumulate in conifer needles and is found in the soil of coniferous forests (Frank 1988). Measurements of soil TCAA concentrations vary widely, from <0.05 to a few $100\text{ }\mu\text{g kg}^{-1}$ (McCulloch 2002, Peters 2003, Stidson et al. 2004a). The PNEC (predicted no effect concentration) in the soil is $2.4\text{ }\mu\text{g kg}^{-1}$. A study in the Black Forest area showed the predicted environmental concentration of TCAA to far exceed the PNEC, indicating a clear risk for the forest ecosystem and a requirement for reduction measures (Fahimi 2003).

The variation of TCAA concentrations in soil is probably due to the considerable heterogeneity of soil properties both within and between sampling locations. There is a general consensus that concentrations of TCAA are highest in the more aerobic soil layer (O horizon) and decrease with depth. Highest TCAA concentrations appear to be particularly associated with soils of high organic matter content underlying coniferous forests (McCulloch 2002, Peters 2003, Stidson et al. 2004a). Differences between analytical procedures also seem likely to contribute to variations in measured soil TCAA concentration. These issues are discussed below.

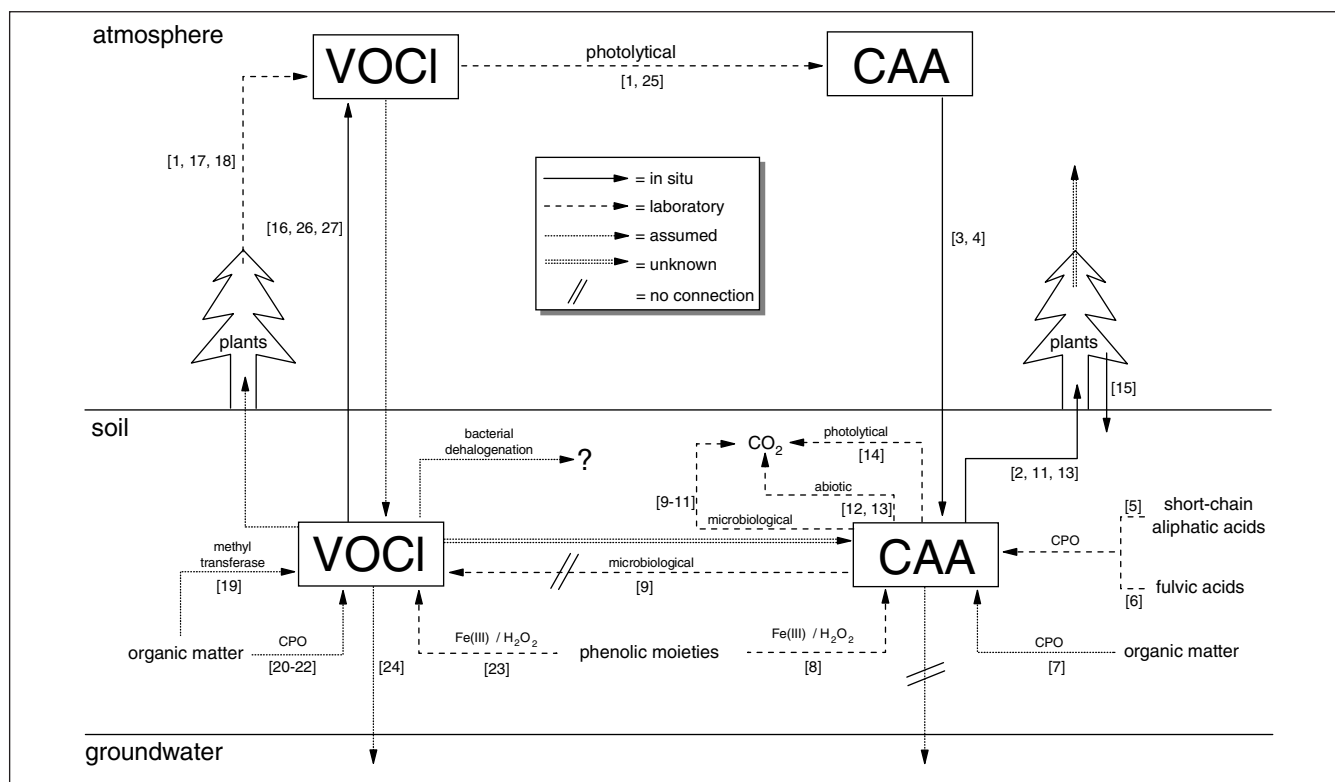


Fig. 1: Pathways and links of chloroacetic acids (CAA) and volatile organochlorine compounds (VOCl) in forest ecosystems. References in brackets: [1] Weissflog et al. (2004), [2] Matucha et al. (2001), [3] McCulloch (2002), [4] Stidson et al. (2004), [5] Haiber et al. (1996), [6] Niedan et al. (2000), [7] Hoekstra (2003), [8] Fahimi et al. (2003), [9] Matucha et al. (2003b), [10] Forczek et al. (2001), [11] Heal et al. (2003), [12] Schröder et al. (2003), [13] Dickey et al. (2004), [14] Lifongo et al. (2004), [15] Stidson et al. (2004b), [16] Haselmann et al. (2000), [17] Yokouchi et al. (2002), [18] Gribble (2003), [19] Wuosmaa and Hager (1990), [20] Asplund et al. (1993), [21] Laturus et al. (1995), [22] Hoekstra et al. (1998), [23] Keppler et al. (2000), [24] Laturus et al. (2000), [25] Frank et al. (1994), [26] Hoekstra et al. (2001), [27] Hamilton et al. (2003)

1.1.2 Biotic and abiotic formation

The existence of natural processes leading to TCAA formation in soils has been inferred indirectly in a number of studies that have sought to account for the observed concentrations of TCAA in soil. For example, attempts to quantify the TCAA budget in forest soil by synthesis of existing literature data (Hoekstra et al. 1999b, Schöler et al. 2003) or by direct measurement of the rain and forest throughfall input at a single location (Stidson et al. 2004) have all concluded that the measured soil TCAA burden was most likely maintained by an in-situ production of TCAA within the soil.

The suggested route of TCAA formation (and of other CAA) in soil is via chlorination of organic material, analogous to the well-known production of CAA via chlorination of humic material during drinking water treatment (Liang and Singer 2003). There is evidence for both biological and non-biological chlorination processes in soils. In laboratory model experiments, Haiber et al. (1996) showed that TCAA was produced when commercial humic acid and a range of short-chain aliphatic acids were incubated with commercial chloroperoxidases (CPO) in the presence of sodium chloride and hydrogen peroxide (H₂O₂). Optimum chlorination occurred at pH 3-6. Similarly, Niedan et al. (2000) showed TCAA and DCAA production via incubation of fulvic acid with commercial CPO (plus chloride and H₂O₂). It is not yet clear whether CPO exists in real soil, although halogen-

ating activity has been reported in soil extracts (Asplund et al. 1993, Laturus et al. 1995). Combining the above observations with the observed positive correlation between TCAA in soil and trichloromethane (CHCl₃) in soil air, Hoekstra et al. (1999a) concluded indirectly that TCAA (and CHCl₃) were probably products of biological activity in soil. Hoekstra (2003) proposed that the mechanism was CPO chlorination mediated by hydrochlorous acid (HOCl). Recently, the production of CAA in laboratory soil experiments without addition of CPO (but still possibly biologically mediated) has been demonstrated via use of ³⁶Cl labelling (Matucha et al. unpublished).

An abiotic route to CAA formation in soil has also been demonstrated in a model system. Fahimi et al. (2003) showed that MCAA, DCAA and TCAA could all be produced probably via Fenton-like reactions between Fe(II), Fe(III) and H₂O₂ acting (in the presence of chloride) on phenolic moieties such as ethoxyphenol and catechol used as model substances of monomeric units of humic acids. The humus, iron and chloride ingredients required for this abiotic route of CAA formation are widespread in soil.

Although all the above mentioned evidence for CAA formation processes in soil is indirect, it seems reasonable to assume that both biotic and abiotic processes can contribute to CAA production in real soil under natural conditions. Both laboratory and field measurements indicate a strong

correlation of the formation of CAA, soil microbial biomass and organic matter content (Heal et al. unpublished), although clearly soil oxidants, such as iron and H_2O_2 seem to be likewise important factors for the abiotic production. There is currently no information as to the extent, if any, of deep-soil transportation of CAA. Instead, it is well-known that TCAA is found in stream and bog waters draining through TCAA-containing soils (Haiber et al. 1996, Stidson et al. 2004a), thus CAA mobility is likely to be dominated by bulk soil hydrology and plant uptake.

1.1.3 Biotic and abiotic degradation

There is widespread evidence that TCAA is degraded when applied to soils. Experiments evaluating the fate of TCAA derivatives applied as a herbicide seem to indicate mineralisation to CO_2 and chloride, although these observations relate to doses of tens of mg kg^{-1} , several orders of magnitude higher than current ambient soil TCAA concentrations (Barrons and Hummer 1951, Foy 1975, McGrath 1976, Lignell et al. 1984). More recent studies have applied TCAA to soil at concentrations closer to, although still higher than, ambient. Extensive work has been undertaken with $[1,2-^{14}\text{C}]$ -labelled TCAA. Using this tracer it has been shown that TCAA applied to fresh forest soil is rapidly degraded in the soil, producing $^{14}\text{CO}_2$ and no other gaseous (i.e. CO , CH_4 , CHCl_3) degradation product (Matucha et al. 2003a). $[1,2-^{14}\text{C}]$ DCAA was degraded even faster than $[1,2-^{14}\text{C}]$ TCAA (Matucha et al. 2003b). Under laboratory conditions a major portion of the radioactivity is released from soil within 2–3 days after application while only a minor part is translocated into and accumulated in needles. A portion of the radioactivity remains bound in the soil. In contrast, the release of $^{14}\text{CO}_2$ from autoclaved soil was negligible (Matucha et al. unpublished). These observations strongly suggest, at least under laboratory conditions, a microbiological (i.e. bacterial, actinomycetous or fungal) degradation, with the radioactivity remaining in the soil probably due to incorporation into microbial biomass. In other experiments in which TCAA was applied to soil/seedling systems it has likewise been inferred that, alongside translocation of TCAA into seedlings, the majority of the applied TCAA was probably degraded in-situ in the soil (Forczek et al. 2001, Matucha et al. 2001, Heal et al. 2003, Dickey et al. 2004). Similarly, TCAA was degraded (on timescale of just a few days) when applied to soil lysimeters, but with degradation slower in the litter layer (Schröder et al. 2003) and in soil sterilised by γ -irradiation (Heal et al. unpublished), again suggesting biological involvement. The rate of degradation of CAA in soils seems to depend on environmental factors such as soil humidity and temperature (Matucha et al. 2003a). The highest rate of degradation was observed at ~30–40% soil water content, which is a humidity level favouring microbial activity. The degradation rate also seems to increase with temperature, being lowest at 4°C, but with almost no difference between 15 and 23°C. Matucha et al. (2004) also report a possible loss of TCAA from soil during soil extraction with water by microbial degradation, which may contribute to the confusing disparity amongst reported soil TCAA concentrations. The wide range of TCAA concentrations presented in the literature that have not yet been satisfactorily explained mainly

due to insufficient data on the characteristics of the soil, which are needed to identify whether any explanatory relationship exists.

The abiotic decarboxylation of CAA is slow but probably not a negligible process at ambient temperatures. Although CAA have been shown to degrade photolytically in aqueous solution with half-lives of less than a few days (Lifongo et al. 2004). This abiotic degradation route will not be important within soil.

The available experimental results suggests that the ubiquitous evidence for the degradation of CAA (TCAA in particular) in soil is most likely due to biotic rather than abiotic processes. The bacteria *Pseudomonas sp.*, *Arthrobacter sp.* and *Pseudomonas dehalogens*, and the fungus *Trichoderma viride* have specifically been identified as capable of degrading TCAA via dehalogenation to CO_2 and chloride (Weightman et al. 1992). Yu and Welander (1995) have also isolated and characterised aerobic bacteria which can grow using TCAA as their sole source of carbon.

1.2 Volatile organochlorines (VOCl)

1.2.1 Occurrence

Recent research has revealed the terrestrial environment as a source for VOCl (Table 1).

Terrestrial emissions of trichloromethane, chloromethane and chloroethene into the atmosphere have been discovered (e.g. Keppler et al. 2000, Keppler et al. 2002, Laturnus et al. 2002, McCulloch 2003, Yokouchi et al. 2002). However, although different soil types such as forest soils, salt marshes, wetlands, and rice paddies have been found to release VOCl (see Table 1), there is almost no information on the specific source(s) and underlying formation processes. Nevertheless, it is believed that the atmospheric emissions from terrestrial sources are large relative to the industrial input (Khalil et al. 1999, McCulloch 2003). For example, it has been calculated that around 30% of the annual global natural emission of trichloromethane is probably released from soil (Laturnus et al. 2002) and that up to 35% of the total annual atmospheric input of chloromethane may originate from natural terrestrial sources (Keene et al. 1999). Overall, it has been estimated that forest soil, especially spruce forest soil, contributes up to 25% of the total natural global emission of VOCl from soil (Laturnus et al. 2002).

The formation of trichloromethane has been detected in laboratory studies of incubated temperate forest soil (Haselmann et al. 2002). There are also indications of a formation of trichloromethane and degradation of chloromethane in tropical forest soils (Khalil and Rasmussen 2000). Tetrachloromethane (CCl_4), 1,1,1-trichloroethane ($1,1,1\text{-C}_2\text{H}_3\text{Cl}_3$), trichloroethene (C_2HCl_3) and tetrachloroethene (C_2Cl_4) are found in forest soil – probably due to a transfer from the atmosphere – but no studies on the natural formation routes of these compounds have been performed (Haselmann et al. 2002, Haselmann et al. 2000, Hoekstra et al. 2001, Laturnus et al. 2002). It appears that forest soils have a dual function with respect to VOCl: acting as a source for organic chlorine released to the atmosphere, and probably also acting as a sink (Khalil and Rasmussen 2000).

Table 1: At present identified terrestrial sources of volatile chlorinated compounds

Source/ecosystem	Identified compounds	References
Coniferous forest soil	CHCl ₃ , C ₂ H ₃ Cl	(Haselmann et al. 2000, Keppler et al. 2002, Hoekstra et al. 2001, Laturnus et al. 2000)
Deciduous forest soil	CH ₃ Cl, CHCl ₃ , C ₂ H ₃ Cl	(Haselmann et al. 2000, Keppler et al. 2002)
Grassland	CH ₃ Cl, CHCl ₃	(Haselmann et al. 2000, Keppler et al. 2000)
Salt marshes	CH ₃ Cl, C ₂ H ₃ Cl	(Rhew et al. 2000, Keppler et al. 2002)
Peatlands	CH ₃ Cl, CHCl ₃ , C ₂ H ₃ Cl	(Dimmer et al. 2001, Keppler et al. 2002)
Wetlands	CH ₃ Cl	(Varner et al. 1999)
Shrublands	CH ₃ Cl	(Rhew et al. 2001)
Rice fields	CHCl ₃	(Khalil et al. 1998, Redeker et al. 2000)
Soil	CH ₃ Cl, CHCl ₃	(Harper 1985, Khalil and Rasmussen 1999, 2000)
White-rot fungi	CH ₃ Cl	(Harper 1993)
Leave decay	CH ₃ Cl	(Hamilton et al. 2003)
Tropical plants	CH ₃ Cl	(Yokouchi et al. 2002)
Termites	CHCl ₃	(Khalil 1990)
Biogas pits	CHCl ₃	(Khalil 1990)
Cultivated mushrooms, potato tubers, pencil cedar, northern white cedar, evergreen cypress	CH ₃ Cl	(Gribble 1996)
Barley	C ₂ Cl ₂	(Gribble 1996)
Deciduous mosses, drill wells, mine gas, minerals, lemon, orange, barley, mushrooms	CHCl ₃	(Gribble 1996)
Terrestrial plants	CCl ₄	(Gribble 1996)
Volcanoes	CFCl ₃ , CF ₂ Cl ₂ , CHCl ₃ , C ₂ Cl ₄	(Isidorov 1990, Jordan 2000)
Earth crust	CHCl ₃ , C ₂ Cl ₄ , CFCl ₃	(Isidorov 1990)

1.2.2 Biotic processes

Forest soil organisms and plants have been investigated as sole emitters of VOCl (e.g. Khalil 1990, Yokouchi et al. 2002). In laboratory experiments wood-rotting fungi produced significant amounts of chloromethane (Watling and Harper 1998). These fungi are the only microorganisms studied for the formation of VOCl so far. Other sources of VOCl identified in forest ecosystems were reviewed by Gribble (1996 and 2003) and include the emission of chloromethane by cultivated mushrooms, by pencil cedar, by northern white cedar and by evergreen cypress, the emission of trichloromethane from deciduous mosses and mushrooms, and the emission of tetrachloromethane by terrestrial plants. In addition, the emission of chloromethane from early decaying leaves was reported in a recent study (Hamilton et al. 2003). The authors suggested chloromethane formation by methylation of chloride through methyl units found in pectin located in the leaf cell walls. However, although this process only occurred at temperatures from 30°C to 350°C, and thus the suggested formation process might only be valid in tropical forest soils or during the abiotic process of biomass burning, suggested the authors that the amounts of chloromethane formed during this process can count for most of the missing chloromethane in the atmospheric budget. In summary, although it appears that a variety of organisms are capable of producing VOCl, the number of performed studies is limited and consequently it is difficult to establish reliable estimates of the contribution and strength of forest soil as a source of these compounds. As described in section 1.3, processes in the (myco)rhizosphere are probably highly rel-

evant for organohalogen production, although this microhabitat has not been much discussed as a possible 'hot-spot' of organohalogen dynamics. Furthermore, biotic production of trichloro- and tetrachloroethene by marine macroalgae which may enter the forest ecosystems in coastal areas was reported Laturnus et al. (2005). A relationship between VOCl, formed in salt lakes by halobacteria, and CAA, formed by oxidation of tetrachloroethene in plants, and their phytotoxic affects on vegetation has recently been reported by Weissflog et al. (2004a, b), Lange et al. (2004) and Kotte (2004), indicating a further link between VOCl and CAA in forest ecosystems.

The exact mechanisms for the biological formation of VOCl in soil remain unclear but are suggested to parallel those in the marine environment (Geigert et al. 1984, Walter and Ballschmiter 1992, Wever and Hemrika 2001). It has long been known that a number of forest soil microorganisms can use chloride for the conversion to organic chlorine (Clutterbuck et al. 1940, Hunter 1987, Öberg 2002). It is also known that some microorganisms are involved in the formation of VOCl (Harper 1985, Hoekstra et al. 1998). Thus chlorination of organic matter by chloroperoxidase (CPO) enzymes is a likely source of VOCl, as postulated for CAA formation in soil. This enzyme group is known to oxidise halide ions such as chloride (Cl⁻), bromide (Br⁻) and iodide (I⁻) in the presence of H₂O₂ to form reactive intermediates such as hypochlorous acid (HOCl) (Neidleman and Geigert 1986). The reactive intermediates could chlorinate organic matter followed by the formation of volatile organochlorines. However, as stated before (see section 1.1.2), so far only

chlorinating-activity of forest soil has been demonstrated (Asplund et al. 1993, Laturnus et al. 1995); the soil enzymes behind the halogenation have not been isolated. Studies of the conversion of chloride to organic chlorine used a chloroperoxidase isolated from the marine fungi *Caldariomyces fumago* (Asplund et al. 1993, Hoekstra et al. 1995, Haiber et al. 1996, Niedan et al. 2000). Another enzyme group, the methyl transferases, is also suggested to be involved in the formation of VOCl. The activity of methyl transferase, which is able to catalyse the methylation of chloride and bromide (Wuosmaa and Hager 1990), has been detected in a white-rot fungi (*Phellinus pomaceus*). The enzyme uses S-adenosyl methionine as a methylating agent to synthesise monohalomethanes such as chloromethane (Saxena et al. 1998, White and Broadley 2001).

1.2.3 Abiotic processes

Natural abiotic halogenation reactions are also established but little investigated, particularly under real soil conditions. Thermodynamic considerations show it is possible that halide ions may form organohalide compounds naturally by purely chemical processes known to occur in vitro. Recently, an abiotic halogenation reaction was proposed by Keppler et al. (2000) in which the oxidation of phenolic moieties containing alkoxy groups by reduction of partner Fe(III) to Fe(II) is coupled to the alkylation of halides (Cl⁻, Br⁻, I⁻) also present. The methyl, ethyl, propyl and butyl alkyl halides so formed thus represent degradation products of oxidised organic matter. As organic matter in soil displays a highly complex polymeric structure, it is difficult to elucidate the chemical reactions taking place, so small molecules – so-called model compounds – are used to represent the structural elements or redox features of the organic matter in laboratory experiments. Widely accepted model compounds for aromatic structures are catechol, hydroquinone, resorcinol, guaiacol and 2,3-dihydroxybenzoic acid. One of these natural monomeric constituents, guaiacol, was used as a methyl-group donor for the oxidation reaction with dissolved Fe(III) or with the mineral ferrihydrite (5 Fe₂O₃ · 9 H₂O) and halides. Methyl halides, Fe(II) and o-quinone have been identified as reaction products. It is assumed that methyl halides are produced in an almost synchronous reaction scheme: (1) the oxidation of guaiacol by ferrihydrite and (2) nucleophilic substitution of the methyl group by halide.

Keppler et al. (2002) recently described a natural formation of the reactive intermediate chloroethene (vinylchloride) in soil. Catechol was used as a model compound for the redox-sensitive functional aromatic groups of soil organic matter and the corresponding o-quinone as the intermediate precursors for chloroethene. Previous laboratory experiments with catechol have shown that it can be oxidised by Fe(II), producing CO₂ and Fe(II) (Pracht et al. 2001) and, if halides are present, alkyl halides are formed. The chloromethane/chloroethene ratio was approximately eight. There was no chloroethene or chloromethane formation when Fe(III) was absent. Moreover, no chloroethene production was observed when using H₂O₂ as sole naturally occurring-oxidant. When both oxidants Fe(III) and H₂O₂ were applied the chloroethane

production increased significantly, probably caused by Fe(III), which initiated a Fenton reaction by which H₂O₂ and Fe(II) generate hydroxyl radicals. The pre-requisite Fe(II) is provided by the reaction of catechol with Fe(III). OH radicals are powerful oxidants and could be responsible for the augmented formation of chloroethene and chloromethane.

From studies on the anthropogenic use of HOCl in disinfection, bleaching and detoxification processes, the trichloromethane/TCAA ratio was found to depend on the structural elements of the humic material present in the water (Hoekstra 2003). At pH < 7 TCAA formation was favoured, and vice versa at pH > 7. Hoekstra et al. (1999c) showed a strong positive correlation between trichloromethane and TCAA in soils. This correlation may indicate that TCAA can be decarboxylated to trichloromethane in soil or that both compounds are products from the same educt. The former is unlikely since chemical decarboxylation of TCAA to trichloromethane under soil conditions is expected to be very slow (section 1.1.3).

1.3 Natural processes in the rhizosphere

1.3.1 Ecology of the rhizosphere soil compartment

The involvement of microbial processes directly or indirectly in the formation and degradation of CAA and VOCl in forest soil implies a prominent role for the rhizosphere. The rhizosphere compartment of soils is characterised by a high availability of labile organic compounds from plant root exudates, which provide favourable nutrient conditions for microbes (Brimecomb et al. 2001). The rhizosphere of forest trees should be mostly considered as mycorrhizosphere because of the abundantly occurring symbiosis of fungi with the roots of forest trees. The (myco)rhizosphere is colonised by a high density of microbes of much higher activity than the non-rhizosphere soil (Hartmann et al. 2004, Mogge et al. 2000). Recently, hitherto mostly unexplored rhizosphere habitats for microorganisms have come into focus: the endorhizosphere (Kobayashi and Palumbo 2000) and the interior of fungal hyphae and spores (Bertaux et al. 2003, Bianciotto et al. 2000). In the root interior – from the rhizodermis to the vascular system – are present endorhizal microbial communities consisting of non-pathogenic bacteria or fungi (Lodewyckx et al. 2002). A diversity of root endophytic bacteria was found both in woody (Brookes et al. 1994) and gramineous plants (James and Olivares 1997). In addition, a systemic colonisation of the whole plant was frequently reported. Therefore, the metabolic activity of the (myco)rhizosphere probably comprises the whole microbial community in interaction with the roots. The high oxygen demand of this 'meta-community' arising from the large carbon supply means that oxygen can get exhausted in this micro-compartment, especially under wet conditions with limit oxygen diffusion. On the other hand, due to the oxygen supply of plant roots, an oxygen gradient is generated in the rhizosphere especially under wet conditions. In this way, microaerobic or anaerobic micro-sites may be temporarily created (likewise in the vicinity of degrading fresh organic debris such as leaves) leading to so-called 'hot-spots' of microbial activity.

1.3.2 Formation of CAA and VOCl in the rhizosphere compartment

The highly active organism community of the rhizosphere and mycorrhizosphere leads to strong competition for macro- and micro-nutrients. For the mobilisation and uptake of essential mineral nutrients and trace elements such as iron, specific scavenging molecules, the siderophores (Neilands 1995), are produced to circumvent limitations in supply. Siderophores are extremely efficient natural Fe(III)-complexing molecules, which can be grouped as dihydroxybenzoate compounds, such as enterobactin, produced by *Enterobacter* spp., or compounds with hydroxamate moieties, such as ferrichrome, produced, for example, by *Ustilago* spp. Siderophores are used by microbial populations to out-compete other populations in the colonisation of the rhizosphere and mycorrhizosphere by iron starvation (Ratledge and Dover 2000) or by pathogens to colonise their host (Wandersman and Delepelaire 2004). Gramineous plants are known to excrete the siderophore mugineic acid under iron-limiting conditions to mobilise iron from soil for the uptake by the plant roots (Sugiura and Nomoto 1984). Therefore, both plant and microbial siderophores are abundantly produced in the rhizosphere and are also stabilised in the soil matrix (Powell et al. 1983). Under anaerobic conditions, solubilised ferric iron can be reduced by numerous bacteria for energy production (Lovley 1991). Thus, Fe(II) which has the potential to generate reactive oxygen species (Halliwell and Gutteridge 1984) occurs in the rhizosphere. As a final consequence, CAA or VOCl could thus be produced at high rates in the rhizosphere in the presence of chlorine and organic substances.

1.3.3 Influence of the rhizosphere on the degradation of CAA and VOCl

The metabolic activity and diversity of the soil microflora is governed by the availability of organic and/or inorganic constituents and the existing oxygen or redox regime (Stotzky 1997). Due to the enhanced metabolic activity in the rhizosphere, endorhizosphere or mycorrhizosphere compartments, co-metabolic degradation of VOCl probably occurs in these 'hot spots' of microbial activity (Sorensen 1997). Oxygenolytic dehalogenation by microbes is catalysed by mono- or dioxygenases and the halogen substituent is replaced by oxygen from O₂ (Lengeler et al. 1999). In the hydrolytic dehalogenation by halohydroxylases, the halogen is replaced by a hydroxyl-group derived from water. Furthermore, a so-called 'thiolytic' dehalogenation can occur in microbes catalysed by glutathione S-transferases (GST), forming a glutathione conjugate which is later hydrolysed. This type of reaction could also be performed by plant GSTs after the compound is taken up by the roots. Organic compounds with a K_{ow} between 0.5 and 3.5 can be taken up and degraded by endophytic microbes or by plant enzymes (Trapp et al. 1994). Microbial dehydrohalogenation by HCl-elimination, leading to the formation of a double bond, and an intramolecular substitution of vicinal haloalcohols by displacement of an OH-group, yielding epoxides are also known to be initial reactions in microbial dehalogenation of organohalogenes.

In the case of limiting oxygen supply, or anaerobiosis, which occurs in 'hot-spot' micro-sites under wet conditions, anaerobic dehalogenation of organohalogen compounds is catalysed by a high microbial diversity (Hollinger et al. 1999, Smidt and de Vos 2004). In these reactions, the halogen is replaced by hydrogen and metabolic energy is generated in this process. However, the efficiency of this type of dehalogenation is usually much lower compared to aerobic conditions and is known to be dependent on the absence of alternative carbon compounds (Gibson and Harwood 2002). Under anaerobic conditions, acetogenic bacteria also contribute to the degradation of organohalogenes (Drake et al. 1997). This diverse group of bacteria (including several *Acetobacterium* and *Clostridium* spp.) produce acetate by reducing CO₂ and oxidising a variety of organic and inorganic (H₂) electron donors. The metabolic versatility of acetogenic bacteria is very high; and organohalogen compounds have been used as electron donors while diverse electron acceptors and reduced end-products are generated (Drake et al. 1997).

2 Perspectives

2.1 Method development

Careful evaluation of the methods used for soil analysis is required to correctly interpret comparisons of the results (for a general review on methods for e.g. TCAA analysis see Lewis et al. 2004). Standard procedures have to be established on how to sterilise, sample and store soils, and how to analyse CAA and VOCl. At present, experiments seeking to quantify biotic and abiotic formation and degradation processes of CAA and VOCl in natural soil systems face the following difficulties: (i) ensuring that the properties of soils used in experiments remain representative of the natural forest soil system from which they were sampled, (ii) adequately characterising the impacts of soil heterogeneity, (iii) understanding the limitations of the applied analytical methodology, (iv) deriving an adequate sterile soil control.

For example, the two main approaches to TCAA analysis in soil are extraction of TCAA into aqueous solution, followed by derivatisation and analysis by gas chromatography (GC) (e.g. Frank et al. 1990), or thermal decarboxylation of TCAA in the whole sample to CHCl₃ and analysis of the latter by headspace GC (e.g. Plumacher and Renner 1993). Since the two methods measure different target analytes (water-extractable TCAA versus whole-soil TCAA), the soil TCAA concentration is unavoidably operationally defined. No inter-comparison study on the same soil sample can resolve this issue, since it is not possible to demonstrate conclusively that extraction methods extract all intrinsic soil TCAA, or that there is no interference in the decarboxylation method. For VOCl, the approach so far to detection in soil is collection of soil air and analysis by GC (e.g. Laturus et al. 2000, Hoekstra et al. 2001). Besides that the method is highly affected by soil temperature, it probably leads to the detection of only a portion of intrinsic soil VOCl. Although this method is suitable to measure the amounts of VOCl released from soil into air, and further into atmosphere, it may give false impressions on the actual VOCl concentrations in soil.

The goal for soil CAA and VOCl measurement is to develop methods to reliably detect the total concentration of these compounds in soil and to standardise methods of sample collection, storage and preparation; for example, parallel measurements of fresh soil parameters, such as pH, water content, organic matter content, temperature of soil storage (e.g. +4°C, -20°C or -80°C), and sieving parameters could be useful, and for extraction methodologies: use of buffered extraction, duration of extraction, method of shaking during extraction should be uniform. Possible methods of soil sterilisation include irradiation, high temperature and pressure (autoclaving), and chemical treatment, but each method has its limitations. Autoclaving leads to profound physico-chemical changes of the soil and may destroy exocellular soil enzymes on the one hand, but not all soil microorganisms on the other. Chemical (or antibiotic) fumigation of soil cannot ensure total sterilisation and usually requires good mixing which again changes the soil character. Irradiation with γ -rays can be performed on intact soil samples, so it is usually considered the most non-destructive sterilisation method, but high-energy free radicals may be generated which can interfere with observations of subsequent chemical processes. As with analyte determination, the practical goal is probably not to standardise just one method of sterilisation but to ensure that workers standardise procedures for each method separately.

2.2 Chloroacetic acids

As extensively discussed above, the knowledge of the biotic and abiotic generation/degradation of CAA in forest soils is very limited. It is not clear whether, and under which environmental conditions, forest soils can act as a sink or source of CAA. To address these issues, strategies that were formerly developed to study the fate of herbicides in agricultural soils could be used to investigate CAA in forest ecosystems, but at the lower concentrations relevant to natural systems.

There are two main strategies used for studying the fate of chemicals in soils. One consists of applying the chemicals in a non-labelled form and determining solely the disappearance of the chemical (Amellal et al. 2001, Boesten and van der Pas 2000, De Primo et al. 2003, French et al. 2001, Higarashi and Jardim 2002, Renaud et al. 2004). Unfortunately, in several cases this disappearance is defined as 'degradation' of the chemical, leading to an overestimation of the real degradation process. Alternatively, by using ^{14}C -labelling of the organic compounds the different processes of dissipation such as mineralisation, formation of non-extractable or bound residues, volatilisation, or formation of metabolites, can be individually identified and quantified (Kördel et al. 1995, Pesaro et al. 2003, Schroll et al. 2004, Schroll and Kühn 2004, Sørensen and Aamand 2001). A mass balance of the ^{14}C -labeled organic compounds is essential to provide quality assurance. The incubation of soil with ^{37}Cl - or ^{36}Cl -enriched chloride with subsequent analysis by mass spectrometry or corresponding radio-analytical methods could also test natural CAA formation in soil (e.g. Matucha et al. 2003b).

When studying the fate of CAA in soils it has to be clarified under which environmental conditions biotic or abiotic processes could dominate the formation and the degradation of CAA. An attempt has to be made to quantify the influence of abiotic soil factors like varying redox potential, H_2O_2 (produced by microorganisms) content and available iron in the soil on the formation and degradation of CAA. As the intensity of microbially-induced redox processes depends mainly on the amount of persistent organic matter in soils, the redox potential could be reduced rapidly in A_h -soil horizons of humus-rich soils after water saturation (Schachtschabel et al. 2004) caused by a precipitation event. This is a frequent scenario in forest soils under European climatic conditions. It is important to try to establish the transferability to real environmental conditions of laboratory-derived data on the influence of the redox potential on the turn-over rate of CAA.

It is known from previous studies that the biotic degradation of organic compounds in soils can be of metabolic or co-metabolic origin (Beigel et al. 1999, Bending et al. 2001, Ottow 1991, Robertson and Alexander 1994, Schroll and Kühn 2004, Torstensson 1980). Metabolic degradation and mineralisation of organic compounds can often lead to higher mineralisation rates in soils (Schroll and Kühn 2004) than the co-metabolic degradation pathway which generates less mineralisation but often produces several extractable dead-end-products, i.e. metabolites. Therefore the metabolic capabilities of microbial communities in soils for mineralising CAA should be studied. The identification of the key enzymes for the mineralisation is required as well as the identification of gene sequences of halogenating enzymes. It is still not at all clear whether the possibility of formation and degradation processes of CAA in deeper soil layers is an issue. Experiments generating CAA via redox processes indicate iron, halide and organic matter are necessary for the abiotic formation of CAA and these components could become limiting factors for the abiotic formation at depth. At present the importance of processes leading to CAA downward transport to groundwater, and hence to contamination of drinking water, are unknown.

If future research confirms that real risks exist for the environment and human health, in some specific ecosystems under specific circumstances, then strategies for steering the degradation of these chemicals in soils will need to be developed. Previous work (Assaf and Turco 1994, El-Fantroussi 2000, Schroll et al. 2004) has shown that specific soil functions such as microbial degradation processes can be influenced by the adaptation of active microorganisms and active microbial communities.

2.3 Volatile organochlorine compounds

Despite the existing knowledge on the biotic formation and degradation of VOCl in forest soil several aspects are still unknown and need to be investigated. So far, most studies on the formation and degradation of VOCl have been done in laboratory experiments using soil collected in the field and exposed to artificial and controlled conditions (e.g. Haselmann et al. 2002). A few studies have been published on direct field measurements of forest soil. However, these studies either only measured the occurrence of VOCl in soil (Haselmann et al. 2002, Kepler et al. 2000, Laturnus et al.

2000, Watling and Harper 1998), or determined the release from forest soil during a defined time period (Haselmann et al. 2000, Hoekstra et al. 2001), and thus leave questions on whether the release of these compounds could have been derived from biotic formation or from desorption processes of VOCl adsorbed to e.g. organic matter unanswered. Furthermore, basic data are still scarce on factors describing different soil types, such as microbial parameters, pH, composition of organic matter in forest soil, organic matter content, halide concentration, redox potential, K_{oc} to define the quality of organic matter, and how environmental factors, such as humidity, and temperature, could influence the formation or degradation of VOCl. All these factors could directly affect the forest soil microbiological communities that are assumed to contribute to the formation and degradation of VOCl, but none of the published studies have so far considered the effect of these factors.

Additional investigations need to be done on the actual processes occurring in the soil. Compared to ambient air, higher concentrations of trichloromethane were detected in soil air, suggesting a formation in the soil (Haselmann et al. 2000, Hoekstra et al. 2001, Laternus et al. 2000). The mechanism suggested for the formation was adapted from investigations of the formation of VOCl by marine organisms (Asplund et al. 1993, Laternus et al. 1995, Wever and Hemrika 2001). Whether these enzymatic processes involving chloroperoxidases are responsible for VOCl formation in forest soil is not yet clear. Although previous studies have shown halogenating activity of forest soil (Asplund et al. 1993, Laternus et al. 1995), pure enzymes have not been isolated from forest soil. Assuming enzymes are involved, it is not known if these are endo-enzymes, or exo-enzymes excreted by microorganisms or released after microorganism death. In fact, it is still even unknown to what extent plants and trees contribute to the possible formation and degradation of VOCl, i.e. to what extent the rhizosphere micro biota supports or hampers the formation of these VOCl. Isolation of the pure enzymes from soil or from plant roots would enable studies of VOCl compound formation in a controlled laboratory environment as the first step in identifying the chlorinating processes in real forest soil systems.

At present, field and laboratory studies only indicate natural formation in forest soil for trichloromethane, chloromethane and chloroethene. Although other compounds such as tetrachloromethane, 1,1,1-trichloroethane, trichloroethene and tetrachloroethene have been detected in forest soils, a formation process has not yet been confirmed and their presence is probably due to an equilibrium with atmospheric concentrations of anthropogenic origin. Future field and laboratory investigations need to be extended to a wider range of VOCl such as dichloromethane, chloroethane, chloroethine, whose biotic formation in forest soil have been assumed but not yet confirmed.

Identification of other VOCl formed in forest soil is important for quantifying the assumed source strength of forest ecosystems to the atmospheric reactive chlorine burden (Khalil et al. 1999). The focus on only selected VOCl may lead to an underestimation of the importance of forest ecosystem on a global scale compared to other natural terrestrial and marine sources of VOCl.

In addition, there should be investigations of possible degradation processes of VOCl in forest soil. A laboratory study has shown degradation of certain VOCl in water-unsaturated topsoil under denitrifying conditions (Borch et al. 2003). Investigating the mechanisms and extensions of possible degradation processes in forest soil are necessary to identify the real formation of VOCl in forest soil, which can be much higher than the usually determined net formation/net release. Application of different redox conditions and the use of model compounds in laboratory experiments to identify possible break-down compounds could be a first step. In a second step, the search for the identified break-down compounds in real soil could be used to confirm the results obtained in laboratory studies.

Alongside identification of the formation and degradation mechanisms VOCl in forest soil it could also be necessary to investigate how human activities may influence the natural processes. As VOCl of anthropogenic origin are widely dispersed in the atmosphere they could affect the concentration of these compounds in forest soil due to the transportation from the atmosphere to the soil by diffusion or wash-out processes. The effect of these processes has to be a point of future investigations especially as humans can control the anthropogenic environmental input of VOCl. A second aspect of human influence that should be considered is the effect of human-induced climate changes, e.g. increasing ambient temperature and/or increasing surface UV radiation due to the destruction of stratospheric ozone on the formation and degradation of VOCl in forest ecosystems. These changes in the global climate may contribute to, or even trigger, a feed-back loop between the atmosphere and forest ecosystem. VOCl are known to participate in the destruction of stratospheric ozone (Keene et al. 1999) and in the warming of the troposphere (Döös 1997). Future studies on the effect of human activities on the formation and degradation of VOCl in forest will help legislators establish appropriate ways of protecting forest ecosystems.

3 Conclusion

This review of the present knowledge of the natural formation and degradation processes of CAA and VOCl in forest soil has revealed gaps in knowledge regarding the actual mechanisms behind these processes. In particular, a quantification of the amounts and rates of formation and degradation of CAA and VOCl in forest soil and reliable budget calculations are still missing. It is concluded that the overall role of forest soil as a source and/or sink for CAA and VOCl is still unclear; the available laboratory and field data reveal only bits of the puzzle. Detailed knowledge of the natural degradation and formation processes in forest soil is important to evaluate the strength of forest ecosystems for the emission and uptake of CAA and VOCl, both on a regional scale and on a global scale. It is important to note that these processes could be influenced by human activities. Evaluation of the extent of this influence would help to identify what actions are needed in future to reduce human influences and, thus, to prevent further damage to the environment and to human health caused by CAA and VOCl.

Acknowledgements. This review was written by participants of the International Workshop on Occurrence and Fate of Organohalogenes in the Environment with Special Emphasis on Chloroacetic Acids in the European Forest Ecosystem held in Garmisch-Partenkirchen, Germany, 24-26 October 2004. Organisation by P. Schröder and financial support of the workshop by the German-Czech Future Funds and from the Impulse and Networking Funds of the Helmholtz Foundation is greatly acknowledged.

References

- Amellel N, Portal JM, Berthekin J (2001): Effect of soil structure on the bioavailability of polycyclic aromatic hydrocarbons within aggregates of a contaminated soil. *Appl Geochem* 16: 1611–1619
- Asplund G, Christiansen JV, Grimvall A (1993): A chloroperoxidase-like catalyst in soil – detection and characterization of some properties. *Soil Biol Biochem* 25: 41–46
- Assaf NA, Turco RF (1994): Accelerated biodegradation of atrazine by a microbial consortium is possible in culture and soil. *Biodegradation* 5: 29–35
- Barrons KC, Hummer RW (1951): Basic herbicidal studies with derivatives of TCA. *Agric Cult Chem* 6: 48–121
- Baehr AL, Stackelberg PE, Baker RJ (1999): Evaluation of the atmosphere as a source of volatile organic compounds in shallow groundwater. *Wat Resour Res* 35: 127–136
- Beigel C, Charnay MP, Barriuso E (1999): Degradation of formulated and unformulated triticonazole fungicide in soil: Effect of application rate. *Soil Biol Biochem* 31: 525–534
- Bending GD, Shaw E, Walker A (2001): Spatial heterogeneity in the metabolism and dynamics of isoproturon degrading microbial communities in soil. *Biol Fertil Soils* 33: 484–489
- Berg M, Müller SR, Mühlemann J, Wiedmer A, Schwarzenbach RP (2000): Concentrations and mass fluxes of chloroacetic acids and trifluoroacetic acid in rain and natural waters in Switzerland. *Environ Sci Technol* 34: 2675–2683
- Bertaux J, Schmid M, Prevost-Boure NC, Churin JL, Hartmann A, Garbaye J, Frey-Klett P (2003): In situ identification of intracellular bacteria related to *Paenibacillus* sp. in the mycelium of the ectomycorrhizal fungus *Laccaria bicolor* S238N. *Appl Environ Microbiol* 69: 4243–4248
- Bhat HK, Kanz MF, Campbell GA, Ansari GA (1991): Ninety day toxicity study of chloroacetic acids in rats. *Fund Appl Toxicol* 17: 240–253
- Bianciotto, V, Lumini E, Lanfranco L, Minerdi D, Bonfante P, Perotto S (2000): Detection and identification of bacterial endosymbionts in arbuscular mycorrhizal fungi belonging to the family Gigasporaceae. *Appl Environ Microbiol* 62: 3005–3010
- Boesten JJTI, van der Pas LJT (2000): Movement of water, bromide and the pesticides ethoprophos and bentazone in a sandy soil: the Vredepeel data set. *Agric Wat Manag* 44: 21–42
- Borch T, Ambus P, Laturus F, Svensmark B, Grøn C (2003): Biodegradation of chlorinated solvents in a water unsaturated topsoil. *Chemosphere* 51: 143–152
- Brimecomb MJ, De Leij FA, Lynch JM (2001): The effect of root exudates on rhizosphere microbial populations. In: Pinton R, Varanini Z, Nannipieri P (eds), *The Rhizosphere*. Marcel Dekker, New York, pp 95–140
- Brookes DS, Gonzalez CF, Appel DN, Filer TH (1994): Evaluation of endophytic bacteria as potential biological control agents for oak wilt. *Biol Control* 4: 373–381
- Collins C, Laturus F, Nepovim A (2002): Remediation of BTEX and Trichloroethene – Current knowledge with special emphasis on phytoremediation. *ESPR – Environ Sci & Pollut Res* 9, 86–94
- Clutterbuck PW, Mukhopadhyay SL, Oxford AE, Raistrick H (1940): Studies in the Biochemistry of microorganisms. *Biochem J* 34: 664–677
- Dewulf JP, van Langenhove HR, Everaert M, Vanthournout H (1998): Volatile organic compounds in the Scheldt estuary along the trajectory Antwerp-Vlissingen: Concentration profiles, modelling and estimation of emissions into the atmosphere. *Wat Res* 32: 2941–2950
- Dickey CA, Heal KV, Stidson RT, Koren R, Cape JN, Schröder P, Heal MR (2004): Trichloroacetic acid cycling in Sitka spruce (*Picea sitchensis*) saplings and the effects on tree health following long term exposure. *Environ Poll* 130: 165–176
- Dickey CA, Heal KV, Cape JN, Stidson RT, Reeves NM, Heal MR (2005): Addressing analytical uncertainties in the determination of trichloroacetic acid in soil. *J Environ Monitoring* 7: 137–144
- Dimmer C, Simmonds P, Nickless G, Bassford M (2001): Biogenic fluxes of halomethanes from Irish peatland ecosystems. *Atmos Environ* 35: 321–330
- Di Primo P, Gamliel A, Austerweil M, Steiner B, Beniches M, Peretz-Alon I, Katan J (2003): Accelerated degradation of metam-sodium and dazomet in soil: characterization and consequences for pathogen control. *Crop Protect* 22: 635–646
- Döös BR (1997): Greenhouse gases and climatic change. In: Brune D, Chapman D, Gwynne MD, Pacyna JM (eds), *The Global Environment*. Scandinavian Science Publisher and VCH, Weinheim, Germany, pp 319–351
- Drake HL, Daniel SL, Küsel K, Matthies C, Kuhner C, Braus-Stroymeyer S (1997): Acetogenic bacteria: what are the in situ consequences of their diverse metabolic versatilities? *Bio Factors* 6: 13–24
- El-Fantroussi S (2000): Enrichment and molecular characterization of a bacterial culture that degrades methoxy-methyl urea herbicides and their aniline derivatives. *Appl Environ Microbiol* 60: 5110–5115
- Fahimi IJ (2003): Natural formation of haloacetic acids and iodinated alkanes. PhD thesis, University of Heidelberg, Germany
- Fahimi IJ, Keppler F, Schöler HF (2003): Formation of chloroacetic acids from soil, humic acid and phenolic moieties. *Chemosphere* 52: 513–520
- Forczek ST, Matucha M, Uhlířová H, Albrechtová J, Fuksová K, Schröder P (2001): Biodegradation of trichloroacetic acid in spruce/soil-system. *Biol Plant* 44: 317–320
- Foy CL (1975): The chlorinated aliphatic acids. In: Kearney PC, Kaufman DD (eds), *Herbicides: Chemistry, Degradation and Mode of Action*, vol. 1, Marcel Dekker, New York
- Frank H (1988): Trichloressigsäure im Boden – Eine Ursache neuartiger Waldschäden. *Nachr Chem Tech Lab* 36: 889
- Frank H, Vincon A, Reiss J, Scholl H (1990): Trichloroacetic Acid in the Foliage of Forest Trees. *J High Resolut Chromatogr* 13: 733–736
- Frank H, Scholl H, Renschen D, Rether B, Laouedj A, Norokorpi Y (1994): Haloacetic Acids – Phytotoxic Secondary Air Pollutants. *ESPR – Environ Sci & Pollut Res* 1: 4–14
- French HK, Van der Zee SEATM, Leijne A (2001): Transport and degradation of propyleneglycol and potassium acetate in the unsaturated zone. *J Contam Hydro* 49: 23–48
- Geigert J, Neidleman SL, DeWitt SK, Dalietos DJ (1984): Halonium ion-induced biosynthesis of chlorinated marine metabolites. *Phytochemistry* 23: 287–290
- Gibson J, Harwood CS (2002): Metabolic diversity in aromatic compound utilization by anaerobic microbes. *Annu Rev Microbiol* 56: 345–369
- Gribble G (1996): The diversity of natural organochlorines in living organisms. *Pure Appl Chem* 68: 1699–1712
- Gribble G (2003): The diversity of naturally produced organohalogenes. *Chemosphere* 52: 289–297
- Haiber G, Jacob G, Niedan V, Nkusi G, Schöler HF (1996): The occurrence of trichloroacetic acid (TCAA) – Indications of a natural production? *Chemosphere* 33: 839–849
- Halliwell B, Gutteridge JMC (1984): Oxygen toxicity, oxygen radicals, transition metals and disease. *Biochem J* 219: 1–14
- Hamilton JTG, McRoberts WC, Keppler F, Kalin RB, Harper DB (2003): Chloride methylation by plant pectin – An efficient environmentally significant process. *Science* 301: 206–209
- Harper DB (1985): Halomethane from halide ion – A highly efficient fungal conversion of environmental significance. *Nature (London)* 315: 55–57
- Harper DB (1993): Biogenesis and metabolic role of halomethanes in fungi and plants. In: Sigl H, Sigl A (eds), *Metal ions in biological systems*. Marcel Dekker, New York, pp 345–388
- Hartmann A, Pukall R, Rothballer M, Gantner S, Metz S, Schloter M, Mogge B (2004): Microbial community analysis in the rhizosphere by in situ and ex situ application of molecular probing, biomarker and cultivation techniques. In: Varma A, Abbott L, Werner D, Hampp R (eds), *Plant Surface Microbiology*. Springer Verlag, Berlin, pp 449–469

- Haselmann KF, Ketola RA, Laturus F, Lauritsen FR, Grøn C (2000): Occurrence and formation of chloroform at Danish forest sites. *Atmos Environ* 34: 187–193
- Haselmann KF, Laturus F, Svensmark B, Grøn C (2002): Formation of chloroform in spruce forest soil – results from laboratory incubation studies. *Chemosphere* 41: 1769–1774
- Heal MR, Dickey CA, Cape JN, Heal KV (2003): The routes and kinetics of trichloroacetic acid uptake and elimination in Sitka spruce (*Picea sitchensis*) saplings via atmospheric deposition pathways. *Atmos Environ* 37: 4447–4452
- Higarashi MM, Jardim WF (2002): Remediation of pesticide contaminated soil using TiO₂ mediated by solar light. *Catalysis Today* 76: 201–207
- Hoekstra EJ, Lassen P, van Leeuwen J, deLeer EWB, Carlsen L (1995): Formation of organic chlorine compounds of low molecular weight in the chloroperoxidase-mediated reaction between chloride and humic material. In: Grimvall A, deLeer EWB (eds), *Naturally-Produced Organohalogenes*. Kluwer Academic Publishers, Dordrecht
- Hoekstra EJ, Verhagen F, Field J, de Leer EWB, Brinkman UAT (1998): Natural production of chloroform by fungi. *Phytochemistry* 49: 91–97
- Hoekstra EJ, de Leer EWB, Brinkman UAT (1999a): Findings supporting the natural formation of trichloroacetic acid in soil. *Chemosphere* 38: 2875–2883
- Hoekstra EJ, de Leer EWB, Brinkman UAT (1999b): Mass balance of trichloroacetic acid in the soil top layer. *Chemosphere* 38: 551–563
- Hoekstra EJ (1999c): On the natural formation of chlorinated organic compounds in soil. PhD Thesis, Free University of Amsterdam, The Netherlands
- Hoekstra EJ, Duyzer JH, de Leer EWB, Brinkman UAT (2001): Chloroform – Concentration gradients in soil air and atmospheric air, and emission fluxes from soil. *Atmos Environ* 35: 61–70
- Hoekstra EJ (2003): Review of concentrations and chemistry of trichloroacetate in the environment. *Chemosphere* 52: 355–369
- Hollinger C, Wohlfarth G, Diekert G (1999): Reductive dechlorination in the energy metabolism of anaerobic bacteria. *FEMS Microbiol Rev* 22: 383–398
- Hunter JC, Belt A, Sotos LS, Fonda ME (1987) Fungal chloroperoxidase method. In: United States Patent, USA
- Isidorov VA (1990): Organic chemistry of Earth's atmosphere. In: *Natural sources of organic components of the atmosphere*, chpt 3, Springer, Berlin, 215 pp
- Jordan A, Harnisch J, Borchers R, Le Guern FN, Shinohara H (2000): Volcanogenic halocarbons. *Environ Sci Technol* 34: 1122–1124
- James EK, Olivares FL (1997): Infection and colonization of sugar cane and other Gramineous plants by endophytic diazotrophs. *Crit Rev Plant Sci* 17: 77–119
- Juuti S, Hirvonen A, Tarhanen J, Holopainen JK, Ruuskanen J (1993): Trichloroacetic acid in pine needles in the vicinity of a pulp mill. *Chemosphere* 26: 1859–1868
- Keene WC, Khalil MAK, Erickson III DJ, McCulloch A, Graedel TE, Lobert JM, Aucott ML, Gong SL, Harper DB, Kleiman G, Midgley P, Moore RM, Seuzaret C, Sturges WT, Benkovitz CM, Koropalov V, Barrie LA, Li YF (1999): Composite global emissions of reactive chlorine from anthropogenic and natural sources – reactive chlorine emissions inventory. *J Geophys Res* 104: 8429–8440
- Keppler F, Eiden R, Niedan VW, Pracht J, Schöler HF (2000): Halocarbons produced by natural oxidation processes during degradation of organic matter. *Nature (London)* 403: 298–301
- Keppler F, Borchers R, Pracht J, Rheinberger S, Schöler HF (2002): Natural formation of vinyl chloride in the terrestrial environment. *Environ Sci Technol* 36: 2479–2483
- Khalil MAK, Rasmussen RA, French JRJ, Holt JA (1990): The influence of termites on atmospheric trace gases. *J Geophys Res* 95: 3619–3634
- Khalil MAK, Rasmussen RA, Shearer MJ, Chen ZL, Yao H, Yang J (1998): Emissions of methane, nitrous oxide, and other trace gases from rice fields in China. *J Geophys Res* 103: 25241–25250
- Khalil MAK, Moore RM, Harper DB, Lobert JM, Erickson DJ, Koropalov V, Sturges WT, Keene WC (1999): Natural emissions of chlorine-containing gases – Reactive chlorine emissions inventory. *J Geophys Res* 104: 8333–8346
- Khalil MAK, Rasmussen RA (2000): Soil-atmosphere exchange of radiatively and chemically active gases. *ESPR – Environ Sci & Pollut Res* 7: 79–82
- Kobayashi DY, Palumbo JD (2000): Bacterial endophytes and their effects on plants and uses in agriculture. Bacon CW, White JF Jr (eds), Marcel Dekker, New York
- Kördel W, Wahle U, Knoche H, Hund K (1995): Degradation capacities of chlorotoluron and simazine in subsoil horizons. *Sci Total Environ* 171: 43–50
- Kotte K (2004) PhD thesis, Beiträge zur phytotoxischen Relevanz von C₂-Chlorkohlenwasserstoffen und C₂-Chlor-carbonsäuren am Beispiel von Tetrachlorethen und Trichloressigsäure, Friedrich-Schiller-University Jena, Germany (in German)
- Krüger BC, Wang GQ, Fabian P (1987): The Antarctic ozone depletion caused by heterogeneous photolysis of halogenated hydrocarbons. *Geophys Res Letts* 14: 523–526
- Krysell M, Nightingale PD (1994): Low molecular weight halocarbons in the Humber and Rhine estuaries determined using a new purge-and-trap gas chromatographic method. *Cont Shelf Res* 14: 1311–1329
- Lange C, Weissflog L, Strasser RJ, Krueger GHJ, Pfenningdorff A (2004): Phytotoxic effects of trichloroacetic acid on Scots Pine and birch by chl a fluorescence and the JIP-test. *South African J Botany* 70: 683–694
- Laturus F, Mehrtens G, Grøn C (1995): Haloperoxidase-like activity in spruce forest soil – A source of volatile halogenated organic compounds? *Chemosphere* 31: 3709–3719
- Laturus F, Lauritsen FR, Grøn C (2000): Chloroform in a pristine aquifer system – Toward an evidence of biogenic origin. *Wat Resour Res* 36: 2999–3009
- Laturus F, Haselmann K, Borch T, Grøn C (2002): Terrestrial natural sources of trichloromethane (Chloroform, CHCl₃) – An overview. *Biogeochemistry* 60: 121–139
- Laturus F, Svensson T, Wiencke C, Öberg G (2005): Volatilization of chlorine by marine macroalgae – A key process in the natural global cycle of chlorine? *Geophys Res Letts* (submitted)
- Lengeler JW, Drews G, Schlegel HG (1999): *Biology of the prokaryotes*. Thieme Verlag, Stuttgart, 955 pp
- Lewis TE, Wolfinger TF, Barta ML (2004): The ecological effects of trichloroacetic acid in the environment. *Environ Int* 30: 1119–1150
- Liang L, Singer PC (2003): Factors influencing the formation and relative distribution of haloacetic acids and rihalomethanes in drinking water. *Environ Sci Technol* 37: 2920–2928
- Lifongo LL, Bowden DJ, Brimblecombe P (2004): Photodegradation of haloacetic acids in water. *Chemosphere* 55: 467–476
- Lignell R, Heinonen-Tanski H, Uusi-Rauva A (1984): Degradation of trichloroacetic acid (TCA) in soil. *Acta Agricult Scan* 34: 3–8
- Lodewyckx C, Vangronsveld J, Porteous F, Moore ERB, Taghavi S, Mezgeay M, van der Lelie D (2002): Endophytic bacteria and their potential applications. *Crit Rev Plant Sci* 21: 583–606
- Lovley DR (1991): Dissimilatory Fe(III) and Mn(IV) reduction. *Microbiol Rev* 55: 259–287
- Matucha M, Uhlířová H, Bubner M (2001): Investigation of uptake, translocation and fate of trichloroacetic acid in Norway Spruce (*Picea Abies* L./ Karst.) using ¹⁴C-labelling. *Chemosphere* 44: 217–222
- Matucha M, Forczek ST, Gryndler M, Uhlířová H, Fuksová K, Schröder P (2003a): Trichloroacetic acid in Norway spruce/soil-system I. Biodegradation in soil. *Chemosphere* 50: 303–309
- Matucha M, Gryndler M, Forczek ST, Uhlířová H, Fuksová K, Schröder P (2003b): Chloroacetic acids in environmental processes. *Environ Chem Letts* 1: 127–130
- McCulloch A (2002): Trichloroacetic acid in the environment. *Chemosphere* 47: 667–686
- McCulloch A (2003): Chloroform in the environment – Occurrence, sources, sinks and effects. *Chemosphere* 50: 1291–1308
- McGrath D (1976): Factors that influence the persistence of TCA in soil. *Weed Res* 16:131–137
- Mogge B, Loferer C, Agerer R, Hutzler P, Hartmann A (2000): Bacterial community structure and colonization patterns of *Fagus sylvatica* L. ectomycorrhizospheres as determined by fluorescence in situ hybridization (FISH) and confocal laser scanning microscopy (CSLM). *Mycorrhiza* 9: 272–278
- Müller G, Nkusi G, Schöler HF (1996): Natural organohalogenes in sediments. *J Prakt Chem/Chem Ztg* 338:23 – 29
- Neidleman SL, Geigert J (1986): *Biohalogenation*. John Wiley and Sons, Chichester

- Neilands JB (1995): Siderophores – Structure and function of microbial iron transport compounds. *J Biol Chem* 270: 26,723–26,726
- Niedan V, Pavasars I, Öberg G (2000): Chloroperoxidase-mediated chlorination of aromatic groups in fulvic acid. *Chemosphere* 41: 779–785
- Ottow JCG (1991): Mikrobiologische und chemisch-physikalische Wechselwirkungen beim Abbau organischer Schadstoffe in Böden. *Mitteilungen Dt. Bodenkundlichen Gesellschaft* 63: 19–26
- Öberg G (2002): The natural chlorine cycle – fitting the scattered pieces. *Appl Microbiol Biotechnol* 58: 565–581
- Öberg G (2003): The biogeochemistry of chlorine in soil. In: Gribble G (ed), *Natural production of organohalogen compounds. The handbook of Environmental Chemistry, Vol 3, part P*, Springer, Berlin, p 43–62
- Pesaro M, Widmer F, Nicollier G, Zeyer J (2003): Effects of freeze-thaw stress during soil storage on microbial communities and methidathion degradation. *Soil Biol Biochem* 35: 1049–1061
- Peters RJB (2003): Chloroacetic acids in European soils and vegetation. *J Environ Monit* 5: 275–280
- Plumacher J, Renner I (1993): Determination of volatile chlorinated hydrocarbons and trichloroacetic acid in conifer needles by headspace gas chromatography. *Fresenius J Anal Chem* 347: 129–135
- Powell PE, Szanislo PJ, Reid CP (1983): Confirmation of occurrence of hydroxamate siderophores in soil by a novel *Escherichia coli* bioassay. *Appl Environ Microbiol* 46: 1080–1083
- Pracht J, Boenigk J, Isenbeck-Schröter M, Keppler F, Schöler HF (2001): Abiotic Fe(III) induced mineralization of phenolic substances. *Chemosphere* 44: 613–619
- Ratledge C, Dover LG (2000): Iron metabolism in pathogenic bacteria. *Annu Rev Microbiol* 54: 881–941
- Redeker K, Wang N-Y, Low J, McMillan A, Tyler S, Cicerone R (2000): Emissions of methyl halides and methane from rice paddies. *Science* 290: 966–969
- Renaud FG, Brown CD, Fryer CJ, Walker A (2004): A lysimeter experiment to investigate temporal changes in the availability of pesticide residues for leaching. *Environ Poll* 131: 81–91
- Rhew R, Miller B, Weiss R (2000): Natural methyl bromide and methyl chloride emissions from coastal salt marshes. *Nature (London)* 403: 292–295
- Rhew R, Miller B, Vollmer M, Weiss R (2001): Shrubland fluxes of methyl bromide and methyl chloride. *J Geophys Res-Atmos* 106: 20,875–20,882
- Robertson BK, Alexander M (1994): Growth-linked and cometabolic biodegradation – Possible reason for occurrence or absence of accelerated pesticide biodegradation. *Pestic Sci* 41: 311–318
- Saxena D, Aouad S, Attieh J, Saini H (1998): Biochemical characterization of chloromethane emission from the wood-rotting fungus *Phellinus pomaceus*. *Appl Environ Microbiol* 64: 2381–2385
- Schachtschabel P, Blume HP, Brümmer G, Hartge KH, Schwertmann U (2004): *Lehrbuch der Bodenkunde*, 15th ed, Spektrum Akademischer Verlag, Heidelberg, 593 pp
- Schöler HF, Keppler F, Fahimi IJ, Niedan VW (2003): Fluxes of trichloroacetic acid between atmosphere, biota, soil and groundwater. *Chemosphere* 52: 339–354
- Schroll R, Brahusi F, Dörfler U, Kühn S, Fekete J, Munch JC (2004): Biomineralisation of 1,2,4-trichlorobenzene in soils by an adapted microbial population. *Environ Poll* 127: 395–401
- Schroll R, Kühn S (2004): Test system to establish mass balance for ¹⁴C-labeled substances in soil-plant-atmosphere systems under field conditions. *Environ Sci Technol* 38: 1537–1544
- Schröder P, Matucha M, Forczek ST, Uhlířová H, Fuksová K, Albrechtová J (2003): Uptake, translocation and fate of trichloroacetic acid in Norway spruce/soil system. *Chemosphere* 52: 437–442
- Smidt H, de Vos WM (2004): Anaerobic microbial dehalogenation. *Annu Rev Microbiol* 58: 43–73
- Sorensen J (1997): The rhizosphere as habitat for soil microorganisms. In: Van Elsas JD, Trevors JT, Wellington MH (eds), *Modern Soil Microbiology*. Marcel Dekker, New York, pp 21–45
- Sörensen SR, Aamand J (2001): Biodegradation of the phenylurea herbicide isoproturon and its metabolites in agricultural soils. *Biodegradation* 12: 69–77
- Squillace PJ, Moran MJ, Lapham WW, Price CV, Clawges RM, Zogorski JS (1999): Volatile organic compounds in untreated ambient groundwater of the United States, 1985–1995. *Environ Sci Technol* 33: 4176–4187
- Stidson RT, Dickey CA, Cape JN, Heal KV, Heal MR (2004a): Fluxes and reservoirs of trichloroacetic acid at a forest and moorland catchment. *Environ Sci Technol* 38: 1639–1647
- Stidson RT, Heal KV, Dickey CA, Cape JN, Heal MR (2004b): Fluxes of trichloroacetic acid through a conifer forest canopy. *Environ Pollut* 132: 73–84
- Stotzky G (1997): Soil as an environment for microbial life. In: Van Elsas JD, Trevors JT, Wellington MH (eds), *Modern Soil Microbiology*. Marcel Dekker, New York, pp 1–20
- Sugiura Y, Nomoto K (1984): Phytosiderophores, structure and properties of mugineic acids and their metal complexes. *Structure Bonding* 58: 107–135
- Torstenson L (1980): Role of microorganisms in decomposition. In: Hance RJ (ed), *Interactions between herbicides and the soil*, Academic Press, London, pp 159–177
- Trapp S, Mc Farlane LC, Matthies M (1994): Model for uptake of xenobiotics into plants – Validation with bromuracil experiments. *Environ Toxicol Chem* 13: 413–422
- UNEP report (1987): The Montreal protocol on substances that deplete the ozone layer. United Nations Environmental Programme (UNEP), Nairobi, Kenya
- Varner RK, Crill PM, Talbot RW (1999): Wetlands – A potentially significant source of atmospheric methyl bromide and methyl chloride. *Geophys Res Letts* 26: 2433–2436
- Walter B, Ballschmiter K (1992): Formation of C1/C2-bromo-/chloro-hydrocarbons by haloperoxidase reactions. *Fresenius J Anal Chem* 342: 827–833
- Wandersman C, Delepelaire P (2004): Bacterial iron Sources: From siderophores to hemophores. *Annu Rev Microbiol* 58: 611–647
- Watling R, Harper DB (1998): Chloromethane production by wood-rotting fungi and an estimate of the global flux to the atmosphere. *Mycol Res* 102: 769–787
- Weightman AL, Weightman AJ, Slater JH (1992): Microbial dehalogenation of trichloroacetic acid. *World J Microbiol Biotechnol* 8: 512–518
- Weissflog L, Elansky N, Putz E, Krueger G, Lange CA, Lisitzina L, Pfningsdorff A (2004a): Trichloroacetic acid in the vegetation of polluted and remote areas of both hemispheres – Part II: salt lakes as novel sources of natural chlorohydrocarbons. *Atmos Environ* 38: 4197–4204
- Weissflog L, Krueger G, Kellner K, Plenaar J, Lange C, Strauss R, Pfningsdorff A, Ondruschka B (2004b): Air pollution-derived trichloroacetic acid contributes to degradation of vegetation in South Africa. *South African J Science* 100: 289–293
- Wellburn A (1994): Air pollution and climate change. Pearson Education, Harlow, 268 pp
- Wever R, Hemrika W (2001): Vanadium haloperoxidases. In: Messerschmidt A, Poulos T, Wieghardt K (eds), *Handbook of Metalloproteins*. John Wiley, Chichester, pp 1417–1428
- White P, Broadley M (2001): Chloride in soils and its uptake and movement within the plant – a review. *Ann Botany* 88: 967–988
- Wuosmaa A, Hager L (1990): Methyl chloride transferase – A carbocation route for biosynthesis of halometabolites. *Science* 249: 160–162
- Yokouchi Y, Ikeda M, Inuzuka Y and Yukawa T (2002): Strong emission of methyl chloride from tropical plants. *Nature (London)* 416: 163–165
- Yu P, Welander T (1995): Growth of an aerobic bacterium with trichloroacetic acid as the sole source of energy and carbon. *Appl Microbiol Biotechnol* 42: 769–774

Received: January 21st, 2005
 Accepted: May 31st, 2005
 OnlineFirst: June 1st, 2005