1 INTRODUCTION: HALOGENATED ACETIC ACIDS (HAAS)

Halogenated acetic acids (HAAs) are important chemical substances because of their high phytotoxity, since there is a presumption that they are responsible for a significant part of forest dieback. Trichloroacetic acid (TCA) was introduced as a weed killer in 1947, destroying preferentially monocotyledonous grasses. It is now forbidden in most of the countries of the European Union, except Ireland and Italy. Although TCA is ubiquitous in the envionment, it is particularly connected with conifers because it accumulates in their needles and is also found in the soils of coniferous forests. The PNEC (predicted no effect concentration) in the soil, 2.4 µg/kg, was compared with the PEC (predicted environmental concentration) found in a soil of the Black Forest area: usually if the ratio of PNEC/PEC > 1, reduction measures should be taken. In the case of the Black Forest this value was exceeded by far, indicating a clear risk to the terrestrial ecosystem.

This first segment of this study describes the properties of HAAs, their sources and fluxes in the environment: their inputs, their occurence, and their sinks will be identified and quantified.

1.1 Properties of chlorinated acetic acids (CAAs)

HAAs, e.g. chlorinated acetic acids (CAAs), i.e. monochloroacetic (MCA), dichloroacetic (DCA) and trichloroacetic (TCA) acid are polar, hydrophilic compounds (Morris and Bost, 1991; Juuti, 1997). The preferred environmental compartment where their emissions accumulate is the hydrosphere (Ballschmiter, 1992; McCulloch, 2002). They are completely ionized at environmental pHs (Morris and Bost, 1991; Juuti, 1997) because of their high acidity (pK_a of TCA 0.22 - 0.26), and therefore evaporation from water is not a significant process (Bowden et al., 1997). They have low octanol/water coefficients; and, hence, they are not considered to bioconcentrate in the food chain (Franke et al., 1994) or to adsorb appreciably to soil constituents. All CAAs are biodegradable (Jensen 1957, 1960; Lignell et al., 1984; Yu and Welander, 1994; Diez et al., 1995; Fulthorpe and Allen, 1995).

Table 1: Chemical properties of CAAs

	MW	bp (^oC)	pK_a	vapor pressure (Pa, 20^oC)	K_H (mol/kg atm)	log K_{OW}
MCA	94.5	188	2.85	27	11.1×10^4	0.22
DCA	128.9	194	1.48	25	38.5×10^4	0.76
TCA	163.4	198	0.26	21	7.4×10^4	< 1 – 1.60

1.2 Sources

The research on the behavior of HAAs in the environment can be divided into three periods, the first being characterized by the use of HAAs as herbicides (Martin 1972; Ashton and Crafts, 1973), the second one by HAAs being considered as secondary environmental pollutants only, affecting forest dieback, especially in coniferous forests (Frank et al., 1990), and finally by the production of natural chlorination of humic substances in soil (Haiber et al., 1996; Hoekstra et al., 1999b).

1.2.1 Usage of chlorinated acetic acids as herbicides

Nowadays the use of TCA in agriculture is forbidden, but 30,000 t TCA were applied in Germany from the late 1940s until 1990. It has been prohibited in Germany since 1989. TCA was used with relative impunity at application rates ranging from 2 - 30 kg/ha, now it has been banned because of its indiscriminate herbicidal effects on woody plant species. MCA was marketed as a preemergence herbicide in aqueous solutions at about 22 - 25 kg/ha from the beginning of the 1950s; it has also been used as a defoliant (Martin and Worthing, 1977).

1.2.2 Sources of HAAs in the atmosphere

There are still large gaps in our knowledge of all the sources of HAAs in the environment, but the formation of HAAs from volatile precursors has been investigated and confirmed. There is sufficient evidence that TCA is a minor product of the atmospheric degradation of 1,1,1-trichloroethane and especially tetrachloroethene (McCulloch, 2002). The yield of chlorinated acetic acids is somewhat controversial (Franklin, 1994); e.g. whereas it was originally believed that the yield of conversion of TCA was 100%, it is presently estimated that approximately 5% of tetrachloroethene released into the atmosphere could be converted into TCA and the upper limit on the conversion of 1,1,1-trichloroethane is 1.3%(McCulloch, 2002).

TCA has been postulated to be produced from the hydrolysis of trichloroacetyl chloride formed as a result of atmospheric degradation reactions of tetrachloroethene (PER) (Gay et al., 1976; Tuazon et al., 1988; Zetzsch and Becker, 1989; Frank, 1991; Frank et al., 1990, 1991, 1992, 1994; Itoh et al., 1994). In addition, TCA may be produced by the degradation of 1,1,1-trichloroethane (1,1,1-TCE) in air (Frank et al., 1992, 1994). DCA may be produced similarly from 1,1,2-trichloroethene (TRI) (Gay et al., 1979; Tuazon et al., 1988; Itoh et al., 1994) and MCA from 1,1-dichloroethene and 1,2-dichloroethene (Tuazon et al., 1988; Gürtel et al., 1994, Itoh et al.,1994).

The volatile C_2-chlorocarbons originate from human activity, e.g. their use as solvents and degreasers, and from dry cleaners (Tichenor et a., 1990; Mroueh, 1992). Emissions from kraft pulp bleaching, when chlorine containing agents have been used, have also been shown to include small amounts of these chlorocarbons (Kringstad et al., 1981; Rosenberg et al., 1991a, 1991b; Comba et al., 1994; NCASI 1994). C_2-chlorocarbons seem to also be produced naturally in oceans and are released from volcanoes (Gribble 1994).

Most C_2-chlorocarbons have atmospheric lifetimes long enough to allow them to be transported over long distances, also to remote areas. The distribution of 1,1,1-TCE is practically uniform over both hemispheres. Long-term data of air concentrations of C_2-chlorocarbons are available only from a site in northern Finland, Pallastunturi ($67^o58'N$, $24^o07'E$), measured in September - December 1995; at that point in time the values were relatively low (Juuti, 1997).

1.2.2.1 Photochemical degradation of C_2-chlorocarbons

Although there has been quite some progress regarding the knowledge of degradation pathways and products of the most chlorinated organic hydrocarbons in the atmosphere, great caution is needed in interpreting the data from laboratory experiments. One has to take deviations from actual tropospheric conditions into account to propose likely breakdown pathways and products in the real environment (Franklin, 1994).

Globally speaking the emissions of C_2-chlorocarbons from anthropogenic sources have declined during the recent years (Franklin 1994; Midgley and McCulloch, 1995; McCulloch and Midgley, 1996).

1.2.2.2 Formation of TCA from tetrachloroethene

As regards the formation of TCA from tetrachloroethene in the troposphere, the first step is the attack by either a chlorine atom (Fig. 1), which leads to the formation of trichloroacetyl chloride (TCAC) or by a hydroxyl radical, which leads to phosgene (Tuazon et al., 1988; Kirchner et al., 1990; Gürtel et al., 1994; Itoh et al., 1994) and chlorine atoms. Using the concentrations of Cl and OH radicals of 500 and 10^6 molecules/cm^3, respectively (Sidebottom and Franklin, 1996), and the reaction constants of 4.2×10^{-11} and 1.2×10^{-13} cm^3/molecules, respectively (Franklin, 1994), one can calculate a 15% yield for the formation of the CCl_3-CCl_2O radical, which in turn forms 85% trichloroacetyl chloride (TCAC) and 15% phosgene (Franklin, 1994).

The atmospheric lifetime for PER with respect to its reactions with the OH radical would be about 0.19 years. PER can also react with atomic chlorine with a reaction rate constant which is about 270 times faster than that occurring with the OH radical.

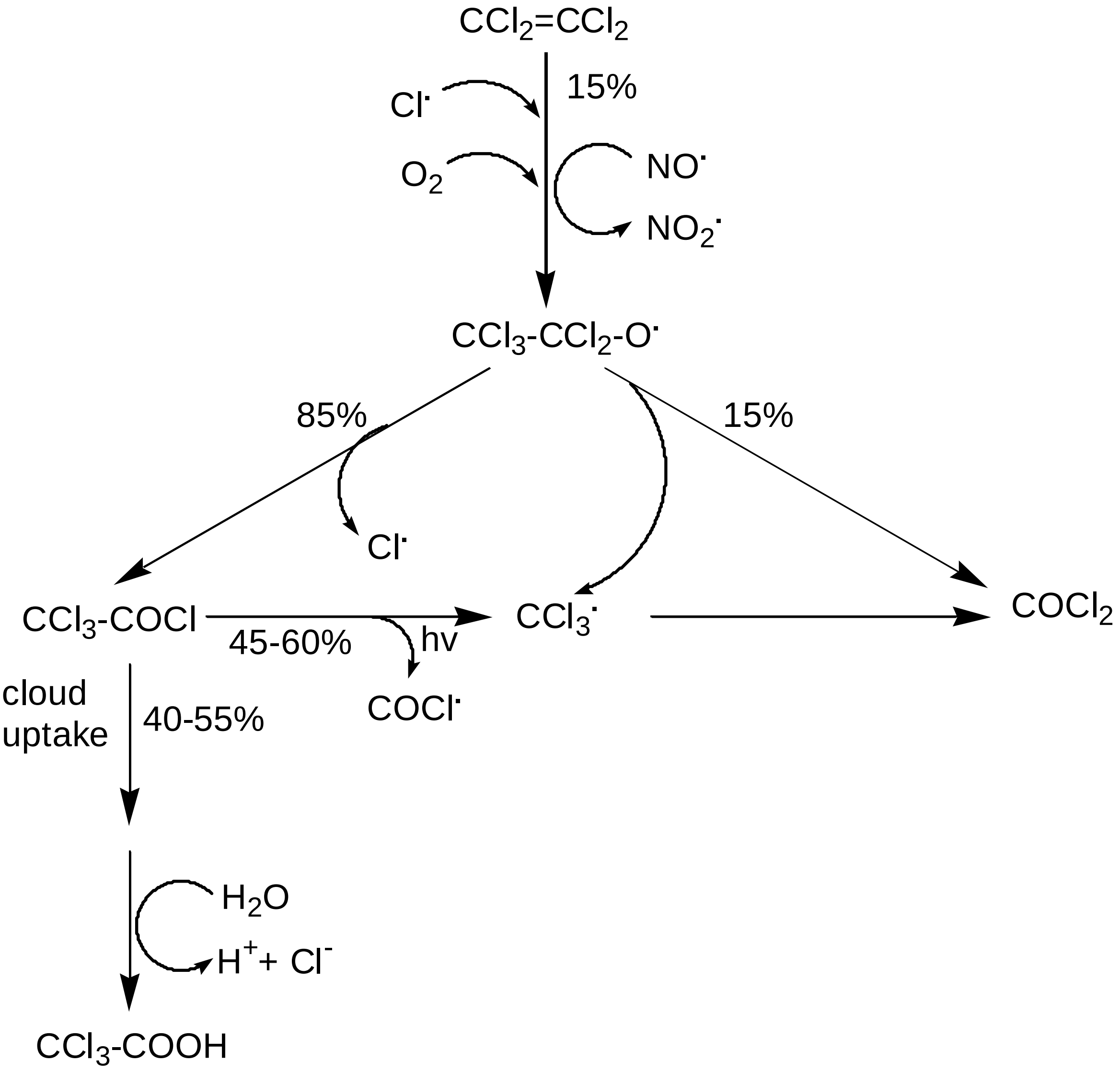

Fig.1: Tropospheric degradation of tetrachloroethene (Sidebottom and Franklin, 1996)

TCAC, which is produced as the main product (Tuazon et al., 1988; Kirchner et al., 1990; Gürtel et al., 1994; Itoh et al., 1994), can be settled by wet or dry deposition and becomes hydrolyzed soon thereafter (estimates vary from 0.2 days to 30 days) in the water droplets, aerosol surface, cloud and rain water to produce TCA (George et al., 1993a; George et al., 1993b; de Bruyn et al., 1995). Use of the calculation procedure of De Bruyn et al. (1995) shows that the lifetime due to uptake of TCAC into the cloud droplet is calculated to be in the range of 4 - 30 h. If one assumes that

TCAC hydrolyzes directly to TCA, the lifetime due to uptake into clouds is limited by the formation of clouds and is therefore about 5 - 10 days.

The degradation of TCAC by photolysis (τ = 6 days (Cox et al., 1995)) generates $COCl_2$ and CCl_4 (Behnke and Zetzsch, 1991). The major fraction of TCAC can be considered to be hydrolyzed to TCA.

At increased Cl concentrations more TCA will be formed. It should be noted that the chlorine atoms produced in the reaction of PER and OH radicals will react much faster with other air pollutants (e.g. ozone, methane) than with PER itself, because of the low concentrations of the latter compounds in the atmosphere (Franklin, 1994).

Taking into account the different reaction pathways, about 4.8 - 7.0% of the tetrachloroethene can be transformed to TCA.

1.2.2.3 Formation of TCA from 1,1,1-trichloroethane

The main degradation pathway of 1,1,1-trichloroethane (Fig. 2) is the oxidation to chloral which starts with the attack of an OH radical (90%) (Nelson et al., 1990; Atkinson et al., 1992; Platz et al., 1995), while 5% are taken up by the oceans and hydrolyzed to acetic acid and another 5% are transported to the stratosphere and photolyzed to acetyl chloride. The relatively stable intermediate chloral (CCl_3CHO) can react further with OH radicals with an atmospheric lifetime of 5.4 days (Rattigan et al., 1998). Concerning the chloral reaction with OH radicals, Hayman (Hoekstra, in press) calculated, using a 2-D global tropospheric model, that the OH radical attack of chloral can lead via the chloralperoxy radical to the formation of very small amounts of TCA, i.e. 0.06% of 1,1,1-trichloroethane.

Photolysis of the chloral leads to C-C bond cleavage (Cox et al., 1995). The lifetime of chloral due to photolysis is 3.4 (Rattigan et al., 1993) to 4 h (Rattigan et al., 1998).

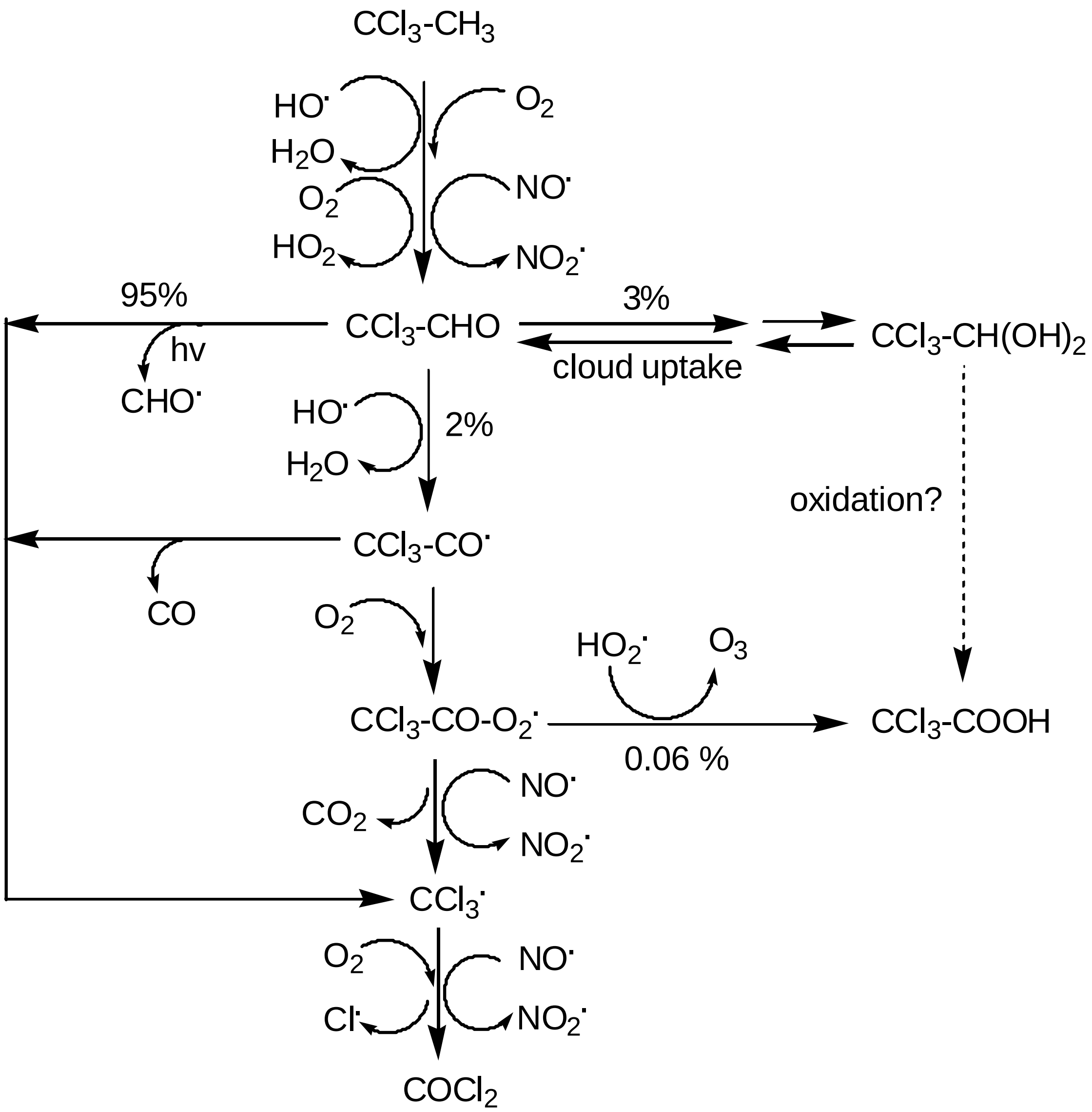

Fig. 2: Tropospheric degradation of 1,1,1-trichloroethane (Sidebottom and Franklin, 1996)

TCA is produced from $CCl_3C(O)O_2$ and HO_2 radicals only when NO_x concentrations are low, because NO_x will compete with HO_2 radicals for oxidation. Thus, this is a feasible TCA source only in clean rural areas. As chloral can also be photolyzed with an atmospheric lifetime of only a few hours (Barry et al., 1994), the OH attack plays only a minor role in the atmospheric degradation of chloral, and the photolysis dominates. Thus, photodegradation of 1,1,1-TCE in the atmosphere represents only a minor source for TCA, and even then only in rural environments.

A further process is the uptake of chloral into clouds where it may be oxidized to TCA. One should realize that the uptake of chloral into clouds is a process dealing with great spatial and temporal heterogeneity while the photolysis and attack of chloral by OH radicals is a more homogeneous process; therefore, the first step of cloud uptake is the formation of clouds and the transport of the gas in the cloud. This step is rate determining for extremely soluble and reactive compounds. The second step is the entry of chloral into the cloud droplets and its hydration, which is determined by mass transfer coefficients in the gas phase and cloud droplet, and the Henry's law constant of chloral ($H\ K_{hydration}$ = 499,000 mole/l atm at 15°C (Betterton and Hoffmann, 1988)). Next, the third step, the oxidation of chloral or chloralhydrate in the cloud droplets, might occur although it has yet to be confirmed through laboratory experiments. Jordan and Frank (1999) assume that this process exclusively leads to the formation of TCA and that complete conversion is achieved on a timescale compatible with the average lifetime of cloud droplets. Chloral may well be oxidized to TCA, but one can imagine that also other products such as chloroform, chloride, formaldehyde and carbon dioxide can be generated. Since gas phase reactions were calculated not to contribute significantly to TCA formation, uptake of chloral in the cloud droplets might be the only formation route of TCA. Concluding, 1,1,1-trichloroethane may be one of TCA's precursors, although the yield does not exceed 2.8%.

1.2.2.4 Formation of DCA from trichloroethene

The generation of DCA in the atmosphere is assumed to be from trichloroethene, which produces phosgene ($COCl_2$) and dichloroacetyl chloride (DCAC, CCl_2COCl) as the main products in the reactions with the OH radical (Tuazon et al., 1988; Gürtel et al., 1994; Itoh et al., 1994). DCAC can be hydrolyzed to DCA, analogously to the hydrolysis of TCAC. No published data, however, exists about the fate of DCAC.

1.2.2.5 Formation of TCA from TRI and PER vs. actual environmental levels

On a global basis, the annual yields of TCA are 13,600 tons from PER and 4300 tons from 1,1,1-TCE, based on the atmospheric burdens and loss rates typical of the late 1990s (McCulloch, 2002).

The transformation percentages of 1,1,1-trichloroethane and tetrachloroethene can be used to calculate the formation rate of TCA in the troposphere. The 5.5-year lifetime of 1,1,1-trichloroethane is sufficient so that it is distributed uniformly across the globe. The lifetime of tetrachloroethene, being a shorter lifetime of 0.5 years, causes an average concentration of 0.07 ng/l in the Northern Hemisphere and 0.01 ng/l in the Southern Hemisphere. The maximum global TCA formation rate from 1,1,1-trichloroethane and tetrachloroethene is calculated to be 22 kt/yr in 1996 and the maximum TCA concentration in rain water about 90 ng/l in the Northern Hemisphere by using an average annual wet deposition of 800 mm. On the Northern Hemisphere the real median TCA levels in rain water seem to be higher than the maximum TCA concentrations calculated from the degradation of 1,1,1-trichloroethane and tetrachloroethene. The real median TCA concentration in rain water, ranging from 100 - 200 ng/l, indicate TCA may originate from other sources than 1,1,1-trichloroethane and tetrachloroethene in the Northern Hemisphere. The additional sources are becoming more important since the contribution from 1,1,1-trichloroethane and tetrachloroethene has been expected to be reduced while the median TCA concentration in rain water has stayed constant since 1996 (Hoekstra, in press).

1.2.2.6 Reaction of Cl radicals with atmospheric organic matter

Recently there have been some reports (Aucott, 1997; Wingenter et al., 1999) about the reaction of Cl radicals, which are present with a global average of 6.5×10^4 molecules/cm^3 in the atmosphere, with atmospheric organic matter which resides on particulates to form pristine TCA.

1.2.3 Other sources of chlorinated acetic acids

Terrestrial sources might also contribute to the formation of HAAs. A backward trajectory study by Römpp et al. (2001) shows that the median TCA concentration in fog originating from air masses of land-based areas is about two times higher (160 ng/l) than in fog from air masses of marine areas. This would indicate that terrestrial origins may be more important to explain the additional sources to 1,1,1-trichloroethane and tetrachloroethene. Examples are chlorination processes, waste incineration, etc. Mowrer and Nordin (1987) detected a median TCA concentration of 1.4 ng/l (0.4 - 3.7 ng/l; n = 4) in flue gases. Higher TCA concentrations were expected in wet deposition or vegetation in the near surroundings of a waste incinerator if incineration processes are indeed an important source. Although they were studied until now, no great difference of TCA concentrations in vegetation and wet deposition has been observed in the proximity of waste incinerators (Juuti et al., 1993; Reimann, 1996). Apart from waste incineration in industrial plants, the emissions of which have been reduced significantly during the past years, biomass burning could also be an important source for TCA as it emits a large range of chlorinated compounds such as chloroform (Rudolph et al., 1995) and other alkyl halides.

TCA emission could also originate from chlorination processes, such as disinfection and pulp bleaching. As TCA does not evaporate significantly from the aqueous phase (Hoekstra et al., 1999a; Juuti, 1997), only emission by aerosols is important. It is unknown if TCA emitted from drinking water disinfection processes or from swimming pools is important. But in general the emission of chlorine from various human activities may lead to the formation of TCA in the atmosphere.

1.2.4 Natural production of TCA in soil

For a long time organochlorine compounds detected in the environment were assumed to be of anthropogenic origin, together with emissions originating from volcanoes and from oceans (Gribble 1994). However, in recent years there has been increasing evidence about the natural production of various organochlorine compounds, e.g. TCA, in the terrestrial environment (Asplund et al., 1993; Hjelm et al., 1995; Öberg et al., 1996a, 1996b, 1997). Organohalogens have been found ubiquitously in various environmental compartments (Asplund et al., 1989; Asplund and Grimvall 1991; Hjelm et al., 1995; Müller et al., 1996; von Sydow et al., 1998), including several plant species (Engvild, 1986) and soil fungi (Harper, 1985; de Jong et al., 1994).

The possibility of natural production of TCA in soil has been proposed relatively recently (Hoekstra and de Leer 1995, Hoekstra et al., 1995; Haiber et al., 1996). Chloroperoxidase enzymes (CPO) can catalyze halogenation of many organic sustances in the presence of hydrogen peroxide and halide ions (e.g. Geigert et al., 1983, Haiber et al., 1996). Asplund et al. (1993) have found a chloroperoxidase-like catalyst in coniferous forest soils, the activity of which was strongly pH-dependent, with an optimum at pH 3.0 - 3.5. Chloroperoxidase has also been found in many plants and soil fungi (Gribble 1994). Studies have shown that formation of organohalogens takes place during degradation of organic matter, in particular the degradation of lignin (Hjelm et al., 1995; Öberg et al., 1996a, 1996b, 1997; Johansson et al., 1997). Niedan et al. (2000) showed that fulvic acid can be chlorinated with CPO, producing, among other compounds, DCA and TCA.

A variety of organochlorine compounds were produced from humic acids, which are involved in several soil processes, and which were incubated with chloroperoxidase in the presence of hydrogen peroxide and sodium chloride in laboratory tests (Hoekstra et al., 1995; Haiber et al., 1996). The reaction products included TCA (5.3% relative to the enzyme), DCA, chloroform and chlorinated acetones, most of them were the same as those produced in the chlorination of drinking water and humic substances (Christman et al., 1983; de Leer et al., 1985; Italia and Uden, 1988), and by bleaching of kraft pulp with Cl_2 or ClO_2 (i.e. chlorination of lignin) (Juuti et al., 1996a). TCA concentrations as high as 7600 µg/l have been shown in the effluent from a kraft pulp mill (Yu and Welander, 1994), but 100 µg/l would be more typical of industrial treated waste water and 1 - 10 µg/l in treated domestic waste water or drinking water (Euro Chlor, 2001). The similarities of the reaction products are apparently due to the similar chemical structure of humic substances and lignin (de Jong et al., 1994). For the natural production of TCA the properties of soil may also play a significant role. Further experiments to assess a natural production of TCA consisted in the incubation of short-chained aliphatic acids which are involved in metabolism or play an important part in soil chemistry, such as acetic acid, malic acid, lactic acid, fumaric acid, malonic acid, citric acid and acetonedicarboxylic acid, with the chlorinating enzyme CPO in the presence of hydrogen peroxide and sodium chloride (Haiber et al., 1996). All reactions resulted in the formation of TCA at concentrations ranging from a few promilles up to 8% relative to the enzyme. Acetic acid produced 8.1% TCA relative to the enzyme; it is the best tested precursor for the TCA formation, because the molecular structure is already present. Even in experiments without CPO, TCA was formed, e.g. humic acid forms TCA without CPO. This may be due to the fact that commercially available humic acids contain short-chained aliphatic acids (1 - 6%), but the TCA concentrations are so high that it is suggested that humic acid itself possesses chlorination potential. Although a natural TCA formation has not been shown to take place in the terrestrial environment, the compounds necessary for a natural formation: hydrogen peroxide, chloroperoxidase and suitable organic substrates are all available in soils.

1.3 Occurrence of chlorinated acetic acids in the environment

In the following sections the occurrence of TCA in various environmental compartments (the hydrosphere, air, biosphere, soil) is discussed in detail.

1.3.1 Hydrosphere

1.3.1.1 Precipitation

Several studies describing the analyses of TCA in snow, rain and cloud water have been published, supporting the ubiquitous presence of TCA in the environment. Most of the determinations originate from Central and Northern Europe (Schöler et al., 1991; Schleyer et al., 1991, 1996; Clemens 1993; Lorbeer et al., 1994; Fillibeck et al., 1995; Plümacher 1995; Haiber et al., 1996; Müller et al., 1996; Reimann et al., 1996; Schleyer 1996; Juuti 1997; Schöler 1998; von Sydow et al., 1999, 2000; Reeves et al., 1999; Berg et al., 2000; Peters, 2000). The data are listed in Euro Chlor (2001).

The main conclusion from these studies is that TCA is ubiquitous in rain water and snow. But, interestingly, its concentrations are highly variable and the variations cannot be correlated with location or date. There is no consistent difference between the concentrations found in cloud, rain and snow and no correlation between quantity of rainfall and the concentration of the highly soluble HAAs. A local reduction in rain water concentration in SW Germany has been demonstrated for the early 1990s, but there is no clear global trend in time.

In general, as has been reported from Central Europe, TCA concentrations in precipitation samples are usually smaller than 1 µg/l (Renner et al., 1989; Lorbeer et al., 1994; Frank et al., 1995; Plümacher 1995; Haiber et al., 1996; Müller et al., 1996a; Reimann et al., 1996a); the mean value of the rural areas in Central Europe is 0.15 µg/l (Schöler et al., in press) and the mean value of TCA concentrations in Northern Europe is 0.1 µg/l: rain water was collected near Kuopio in Eastern Finland, the average was 0.1 µg/l (Juuti, 1997). Measurements performed in Switzerland and Austria are within the range of 0.1 - 0.2 µg/l, as well. Schleyer et al., (1996) measured TCA in rural or semirural sites in the Rhein-Main area and found mean values of 0.17 to 0.28 µg/l.

In the Northern Hemisphere the median TCA concentration in rain water as measured at different sites has decreased over the last 15 years to a median in the range of 100 - 200 ng/l until 1995 and then remaining relatively constant (Renner and Mühlhausen, 1989; Renner et al., 1990; Fillibeck et al., 1995; Frank et al., 1995; Plümacher, 1995; Schleyer et al., 1996; Reimann et al., 1996; Juuti, 1997; Klein, 1997; Berg et al., 2000; Peters, 2000; Römpp et al., 2001). In semirural forest areas surrounding Berlin the highest TCA concentrations - up to 20 µg/l - were measured (Plümacher and Renner 1993). The results reported by Reimann et al. (1996a) and Haiber et al. (1996) suggest that rural areas have lower TCA concentrations in rain water than urban areas, although systematic studies on the differences between rural and urban areas have not been performed, and there is data indicating the contrary, e.g. no significant differences in concentrations were found between the semirural area of Alpthal and the urban area of Zürich. But there seems to be some evidence suggesting a correlation between the TCA concentration in precipitation and the pollution level of the atmosphere.

Studies of Schöler et al. (in press) show that there are differences in the TCA concentrations in urban and rural areas. Their samples from 1990/91 were collected at three locations near the city of Bonn (two rural and one relatively urban site). Measurements showed concentrations of up to 7.5 µg/l (mean concentration 0.8 µg/l). In 1991/92 rain water samples were taken from Grossenbach near Siegen/Germany (Haiber et al., 1996)- the urban site. The rain water samples showed TCA concentrations ranging from < 0.1 µg/l in Nov./Dec. to almost 2 µg/l in June with an annual average of 0.57 µg/l. An explanation for the high values could be the heavy metal industry which is situated around the city of Siegen: Prevailing westerly winds transport polluants in direction of this site.

In contrast, data was also collected 1991/93 from a rural site (Schöler et al., in press): Bleche near Gummersbach/Germany. The TCA concentration ranged from 0.05 to 9.7 µg/l with a median of 0.16 µg/l. The TCA input via precipitation can be influenced by two factors: TCA concentration and rain amount. The input of TCA is relatively uniform excepting Nov. 91. In this month the rain amount was high and TCA concentration was elevated as well. Heavily polluted air masses might have passed the sampling station in that month. In Hau which is situated 30 km west of Siegen and only marginally influenced by TCA precursors from industry 0.15 µg/l (mean value) TCA were found as an average.

When studying Hau, Bleche and Grossenbach we compare two rural and a relatively urban site. Bleche and Hau are located in a rural area dominated by agriculture, far from industry using chlorinated solvents, and Grossenbach is located 10 km east of the city of Siegen. Bleche and Hau only had a yearly input of 1 - 1.5 g/ha a of TCA (except the extraordinary rain event) and showed no seasonal height in summer which was typical for the sampling site Grossenbach.

Also, if the input of TCA were predominantly of anthropogenic origin, one might expect higher concentrations in the Northern than in the Southern Hemisphere. But this is not the case, since the concentrations found in Antarctica and Switzerland do not differ significantly. This could be explained by differences in rainfall patterns: Reimann et al. (1996) describe a positive correlation between the scarcity of rain and the concentrations of HAAs found in rain water.

It has been suggested that photodegradation reactions of tetrachloroethene (PER) and 1,1,1-trichloroethane (1,1,1-TCE) are a probable source of TCA in precipitation samples (Fuchs and Bächmann, Frank et al., 1994; Plümacher 1995). This is partly based on the fact that some measurements of TCA concentrations in precipitations show seasonal variations with higher values in summer (Plümacher 1995; Müller et al., 1996a; Haiber et al., 1996; Reimann et al., 1996a). This is inversely related to the concentrations of PER and 1,1,1-TCE in the atmosphere (Plümacher 1995); which reach their highest levels in precipitations in winter. The diminished levels of TCA in winter could be due to the reduced photochemical activity and the diminished air exchange in the atmosphere due to temperature inversions (Plümacher 1995; Reimann et al., 1996a). However, data from other studies (Plümacher, 1995; Berg et al., 2000) did not show a similar trend in all cases, e.g. data from sites in rural areas in Central and Northern Europe show no seasonal trends.

The temporal trends of TCA in rain water also do not correlate closely with the levels of PER and 1,1,1-TCE. Schleyer et al. measured TCA in rain water over the periods of 1988 - 1989 and 1993 - 1994 at the same site in SW Germany and found that, at the same set of sites, the median concentration dropped from 0.44 to 0.12 µg/l (Schleyer et al., 1991, 1996). But one has to be cautious as Schleyer's group (1996) changed its analytical methods and improved their analytical performance with time. Whereas the reduction of TCA by a factor of 4 is significant, European PER emissions dropped only by 20% and that of 1,1,1-TCE by 50% over the same period (Midgley and McCulloch 1995; McCulloch and Midgley 1996). Given that the yield from chlorinated solvents depends linearly on releases, even after allowing for transport effects, the discrepancy between the reduction levels indicates that additional factors have a significant influence on local TCA concentration in precipitations.

1.3.1.2 Throughfall

Rainfall percolating through forest, throughfall, has been studied and was found to contain distinctively higher TCA concentrations (by a factor of 2 - 3) than the rain water collected from open fields (Renner et al., 1990; Plümacher and Schröder 1994; Reimann et al., 1996a). This could be due to TCA that has been sequestered from the atmosphere and is washed off the leaves, or generated in and on the leaf and needle surface. An aqueous TCA solution sprayed on spruce needles remains on the surface and can be rinsed with water (Frank 1991); this could simulate the evaporation of raindrops and adsorption from air. Rain water measurements from Schleyer et al. (1996) were monitored in 1993/1994 in open fields and in forested areas at 9 rural and semirural sites: the mean values in the forests ranged from 0.2 to 0.85 µg/l and the mean values in open fields ranged from 0.17 to 0.28 µg/l.

1.3.1.3 Firn and snow

Determinations of TCA measured in old ice and firn samples were reported by Haiber et al. (1996), Schöler (1998), and von Sydow et al. (1999, 2000) and relatively high concentrations were found, even in remote areas and preindustrial layers.

Haiber et al. (1996) found an average of 100 +/- 40 ng/l (n = 3; the measurements ranged from 0.016 to 0.14 µg/l) in a glacier ice from the glacier Monte Rosa, Italy, that was dated to around 1900. Von Sydow (1998) measured 1- 13 ng/l (n = 2) in glacier ice that originated from before the 16. century in northern Sweden (Storglaciären); she found similar concentrations in glacier ice samples of Marmaglaciären dated to be 180 to 200 years old. She also found TCA at concentrations of 7 - 10 ng/l (n = 3) in firn sampled at 36 - 46 m depth in Antarctica from approximately 1900. In another 20 m firn core taken by von Sydow et al. (2000) and formed about 1800 in Antarctica the TCA concentrations ranged from the detection limit to 38 ng/l (n = 25) with an average of 12 ng/l. The TCA concentration was diverse at different depths; it is not clear if this was due to temporal variation in deposition or to degradation. The possibility of TCA degradation in older snow has to be taken into account when looking at preindustrial layers.

Considerable care was taken to ensure that during sampling and analysis the old ice and firn samples were not contaminated by the present environment. It was shown that contamination through the years was highly unlikely in firn due to the involatility of the trichloroacetate, which was present as salts, and very low ionic mobility in general in frozen firn at -51 ^{o}C.

All three of the CAAs have also been found in precipitations collected at different remote sites including Antarctica (Boren et al., 1995; Grimvall et al., 1995, von Sydow et al., 1999). TCA was found at Queen Maud's Land (Antarctica) at elevations ranging from 850 - 3100 m above the sea level at 2 orders of magnitude higher than the detection limit. The TCA concentrations in fresh snow are similar to those in rain water (Haiber et al., 1996; Reimann, 1996; Juuti, 1997; von Sydow, 1998). TCA concentrations measured in fresh snow in Antarctica (von Sydow, 1998), (22 - 118 ng/l, median 38 ng/l, in January 1994 and 58 - 348 ng/l, median 168 ng/l, in January 1997), are higher than those on the Northern Hemisphere in some cases (von Sydow et al., 2000).

In certain snow samples from the Russian Tundra, from British Columbia, from Northern Sweden and from New Zealand TCA was not detectable. A closer examination of the data showed that TCA was primarily absent in those samples collected after major snowmelt periods. The TCA contents in all other samples ranged from 0.035 to 0.055 µg/l for the measurements in the Russian Tundra, from 0.02 to 0.05 µg/l for the measurements in British Columbia, from 0.015 to 0.04 µg/l in Northern Sweden and below the detection limit in New Zealand. The data suggest that TCA is degraded when the snow gets older.

1.3.1.4 Fog

Fog water was shown to have elevated concentrations of HAAs relative to rain. Fog water (96 samples) was collected from July 1998 to March 1999 at an ecological research site in northeastern Bavaria, Germany (Römpp et al., 2001). Higher concentrations, up to 11 µg/l MCA, 5 µg/l DCA and 2 µg/l TCA were found in fog water associated with westerly winds. The increase of TCA from fog water to rain water might be plausibly explained by the difference in formation mechanism of the droplets.

1.3.1.5 Sewage waters

Conflicting results were found in two studies of the TCA concentrations in the influent and the effluent of sewage plants. 5 Swiss communal sewage plants were investigated and the TCA concentrations ranged from 0.27 to 3.6 µg/l with an average of 1.4 µg/l in the influent and 0.04 to 1.1 µg/l with an average of 0.43 µg/l in the effluent (Müller et al., 1996; Berg et al., 2000). The mean elimination rate was 60%. The elimination was probably due to microbial degradation. Schöler et al. (in press) investigated a small domestic sewage treatment plant and found 0.3 µg/l in the influent and 1 µg/l in the effluent. This would represent a formation of 300%, suggesting the input of TCA from sewage waters to surface waters might be important. Further studies of the input of TCA from sewage water to surface water are necessary.

1.3.1.6 Seawater

Measurements of Tokyo Bay by Hashimoto and Otsuki (1998) and Hashimoto et al. (1998), show a mean of 1.7 µg/l TCA which is significantly higher than the concentrations measured in lakes and rivers in Europe. Judging from contemporary measurements in rivers feeding Tokyo Bay, the source of this material would seem to be polluted drainage from the Tokyo metropolitan area.

1.3.1.7 Peat bog waters

To investigate a possible decomposition or physical or chemical binding to humic substances the fate of TCA in bog waters was examined. Water samples with a high humic acid content were used to study the recovery of TCA (Haiber et al., 1996). Depending on the humic acid contents the recoveries decreased quite substantially: TCA is probably bound chemically or physically to the humic acid or decomposed. Radical polymerisation reactions may be important in this case. Interestingly, samples of peat bog water from the natural reserve Rotwasser in Odenwald (up to 0.55 µg/l), the Hohlohsee in Black Forest (up to 1 µg/l) and Georgenfelder Hochmoor in Osterzgebirge (up to 0.53 µg/l) showed high concentrations. These regions are far from industries which could emit possible precursors. The peat bog waters are acidic (3.5 to 4.5 pH) which is close to the optimum of chloroperoxidase enzyme. Interestingly, the lowest TCA values were found in winter, indicating a natural biological process as the activity of microorganisms is relatively low at that season as well.

1.3.1.8 Lakes and rivers

The concentrations in lakes and rivers in Germany and Switzerland are, in general, similar to or below the concentrations in contemporary rainfall in the same area. But, it must be admitted that there is not a significant number of measurements of TCA, although Frank et al. (1995), Müller et al. (1996), Hashimoto et al. (1998), Hashimoto and Otsuki (1998), Schöler (1998) and Berg et al. (2000) performed determinations. In 1992/93 concentrations in Lake Greifensee/Switzerland were measured, ranging from 0.06 µg/l in the hypolimnion and 0.13 µg/l in the epilimnion. This variation in TCA contents shows the stratification of the lake and indicates that the introduction of TCA occurred mainly into the epilimnion. The vertical TCA distribution did not vary significantly during the study period. The TCA levels of other Swiss lakes were < 0.1 µg/l. In ten Swiss rivers the TCA contents varied between < 0.03 and 0.34 µg/l, with an average of 0.14 µg/l; clean Alpine rivers mostly had less than 0.03 µg/l, and the river Aare had an elevated value of 0.32 µg/l. German river measurements ranged from 0.12 to 0.6 µg/l. German surface waters spanned from < 0.03 µg/l (springs and pristine brooks) to high levels in the polluted rivers at Chemnitz (1.9 µg/l). Similarly high values were found in Tokyo, Japan, the high levels are readily explained by the generation of TCA via oxidative water treatment processes. The measurements do not cover a sufficiently wide geographical area for any global significance to be assessed, although most TCA levels in surface waters were below 0.2 µg/l.

The residence time of TCA in lake and river waters has been estimated: the shortest was 8 days for the disappearance of TCA during infiltration of river water into groundwater [Switzerland] (Berg et al., 2000), and the highest residence time was determined by Müller et al. (1996), deducing a half-life of more than 230 days for a Swiss lake. Ellis et al. (2000), working in field aquatic microcosms found disappearance over 40 days including an induction period. Other rates were much slower, with Hashimoto et al. (1998) finding no loss in river water after 30 days (20% loss in seawater over 9 days).

1.3.1.9 Groundwater

The occurrence of TCA in groundwater and bank infiltration in Switzerland was investigated 1993 (Müller et al., 1996; Berg et al., 2000) and 61 groundwater and well water samples were measured; the TCA concentrations were always below 0.03 µg/l. The bank infiltration of the Swiss river Glatt revealed a TCA concentration in the river water of 0.15 µg/l but after a 2.5 m bank infiltration the TCA concentrations dropped to < 0.03 µg/l. The TCA is probably eliminated by microbial processes.

Scheyer et al. (1996) also investigated TCA levels in spring water and groundwater. TCA could be measured above the detection limit - 0.03 µg/l - with a maximum value of 0.2 mg/l in only 10% of the samples. No relation between TCA concentrations in groundwater and the TCA input into the catchment area (forest - fir or beech stands - or open fields) could be found. Data from Haiber et al. (1996) and Bertram (1996) showed TCA concentrations between the detection limit and 0.09 µg/l. While in 1995 TCA concentrations in 2 groundwater samples were below the detection limit, TCA traces were detected in 4 of 5 samples ranging between 0.04 and 0.09 µg/l in

1996. The TCA measurements from the natural lysimeter system in Grossenbach (see above) varied between < 0.03 µg/l and 0.06 µg/l.

Due to its high water solubility, TCA is mobile in soil and can become leached by heavy rain events. TCA is transported in the soil to the groundwater. During 1989 and 1995 no temporal trend was found and the overall median concentration was 54 ng/l (Renner and Mühlhausen, 1989; Renner et al., 1990; Schleyer et al., 1996; Juuti, 1997).

Gaber et al. (1974) performed a detailed investigation about leaching: the mobility of TCA in soil was explained as a function of soil humidity. At a humidity of 33% TCA penetrated up to 15 cm depth within one day, at a humidity of only 5% TCA remained in the upper soil layers for 25 days. When adding 25 or 60 cm of rain water to these lysimeters, TCA penetrated to a depth of 20 - 25 cm and 40 cm, respectively.

The median TCA levels in pore water are higher than in groundwater, but the concentration range is not significantly different. The median TCA pore water concentration is generally constant or decreases with depth.

1.3.2 Air

All three chlorinated acetic acids are detected in the air in fairly low concentrations (Frank et al., 1994, 1995). TCA cannot be expected to be found in the gas phase due to its great water solubility (Bowden et al., 1997). Instead, one would expect TCA to be attached to aerosol surfaces, being present in the particular phase of the atmosphere (Fuchs and Bachmann 1987; Behnke and Zetsch 1991). There are very few measurements of TCA in air; the data ranging from 6 - 2600 fg/l (Frank et al., 1994 and 1995; Klein, 1997; Peters, 2000). The observations are quite consistent as related to the precipitation of the same place and time (Peters, 2000). The TCA concentration in urban air ranges from 6 to 500 fg/l in Bayreuth during March 1995 till October 1996, 52 fg/l in Zürich in September 1995 (Klein, 1997), 25 - 160 fg/l in Tübingen from December 1993 till June 1994 (Frank et al., 1995), and < 500 fg/l in Rotterdam in October till December 1999 (Peters, 2000). The TCA concentration in rural air ranges from 390 - 2600 fg/l in spruce fir forest at Schönbuch near Tübingen during March till June 1992 (Frank et al., 1994), 32 - 75 fg/l in Waldstein in June 1995, 34 fg/l at Mace Head, Ireland, in October 1995, 70 fg/l at Jungfraujoch in June 1996, 550 fg/l about 100 km north of Pretoria, South Africa, in August 1996, 80 fg/l at Cape of Good Hope, South Africa, in October 1996 (Klein, 1997) and 700 fg/l in a coniferous forest near Apeldoorn (NL) (Peters, 2000).

No great differences of TCA concentrations between urban and rural sites can yet be found. But, interestingly, the rather high TCA concentrations were measured in coniferous forests. Especially in mountainous areas with enhanced fog and high precipitation levels the TCA input can be relatively high.

There is no clear trend at a large time scale, but the air measurements from Bayreuth show a seasonal variation of the TCA concentrations similar to the trend found for TCA concentrations in rain water (Reimann et al., 1996a; Klein, 1997). From April to September in 1995 and 1996 the average TCA concentration in air was 75 and 48 fg/l, respectively, while from October 1995 until March 1996 the average was 18 fg/l.

1.3.3 Biosphere

1.3.3.1 Concentrations of TCA in needles and leaves

The concentrations of TCA found in plant tissue are certainly region-specific and may also be plant-specific, since conifers seem to contain more than other species. Concentrations in conifers range from 0.6 -178 µg/kg, the values have not been found to be related to the general pollution level of the atmosphere (Euro Chlor 2001; Frank, 1988, 1991; Frank et al., 1990, 1992, 1994, 1998; Juuti et al., 1993, 1995, 1996b; Plümacher and Renner, 1993; Plümacher and Schröder, 1994; Plümacher, 1995; Norokorpi and Frank, 1995; Reimann, 1996; Juuti, 1997; Matucha et al., 1999; Weissflog et al., 1999; Franzaring et al., 2000; Peters, 2000).

Pinus sylvestris (Scots pine) contained several times as much as *Picea abies* (Spruce) in the same area. In addition to conifers, TCA (< 1 - 40 µg/kg) has also been found in the leaves of *Betula pubescens* (birch) (Norokorpi and Frank, 1993).

The concentrations of TCA in Finland or Czechoslovakia were an order of magnitude higher than the concentrations in the Caucasus/Russia, in fact these were generally lower than the background level evident in Finland. The latter showed little variations either with height (at 1 standard deviation) or with season (April vs. July/August). Significant differences were found within the delta of the river Volga and the shores of the Caspian sea (McCulloch, 2002).

1.3.3.2 Age-dependency and seasonal dependence of TCA in needles

TCA concentrations tend to increase with needle age, but the concentrations of individual trees vary considerably, and typically show a weak seasonal variation. The lowest values are found in late winter and the maximum values in autumn (Frank et al., 1994; Plümacher, 1995). However, the data of different studies (Frank et al., 1990 and 1994; Plümacher, 1995; Reimann, 1996; Weissflog et al., 2001) did not show a similar trend in all cases as noted above for rain water.

The age-dependency of the needles (Frank and Scholl, 1990; Frank et al., 1990, 1994; Plümacher, 1995) is shown distinctly by Plümacher (1995) where the median TCA concentration in one year old needles was 13 µg/kg and that of two year old ones 27 µg/kg during June 1990 and May 1991. This may be an indication of metabolism or mobilisation of TCA from the needles, as shown by Frank et al. (1992). Experiments performed with barley and oats have revealed that TCA can be transported within the plants from roots to shoots and vice versa (Schroll et al., 1994). Blanchard (1954) has reported that TCA could be translocated from foliage of maize to the roots.

1.3.3.3 Influence of kraft pulp mills on TCA concentrations of conifer needles

The influence of an established anthropogenic source of TCA is studied by Juuti et al. (1995) who measured the TCA levels in transects down- and crosswind of four kraft pulp mills using chlorine dioxide in the bleaching process. There was no increase of the TCA concentrations in needles found when approaching two out of the four kraft mills. For the other two kraft pulp mills an increase was observed until 5 km, but in the close area of the mills the TCA concentrations in the needles were as low as background levels.

The differences between the measurements are not significant in the downwind series from about 20 km onwards. Moreover, serial measurements on the parallel track at the same distance are statistically similar, indicating that, although the pulp mills might have exerted an influence locally (within the first 20 km), this was additional to a background level of 20 - 40 µg/kg. The route by which TCA enters the atmosphere from a pulp mill is not obvious from these results. TCA has been identified only in aqueous effluent and, judged solely by its Henry's law constant ($7.4\text{x}10^4$ mol/kg atm), it should remain in the aqueous phase. However, it is known to be carried through plant tissue from the root system (Sutinen et al., 1995; Matucha et al., 2000) and to have higher loadings in precipitation beneath the forest canopy (Schöler, 1998). These processes alone could result in a short range migration of TCA into the forest local to the pulp mill and away from contaminated water courses. TCA is produced during oxidative water treatment and could amount to 55,000 tons yr^{-1} (from pulp and paper manufacture, potable water and cooling water treatments) as estimated by McCulloch (2002). This flux would be introduced directly into the aqueous environment and, because TCA is so soluble and is fully dissociated in water, it should be expected to remain in that phase.

1.3.3.4 Conversion of precursors in the plant

Both tetrachloroethene and 1,1,1-trichloroethane, which are precursors of TCA, are widespread in environment, suggesting that TCA might be formed in situ. However, their concentrations are variable both between sites and within the same site with hardly any data to establish geographical trends or differences between species. It is not even clear that trees in urban environments accumulate a different loading from those in remote rural environments (Diezel et al., 1988; Frank and Frank, 1989; Plümacher and Renner, 1993; Plümacher and Schröder, 1994; Dewulf et al., 1996; Brown et al., 1999).

The uptake of gaseous lipophilic C_2-chlorocarbons and their reaction intermediates (e.g. chloral, trichloroacetyl chloride) via the needle cuticle with subsequent transformation to TCA inside the needles is a source of TCA in needles (Frank et al., 1992; Plümacher, 1995) which has been investigated by a number of researchers. The cytochrome-450 monooxygenases have been postulated to enzymatically detoxify the C_2-chlorocarbons to TCA (Frank et al., 1992; Plümacher and Schröder, 1994; Plümacher, 1995). Tetrachloroethene is converted to TCA via epoxy-tetrachloroethene and trichloroacetyl chloride, trichloroethene via epoxy-trichloroethene and chloral; but chloral can also be reduced to 2,2,2-trichloroethanol. A similar process has been known to occur in the liver of humans and animals, leading to the formation of TCA by enzymatic detoxification of 1,1,1-TCE, PER and TRI by cytochrome P-450 (Ikeda, 1977; Koppen et al., 1988; Skender et al., 1991; Back and Süsser, 1992; Vartiainen et al., 1993). Humans exposed to trichloroethene have been studied and are known to have elevated TCA concentrations in their urine. The earthworm *Lumbricus terrestris* is also able to convert trichloroethene into TCA in laboratory experiments (Back and Süsser, 1992) and excrete TCA, since an increase of the TCA concentration in soil was observed. The degradation intermediates of C_2-chlorocarbons in conifers are considered to be hydrolyzed or oxidized inside the needles to produce TCA (Frank et al., 1992; Plümacher, 1995), although the extrapolation from humans and earthworms to plants is a bit risky and one should also consider other uptake pathways, e.g. soil. Hybrid poplar has been reported to be capable of degrading TRI to produce several metabolites, including

TCA (Newman et al., 1997); this is the first time that such metabolic processes have been reported to occur in plants. As a fast growing plant, with an extensive development of root systems and high transpiration rate, poplars are very suitable for usage in phytoremediation. Poplars do not only seem to transpire trichloroethene but also to convert it to 2,2,2-trichloroethanol, DCA and TCA. Trichloroethene doses of 50 mg/l resulted in TCA concentrations of 1 - 7 mg/kg in the leaves (about three orders of magnitude higher than found in the environment), 20 - 100 mg/kg in the stems and 20 - 40 mg/kg in the roots. Exposure of poplar cell cultures to trichloroethene showed that poplar cells were able to transform and to mineralize trichloroethene (Newman et al., 1997). However the ratio of DCA and TCA was reversed. Whereas in the *in vivo* experiments more TCA was formed, in the cell exposure experiments more DCA was observed. These processes may, however, be specific to certain plants, just as certain kind of bacteria are capable of degrading different compounds.

1.3.3.5 CAAs in vegetables, fruit, grain and tobacco

In various vegetables, fruits and grain collected from different parts of the world all the chlorinated acetic acids have been found (Reimann et al., 1996b). The median TCA concentration is 2 µg/kg (< 0.2 - 6 µg/kg, n = 15), < 0.2 µg/kg (n = 3) and 1.3 µg/kg (0.6 - 4 µg/kg, n = 10), respectively. The latter samples, however, could have been contaminated during the transportation and storage, giving rise to these high values. There is little data about the metabolism of TCA inside plants. In tomato and tobacco plants harvested after 15 days of TCA exposure, trichloromethyl compounds have been detected (Mayer, 1957).

1.3.3.6 Physiological effects of TCA on plants

TCA is absorbed into Scots pine (*Pinus sylvestris*) via both the roots and the needle surfaces (Sultinen et al., 1995). It passes through the roots with the transpiration stream and there is some evidence for metabolism during its transport, up to a threshold which is unspecified. Concentrations in needles up to 750 µg/kg were achieved by sequential dosing but with this route into the plant, there was no statistically significant change in the mean area of the chloroplasts of the mesophyll cells (10.5 +/- 0.6 µm^2 for the control and 10.3 +/- 1.5 µm^2 in test plants with a needle loading of 750 µg/kg). By contrast, when applied to the needles, TCA solutions at 50 mg/l gave concentrations up to 283 µg/kg in the needles and reduced the mean area of the chloroplasts from 12.2 +/- 2.4 to 7.8 +/- 1.3 µm^2.

Physiologically, application of TCA to the needles disintegrated the structure of the epicuticular waxes and that of the stomatal cells. The extent of the effect was concentration- and time-dependent. A large fraction of the TCA (80%) remains on the needle surface and continues to cause disintegration of the stomatal cells and deterioration of the epistomatal waxes. However, the dosing concentrations used were 1 and 50 mg/l (roughly 1000 times environmental concentrations and corresponding to pH in the range 3.5 - 5.2). It is possible that the needle effects were simply a response to acid attack.

It has been suggested that TCA might interfere with the biosynthesis of pantothenic acid, a precursor of coenzyme A (Hilton et al., 1959), which is needed for several essential metabolic processes in higher plants, e.g. in the development of epicuticular waxes. Juniper (1958) has observed that the use of TCA changed the character of the surface wax of peas, making them more wettable and susceptible for subsequent sprays of other herbicides. In a study carried out in Berlin and its surroundings the most eroded wax structure was found in those needles with the highest TCA concentrations (Plümacher et al., 1995).

Juuti (1997) et al. reported that exposure via both roots and needles to 0.5 and 1 mg/l solutions at pH 5.5 - 5.2 resulted in reversible adsorption of TCA. After three weeks of exposure the needle concentration rose from 16 µg/kg to 250 µg/kg at the higher dose rate and 60 µg/kg at the lower dose rate. However, those concentrations fell to 35 µg/kg in the needles of the seedlings treated with the lower concentration TCA and to 60 µg/kg in the plants treated with 1 mg/l when the dosing stopped. At the higher dose rate a small but significant *increase* in chlorophyll concentration was measured. Net photosynthesis and chlorophyll *a/b* ratio did not significantly differ from the control and there was an insignificant drop in transpiration rate which was seen with both TCA treatments. In these tests ultrastructural changes (chloroplast area and number, and starch grain area) were minimal, and there was an insignificant reduction in dry weight after TCA treatment.

In the same dose regime, alterations in oxidative metabolism (peroxidase, POX) and conjugation (glutathionine S-transferase, GST) were observed (Schröder et al., 1997). Induction of these enzymes of xenobiotic metabolism may be a stress response to TCA, although none of the treated plants showed visible stress symptoms. It was suggested that the enhancement of enzyme activation might indicate a possible involvement of glutathionine-dependent detoxification but more research would be needed to prove that hypothesis.

In conclusion, these controlled experiments revealed very little pathogenic alterations, in contrast to some of the early work where extensive chlorophyll bleaching was imputed to aerial incorporation of chlorinated solvents into Spruce (*Picea omorica*) needles and subsequent degradation to halogenated acids by UV light (Frank and Frank, 1985, 1986). The experimental controls in those studies were such that confounding effects of parameters (such as the use of UVC to simulate environmental UV) could not be ruled out.

1.3.3.7 Phytotoxicity of CAAs

Monocotyledons, such as grasses, are the main type of plant which chlorinated acetic acids were used against, since most other plants, such as potato, oil-seed rape, kale, turnip, spinach and flax are resistant to them. Some other plants may be grown after the ground has been treated with TCA, e.g. tomato, lettuce, alfalfa, clover, cotton pea, sugar beet and bean plants. Application rates were 5 - 10 lbs/acre (6 – 11 kg/ hectare) for annual grasses and up to 50 - 100 lbs/acre for perennials (Crafts, 1961). It was not recommended for control of weeds in forests, since it was not effective. TCA has been abandoned in several European countries, since more effective herbicides have become available which require much lower rates of application.

Usually the forest health is assessed by the visual examination of the trees which is a very crude method for establishing any causal relationships. On the other hand, visual symptoms represent the final stage in a sequence of responses to stress. Thus, experimental exposures with microscopic analysis provide a superior basis for such an assessment. If the experimental conditions differ from that in the field, however, results should be interpreted with caution. The effects of a 14-day fumigation with high TCA concentrations on needles of Norway spruce (*Picea abies* L. Karst) were studied by Kristen et al. (1992), who noted increased numbers of plastoglobuli and reduced thylakoids in the needle ultrastructure. However they used 4 - 6 mg/m^3 which is about a 10^7 - 10^8 times higher than the TCA levels determined in urban air; such exposures could well cause irrelevant effects. Submersion of Norway spruce in an aqueous solution of TCA (72 - 7200 µg/l) for one minute induced tissue damage in the mesophyll and the subcuticular region, with alterations in the epicuticular wax layer (Schell and Kristen, 1992). Those TCA concentrations were about 10^2 - 10^4 times higher than the typical levels found in precipitation. The effects of long-term exposure with environmentally relevant TCA doses in coniferous species have yet to be investigated.

The experiments on the phytotoxicity of TCA are based either on short-term exposures, usually performed with agricultural species and with high doses, or on the effects noted during its formative and herbicidal effects (Mayer, 1957; Ashton and Crafts, 1973; Aberg, 1982). It has been reported (Ashton and Crafts, 1973) that TCA can cause damage to epidermal, vascular and cortical cells and reduce the nuclear size of the meristem cells. In addition, derangements of metabolic pathways, involving carbohydrate (Rebstock et al., 1953) and nitrogen (Mashtakow et al., 1967) as well as increased respiratory activity of wheat (Rebstock et al., 1953) have also been reported (Ashton and Crafts, 1973). Relatively little data is available about the phytotoxicity of MCA compared to TCA.

1.3.3.8 TCA and forest decline

The question of the possible role of volatile chlorinated hydrocarbons (Frank and Frank, 1985, 1986) and their atmospheric reaction product, TCA, on forest decline symptoms (Frank et al., 1990, 1992, 1994, 1995; Norokorpi and Frank, 1993, 1995; Gullvag et al., 1996) was first raised by Frank and his coworkers. Alterations of the photosynthetic pigments were found after the initial exposures of conifers to chlorocarbons, done with simple, uncontrolled experimental setups (Frank and Frank, 1986) or with fairly high doses (Frank and Frank, 1986). Schröder and Weiss (1991) confirmed that spruce needles (*Picea abies* L. Karst) which were exposed to relatively high concentrations (about 10 to 100-fold higher than the atmospheric levels in rural areas) of tetra- and trichloroethene showed a decrease in their chlorophyll content.

Much interest has been raised on monitoring TCA in tree needles and leaves in forests in order to study possible phytotoxicity since the beginning of the 1990s (Frank et al., 1990, 1992, 1994; Plümacher and Renner 1991, 1993; Juuti et al., 1993; Norokorpi and Frank, 1993, 1995; Plümacher and Schröder, 1994; Plümacher, 1995). The TCA concentration of the needles and the degree of branch damage of Scots pine (*Pinus sylvestris* L.) correlated in a study conducted in a Northern Finnish forest area (Scholl, 1993; Frank et al., 1994). Two groups of trees with different sensitivities to TCA were studied by Norokorpi and Frank (1995). The authors concluded that the degree of defoliation correlated well with the TCA content of needles. The site at which the trees were located had relatively homogeneous growth conditions. On the other hand, no relationship between the TCA concentrations in Scots pine needles and the extent of defoliation of the trees was found by Plümacher (1995). It is relatively unlikely that one could find a causal relationship with only one air pollutant, as the defoliation of trees is a highly nonspecific process and is influenced by a number of biotic and abiotic factors as well as by several different air pollutants which affect the trees (Salemaa et al., 1991; Innes, 1993).

1.3.3.9 Animal tissue

Clams (*Tapes japonica*) sampled from three Japanese rivers in 1995 and 1996 (Gotoh et al., 1998) appeared to have concentrated TCA from water that was contaminated with industrial effluent and municipal waste water. However, samples of the river sediment failed to show TCA and neither the clams nor the sediments contained significant amounts of chlorinated solvents. Furthermore, metabolism of trichloroethene or tetrachloroethene by clam tissue was not confirmed in *in vitro* experiments.

1.3.4 Soil

Recent determinations in soil samples, including those of a comprehensive survey of European soils, show TCA to be ubiquitous, as in precipitation. In only 13% of the 114 determinations listed TCA is found below the detection limit (generally 0.05 µg/kg). Concentrations in soils are very variable and 40% spanned a wide range (up to 380 µg/kg) while the rest of the concentrations were less than 0.5 µg/kg. Soils under coniferous trees (particularly *Pinus sylverstris*, Scots pine) seem to contain higher amounts. See also Table 2 (Frank, 1988; Hoekstra and de Leer, 1993; Plümacher, 1995; Schöler, 1998; Hoekstra, 1999; Weissflog et al., 1999; Peters, 2000; Euro Chlor, 2001).

The O-horizon (O_h) is an organic horizon, situated above the mineral soil horizons (according to FAO > 35% mass percent organic substance). The A-horizon (A_h) is a mineral horizon in the upper soil layer which accumulates humic material and/or is depleted in minerals. The B-horizon (B_h) is a mineral horizon located below the A_h, it has a low accumulation of organic material. One can observe a change of color and material in comparison to the parent rock through weathering or accumulation of soil matter.

Table 2: TCA measurements in soil (Frank, 1988; Plümacher, 1995; Peters, 2000)

Date	Location	Depth(cm)/ horizon	Mean (µg/kg)	Vegetation
1986	Freudenstadt, Germany	n.s.	100	Coniferous forest
	Berlin, Germany	O_h	40	Pine
	Berlin, Germany	A_h	7	Pine
	Berlin, Germany	B_h	3	Pine
	Berlin, Germany	O_h	8	Agricultural
	Berlin, Germany	A_h	0.92	Agricultural
	Berlin, Germany	B_h	0.08	Agricultural
20 Oct. 1999	Freudenstadt, Germany	10	2.1	Spruce, humic soil
	Freudenstadt, Germany	30	5.4	Spruce, humic soil
	Freudenstadt, Germany	10	12	Spruce, humic soil

n.s.: not specified

TCA has been found in varying concentrations. In non-agricultural soils from the Netherlands (Hoekstra and de Leer, 1993) TCA was detected in relatively low concentrations: 0.2 - 1.3 µg/kg in soil of a Douglas forest near Apeldoorn, and similar levels of 0.2 - 0.9 µg/kg in soil of a nearby beech forest. Weissflog et al. observed closely resembling concentrations of 0.04 - 1.09 µg/kg in soils of Scotch pine fir forests in southern Russia. This is much lower than in coniferous forests in the area around Berlin where 9 – 120 µg/kg were measured in the organic soil layer and 2.4 - 14 µg/kg in the A_h (Plümacher, 1995); in southern Germany even 20 - 380 µg/kg were found (0 - 20 cm) in German spruce fir forests (Schwarzwald) near Freudenstadt (Frank, 1988). Since there is a vertical distribution of TCA concentrations in soil, with the highest values found in the top soil layer (Plümacher, 1995), and as these samples were taken at different depths, these results are not directly comparable. Peters investigated soils (0 - 15 cm) in coniferous forests in various European countries and found concentrations of < 0.05 - 2.1 µg/kg. Hoekstra and De Leer (1993) found concentrations of 1.0 - 2.7 and 2.6 - 4.6 µg/kg in soils of a peat moor near Fochteloo and peat De Wieden, respectively, in the Netherlands. This fits to the values found by Schöler et al. (in press) in soils from Rotwasser (Germany) with an average TCA level of 3.8 µg/kg.

The measured concentrations of TCA can probably not be accounted for by the usage of TCA as a herbicide as it is usually not applied in forests and because it has a short half-life. However, Frank (Hoekstra, in press) reported that it could not be excluded that the measured concentrations, as found in the spruce fir forest soils of the Schwarzwald, might be due to the application of herbicides containing TCA still present at the forestries (Hoekstra, in press). Peters' (2000) recent observation of a significantly lower concentration of 2.1 µg/kg in a spruce fir forest in Schwarzwald in 2000 could support Frank's statement.

TCA values vary with depth, location, and possibly, with time. The TCA concentrations usually decrease with depth or remain constant at all individual coniferous forest sites. The concentrations in open fields decrease (Plümacher, 1995) or are rather constant (Peters, 2000) with depth. The median concentration in the top soil layers found by Peters is lower since half of the concentrations were below the detection limit. The median concentration in coniferous forest soils is higher than the median concentrations in open areas measured near the coniferous forest soils (Peters, 2000) while the 90% range of the data is similar. The few available data sets do not permit any conclusion whether the TCA concentrations really decreased during the last fifteen years. The concentrations may have decreased until 1991 and the Dutch data indicate that the TCA concentration in soil did not decrease significantly in the period 1991 - 2000 (Hoekstra, in press).

Data indicate that TCA is generated in forest soil. From environmental measurements (Schöler, 1998) a typical production rate for European forest soil is calculated to be in the range of 1600 g ha^{-1} yr^{-1} (range 8 – 31,000 g ha^{-1} yr^{-1}). Thus the flux from the 102 million hectares of forest soils in Europe could be in the region of 160,000 tons yr^{-1}. The highest TCA values were found in areas with a high input of acidity in the form of acid rain. The acidity input and additional acidification from the decomposition of needle litter often leads to a shift of the soil pH to values between 3 and 4, which is the optimum for the activity of the chlorinating enzyme chloroperoxidase.

1.4 Removal Processes

1.4.1 Removal processes from soil

Schleyer et al. (1996) studied soil leachate, passing through a 15 cm natural soil layer at four sites. The TCA measurements ranged from < 0.03 to 0.45 µg/l. Soil leachate usually showed a pronounced decrease in TCA compared to rain water from the same sampling sites. At the site Witzenhausen (Germany) the highest rain water mean of 0.8 µg/l corresponds to the highest leachate mean of 0.09 µg/l, suggesting 90% of the TCA was eliminated during seepage through a 15 cm soil layer.

Several studies reveal that the TCA concentrations found in soil decrease with soil depth. At the same time the concentrations of DCA increase, pointing to dechlorination processes (Hammer et al., 1995). Another possible reaction is the formation of trichloromethane, which has been reported from lysimeter experiments in which TCA is rinsed through columns filled with different soil types (Jacob, 1993). Another possibility for the reduction of TCA in soil is the physical or chemical binding of TCA to humic substances.

In 1992 rain water (Schöler et al., in press) and water samples of peat and soil lysimeters were collected from the site Hau near Bonn/Germany (Jacob, 1993). The peat lysimeter and the soil lysimeter consisted of a discharge funnel filled with peat (30 cm) or with excavated undisturbed soil (30 cm). The lysimeter experiments indicated that almost all of the TCA disappeared in the soil or in the peat layer. Increasing retention capacity was found in the order soil lysimeter (~ 80%), peat lysimeter (~ 90%) and natural seepage system (~ 100%). TCA was apparently decomposed and/or adsorbed in the soil and in the peat.

The mobility of TCA in soil is high (Loutstalot and Ferrer, 1950; Ogle and Warren, 1954). This can be explained by its high water solubility and acidity; therefore the adsorption onto anionic soil colloids (Kearney et al., 1965) and clay minerals (Göring, 1967) is not very important, but an adsorption onto iron and aluminium oxides is possible.

The literature data about the degradation of TCA in soils differs somewhat. This is due to the different investigation methods and soils. As several researchers report, TCA is subject to biodegradation in soil (Jensen, 1957, 1960; Smith, 1974; Audus, 1980; Lignell et al., 1984), although, in general, TCA decomposition in soil is low: Phytotoxic residues of TCA "usually disappear" from soil within 14 – 90 days (Foy, 1975) depending on soil type, moisture and temperature (Martin, 1972). In twelve weeks there was little degradation on sandy soil, most had disappeared on silt within twelve weeks and decomposition was "rapid" on a "muck" containing 82% organics (Crafts, 1961), probably because there is a larger population of microorganisms in this soil (Barrons and Hummer, 1951). Warm, moist conditions, high organic content and other conditions conducive to microbial activity have been reported to be necessary for breakdown (Loustalot and Ferrer, 1950; Ogle and Warren, 1954). Torstensson and Hammarström (1979) studied the influence of soil organic matter on TCA degradation: In all five studied soils, the degradation was highest in the upper 0 - 5 cm soil layer, because the organic content is higher and the nutrients are more easily accessible. Lignell et al. (1984) reported that liming (i.e. increasing soil pH) accelerated the degradation of TCA in soil. Thus, the residues from possible herbicide application onto soil several years ago cannot account for the TCA concentrations detected presently in soil.

Based on full application rates (50 - 100 lbs/acre, equivalent to 55 - 110 kg/ha) and the most sensitive crop species (cereals), phytotoxicity of TCA persists in the soil for

3 - 6 months (Riley and Eagle, 1990). However, more recent studies using 1,2-^{14}C-TCA have shown that microamounts of TCA, such as those found environmentally, are rapidly degraded in soil (Forczek et al., 2000). The same group also found that TCA was rendered less labile (and so less available) by absorption onto old wood, compost and similar carbonaceous components of the soil (Matucha et al., 2000).

Soil microorganisms dehalogenate chlorinated aliphatic acid herbicides, particularly dalapon (2,2-dichloropropionic acid) and TCA. This function has been identified in eight active soil bacteria (*Arthrobacter sp., Pseudomonas sp.* and *Pseudomonas dehalogens*), seven fungi (*Chlorostachys sp., Trichoderma viride* and *Acrostalagmus sp.*) and two actinomycetes (*Nocardia sp.*) (Foy, 1975). The final proof of the role of bacteria or other microorganisms in detoxification is the isolation of a responsible organism, its growth in a pure culture, using TCA as a carbon source and the inactivation of TCA. A first report on TCA decomposition in a pure culture was given by Jensen (1957, 1960): a bacterium of undefined taxonomic position was found to decompose TCA in co-culture with *Streptomyces* strains or when soil extracts or vitamin B_{12} were added to the medium. These additions were necessary for the decomposition, and the growth of the isolates on TCA was extremely weak. Recently, Yu and Welander (1995) isolated, enriched and characterized an aerobic bacterium which is able to grow with TCA as a sole source of energy and carbon; the growth of the organisms was also low.

TCA has been shown to be cometabolized by microorganisms degrading ethanol under anaerobic conditions. The organisms appear to be dechlorinating TCA and will completely metabolize it at loadings up to 35 mg/l (Kim et al., 2000).

1.4.2 Uptake of TCA into plants

Since TCA is very hydrophilic, its uptake into needles via the lipophilic cuticle may not be an important mechanism. Instead, for TCA the uptake via roots from soil would be a more feasible entry route. This has been shown for several agricultural plant species (Ashton and Crafts, 1973). Indeed, the sodium salt of TCA was applied via soil when it was used for herbicidal purposes (Martin, 1972).

The uptake of TCA into vegetation from soil via roots by the transpiration stream of the xylem is probably more important than the uptake from the atmosphere via the cuticles or stomata of the plants.

This entry is a function of

- the plant species, which determines the surface area and lipids available for accumulation
- the chemical and physical properties of the pollutant, such as its lipophilicity, water solubility, vapor pressure and Henry's law constant
- environmental conditions, such as temperature and organic content of the soil

(Paterson et al., 1990; Paterson and Mackay, 1994; Simonich and Hites, 1995).

Gaseous compounds can penetrate through the conifer needles via stomata (e.g. Schreiber and Schönherr, 1992), but aerosols and water drops (due to their surface tension) are not able to intrude into the stomata. Wetting of needle surfaces by the formation of thin water films (thickness less than 100 nm) will permit some transportation of ions across the concentration gradient. This may allow the uptake of various ionized compounds into the needles by the formation of liquid junctions from the needle surface to the substomatal cavities (Burkhardt and Eiden, 1994). However, the importance of this mechanism for the uptake of compounds into needles has still not been verified.

Uhlirova et al. (1996), Schroll et al. (1994) and Schröder et al. (in press) reported about ^{14}C-marked TCA uptake, as shown by radioactivity monitoring, by roots and its distribution within the plants, e.g. in fir trees. TCA is distributed rapidly, within a few hours, up into the current needles and is subsequently transported to older needles. The only metabolism/degradation product of TCA within the plant/soil system is $^{14}CO_2$, which means a complete mineralization takes place; no $^{14}CCl_3$ entities could be detected (Schröder et al., in press).

1.4.3 Degradation of TCA in plants

Concentration patterns of TCA and chloroform in pine needles suggest that TCA may be partly decarboxylated to chloroform inside the needles (Frank, 1991; Plümacher, 1995). Frank (1991) has reported a half-life of 10 days for TCA in spruce needles, which is similar to the rate determined for other plants (Chow, 1970). Thus, TCA needle levels represent a steady state between uptake and loss. The median of TCA concentrations in needles is 14 µg/kg (Frank, 1990; Frank et al., 1990, 1992 and 1994; Hoekstra and De Leer, 1993; Plümacher, 1995; Reimann, 1996; Reimann et al., 1996; Norokorpi and Frank, 1995; Juuti et al., 1996b; Weissflog et al., 1999 and 2001). TCA is fairly stable in higher plants (Blanchard, 1954; Ashton and Crafts, 1973; Aberg, 1982).

1.4.4 Removal processes from water

The removal of HAAs from aquatic systems was also investigated. Foy (1975) spiked a river with a pulse dose of TCA and noted its disappearance after 48 h and 14.5 km below the injection site. Since adsorption of TCA into the river bank and sediments could produce the same result, it is not clear if this shows chemical or biological removal.

In the laboratory decarboxylation by conventional methods was shown to be rather slow. A rate constant of $1.6 \times 10^{-5}\ s^{-1}$ at 70 ^{o}C (Hine et al., 1957) and $4 \times 10^{-5}\ s^{-1}$ at 76 ^{o}C (Fairclough, 1938) was determined. TCA was shown to decarboxylate at 25 ^{o}C with a rate constant of $6 \times 10^{-3}\ s^{-1}$ (Atkins et al., 1984) in the presence of water in solution in dimethyl sulphoxide and using 1,3,5-trinitrobenzene to trap the CCl_3^- carbanions formed.

1.4.5 Removal processes of TCA in air

The main mechanism of removal of airborne TCA is dissolution in cloud or rain water. The lifetime of TCA by this removal process, including uptake by the oceans, is governed by atmospheric mixing and is about 10 days due to its very high water solubility and Henry's law constant (Kindler et al., 1995; Kolb et al., 1995). Salts of TCA (e.g. ammonium trichloroacetate) are similarly soluble and would have similar lifetimes. The reaction with hydroxyl radicals, which is a secondary removal process, has a lifetime of 84 days and has relatively little influence on atmospheric concentrations (Carr et al., 1996).

1.5 HAAs in the context of other halogenated substances

Next to the halogenated acetic acids there are many other naturally formed organohalogen compounds, e.g. dioxins, vinyl chloride or halogenated alkanes. Numerous other chlorinated and brominated compounds are produced naturally, to a lesser extent fluorinated and iodinated compounds, e.g. volatile iodinated alkanes. There is still much to be learned about the formation of these compounds (Van Pee, 1998). Many halogenated compounds are not only an incidental natural byproduct; but they often play an important role for the organism itself. For example peas produce 4-chloroindolacetic acid as a growth hormone, the nonhalogenated acid is ineffective.

For a long time it was thought that naturally produced organohalogen compounds were mostly formed through enzymatic processes, e.g. by haloperoxidases. Abiotic mechanisms are now being considered and investigated systematically. They are important especially for compounds of low molecular weight , e.g. iodomethane.

1.6 Iodinated alkanes

The atmospheric impact of volatile iodinated organic compounds (VIOC) has received much less attention than that of other halogens until now, because, unlike fluorinated, chlorinated and brominated compounds they have a shorter atmospheric lifetime. Methyl iodide, for example, has a lifetime of 2 – 6 days (Chameides and Davis, 1980), whereas methyl bromide and methyl chloride have a lifetime of 1.3 years, in the case of methyl chloride, and 2 years in the case of methyl bromide. The lifetime of the many other iodinated alkanes is also in the order of days, or even less. A major reaction pathway of iodine atoms in the atmosphere is the reaction with ozone. It is generally assumed that the short-lived organic iodine compounds are not transported to the stratosphere and the role of iodine is confined to the troposphere (Chameides and Davis, 1980; Chatfield and Crutzen, 1990; Davis et al., 1996), however, Solomon et al. (1994b) noted that iodine may play a part in the depletion of lower stratospheric ozone.

Since the discovery of CH_3I in the marine atmosphere, the ocean has been identified as the principle source of atmospheric iodine. The first observations of atmospheric iodine by Heymann, von Fellerberg and Cauer (reviewed by Duce et al., 1965) was in the 1930s. Interestingly, during this period most of the atmospheric iodine over Europe originated from the burning of seaweed. Various types of macroalgae and phytoplankton take up iodide (concentration in seawater in the range of 0.7×10^{-7} mol/l (Tsunogai, 1971)) or iodate (3×10^{-7} mol/l (Tsunogai, 1971)) and transform it to different iodine compounds: besides methyl iodide, a number of other iodocarbons, such as diiodomethane, chloroiodomethane and iodopropane have been detected in seawater (Schall and Heumann, 1993). Little is known about the function of these compounds in macroalgae. They are possibly formed because of their antimicrobial effectiveness (Schall et al., 1994) or alternatively their function may be to control the growth of epiphytic microorganisms. Sometimes the water becomes super-saturated locally with iodocarbons, causing a flux from the aqueous to the gas phase (Singh et al., 1983).

There is also some evidence for a photochemical production mechanism of CH_3I in ocean water. Recombination of photochemically formed CH_3 and I radicals form CH_3I; this source contributes significantly to the global iodine flux from the ocean (Moore and Zafiriou, 1994). Light-induced halogen exchange from CH_2I_2 by seawater Cl^- is possible (Class and Ballschmiter, 1987). A much less determined source of atmospheric iodine may arise from the oxidation of iodide in seawater, producing volatile species such as I_2 or HOI (Thompson and Zafiriou, 1983).

Anthropogenic activity may also be a source of atmospheric iodine. Iodine is released to the atmosphere from the combustion of fossil fuels. However, the total source of iodine emitted from the combustion of fossil fuels is small on a global scale (Chameides and Davis, 1980). Very recently, CF_3I has been discussed as one of the most promising replacements for ozon-depleting compounds. Like other iodocarbons the photolytic lifetime of CF_3I is about two days (Solomon et al., 1994a) and it is not expected to penetrate to the stratosphere. Solomon al. (1994a) concluded that, even if CF_3I were to be applied as a widespread halon replacement, the amount of iodine released to the atmosphere would be at most 3 – 7% of the global natural sources of iodocarbons.

Once released to the atmosphere, photolytic decomposition is the dominant fate of organic iodine compounds:

$$R\text{-}I + \lambda\nu \rightarrow R + I \quad (1)$$

The interchange of I between the reservoir species and the interaction of I with aerosol particles is important. The predominant fate of I atoms is the reaction with ozone:

$$I + O_3 \rightarrow IO + O_2 \quad (2)$$

Substantial ozone depletion is possible in the troposphere and in the lower stratosphere (Solomon et al., 1994b).

VIOC are also believed to play a significant role in the global iodine cycle (Chameides and Davis, 1980; Manley, 1994). No major anthropogenic sources of iodinated compounds are known whereas various natural sources have been identified. Important terrestrial sources include: Rice fields (Redeker et al., 2000), peat bogs (Dimmer et al., 2001), wood-degrading fungi (Harper, 1985) and volcanic emissions (Jordan et al., 2000). Another important terrestrial source of iodinated alkanes also has to be considered: iodinated alkanes are also formed abiotically in soil.

2 RESEARCH OBJECTIVES

There have been no detailed investigations of the abiotic natural formation of HAAs and alkyl iodides in soil.

One of the aims of the present study were to investigate the mechanisms of the abiotic formation of HAAs with soil, humic substances and model compounds, and the effects of the addition of Fe(III), Fe(II) and H_2O_2. The influence of the iron species and H_2O_2 indicate that the formation of OH radicals might be important in the production of HAAs.

In a second study, the generation of OH radicals from iron-containing soils and humic substances was investigated, showing that OH radicals can be easily formed if iron is present.

In a third study, the natural abiotic formation of alkyl iodides in soil is studied. Iron plays a key role in this process, pointing to a coupled oxidation/halogenation reaction. Different organic-rich soils, humic acid and model compounds were investigated to study the mechanism and the release rates of volatile organoiodides. The relationship of iron(III), pH and iodide on the formation of alkyl iodides was investigated.

The results of these investigations are presented in chapter 3,4 and 5 of this work, with corresponding discussions and summaries.

3 CAA FORMATION STUDIES IN SOIL AND ENVIRONMENTAL SAMPLES

3.1 Summary

The mechanism of formation of CAAs, which are important toxic environmental substances, has been controversial. Whereas the anthropogenic production has been well established, a natural formation has also been suggested. In this study the natural abiotic formation of CAAs from soil, as well as from humic material which is present in soil and from phenolic model substances has been investigated. It is shown that CAAs are formed from humic material with a linear relationship between the amount of humic acid used and CAAs formed. More DCA than TCA is produced. The addition of Fe(II), Fe(III) and H_2O_2 leads to an increased yield. NaCl was added as a source of chloride. We further examined the relationship between the structure and reactivity of phenolic substances, which can be considered as monomeric units of humic acids. Ethoxyphenol with built-in ethyl groups forms large amounts of DCA and TCA. The experiments with phenoxyacetic acid yielded large amounts of MCA. With other phenolic substances a ring cleavage was observed. Our investigations indicate that CAAs are formed abiotically from humic material and soils in addition to their known biotic mode of formation.

3.2 Experimental Section

3.2.1 Materials

The humic acid (prakt.), the TCA (99.5%) and the hydroquinone (> 98%) were obtained from Fluka. The resorcinol (p.a.), MCA (> 99%), DCA (> 98%), and the phloroglucinol (> 99%) were from Merck, the methyl chloroacetate (99%), the methyl dichloroacetate (> 99%), the methyl trichloroacetate (99%), the N-methyl-N-nitroso-p-toluene-sulfonamide (99%), the tetrabutylammonium hydrogensulfate (~ 99%), the guaiacol (98%), the phenoxyacetic acid (99%) and the ethoxyphenol (98%) were from Aldrich. The catechol (> 99%) was from Lancaster, the KOH (> 85%),

H_2SO_4 (95 - 97%) and $FeCl_2 \cdot 4\ H_2O$ (p.a.) were from Riedel-de Haen, and the Na_2SO_4 (> 99%) was from Applichem, the $Fe_2(SO_4)_3$ (purum, > 76%) was from Fluka (heated at 400 °C for several hours) and the NaCl (p.a.) and the H_2O_2 (p.a.) were from J.T. Baker (NaCl was heated overnight at 600°C).

Coniferous forest soil was collected in May 2001 from a rural area located in the Odenwald/Germany (49°36'39"N/8°53'11"E); soil samples were taken from the A-horizon (A_h). The soil was freeze-dried and stored in a freezer (-24°C) until laboratory experiments were conducted.

3.2.2 Synthesis of diazomethane

Diazomethane was prepared using the method of de Boer and Baker (1954).

Every step of this reaction has to be performed under a hood with a security glass pane. Diazomethane is poisonous, cancerogenic and mutagenic.

10 ml of a 60% ethanolic KOH solution were added to a 250 ml three-neck flask. 2.5 g N-methyl-N-nitroso-p-toluene-sulfonamide (Aldrich, Steinheim) were dissolved in 25 ml diethylether under stirring and transferred to a dropping funnel. After heating the reaction vessel to 60°C (oil bath), the etheric solution was added drop by drop. The formation of bubbles and yellow colouring indicated the formation of diazomethane. The diazomethane condensed with the simmering ether over a 15 cm Vigreux-column into a collecting main which was cooled with acetone and dry ice. The diazomethane which was not condensed was destroyed with 30% acetic acid in a wash bottle which was connected in series to avoid diazomethane emission into the environment. We obtained a ~ 0.2 molar etheric solution, which was stable for several months at -18°C. The lightening of the solution over the weeks showed a lessening of the diazomethane concentration.

3.2.3 *Method: Extraction, volume reduction and derivatization: humic acid and model substance experiments, environmental samples*

As the HAAs are found at low concentrations, a sensitive analytical method is needed to measure them. An effective method is the combination of gas chomatography (GC) and an electron capture detector (ECD) in combination with extraction and subsequent volume reduction.

200 ml bidistilled water and additives were shaken for 1 hour. To extract the acetic acids the mixture was acidified with concentrated H_2SO_4 to pH 0.8, and shaken with 20 ml of tert-butyl-methyl ether in a separatory funnel. After saturation with NaCl the aqueous solution was extracted two times and the solution was then centrifuged in the case of soil and humic material. The extracts were combined, dried over anhydrous Na_2SO_4 and reduced to 7 ml in a graduated pear shaped flask with a rotary evaporator and subsequently with a gentle stream of nitrogen to a volume of 1 ml. The obtained extracts were derivatized with diazomethane and measured by GC/ECD. The determinations of the model substances (except the experiments of resorcinol with varying concentrations) were carried out in triplicate, the other measurements were carried out in duplicate.

3.2.4 *Gas chromatography*

Fused silica capillary columns are used to separate the different substances; they are easy to use and available with different stationary phases. Quick separations with high sensitivity are possible through an optimization of the temperature program.

The GC/ECD parameters are: GC: Fisons HRGC 8265, injection mode splitless, 1 µl, carrier gas nitrogen, 2.0 ml/min, column BP10, 30 m, 0.25mm ID, 0.25 µm film thickness, temperature program: 35^oC (10 min), 8 ^oC min^{-1} to 200 ^oC.

Next to the gas chromatographic separation the analysis is performed with a detector which is selective and sensitive for the analytes: the electron capture detector. This is a detector with an especially high sensitivity for halogenated compounds. It contains a ß-emitter, in our case ^{63}Ni, which ionizes an auxilliary gas; this liberates thermic electrons. The slow electrons are conducted to the anode via a direct voltage and generate a current. When electronaffinic molecules are eluated from the column, they assimilate these electrons and the current is reduced. The measured current is compared with a reference current and the pulse rate is adjusted so a constant current runs. The pulse rate is converted into a voltage, which is proportional to the concentration of electron-affinic substances. As the ECD is only a selective, but not a specific detector, the analytes are exclusively identified through their retention time.

ECD: Carlo-Erba ECD 400, ^{63}Ni, 270 °C, make-up gas argon/methane (95/5) 50 ml/min. The compounds were quantified via external standard. A chromatogram of a standard solution of the methyl esters (1 µg) is shown in Fig. 3a; of an experiment in Fig. 3b.

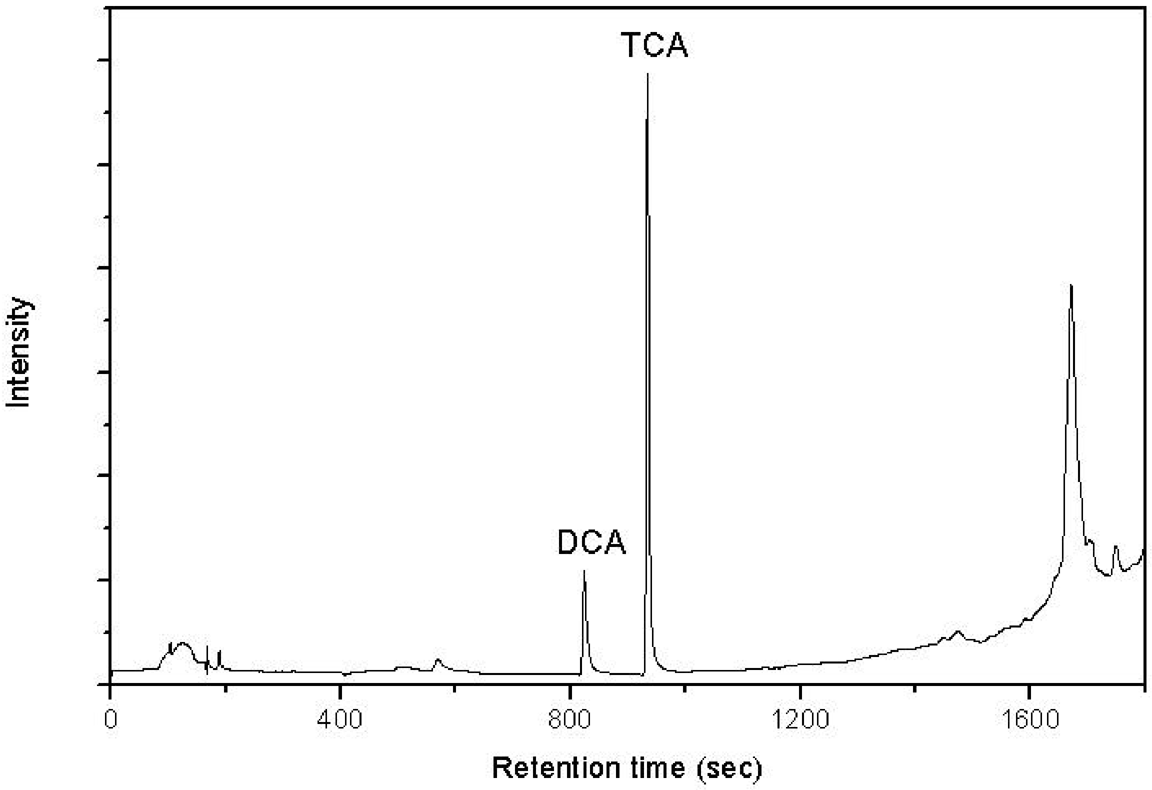

Fig. 3a: Chromatogram of DCA and TCA methyl esters (1µg) from a standard solution measured by GC/ECD.

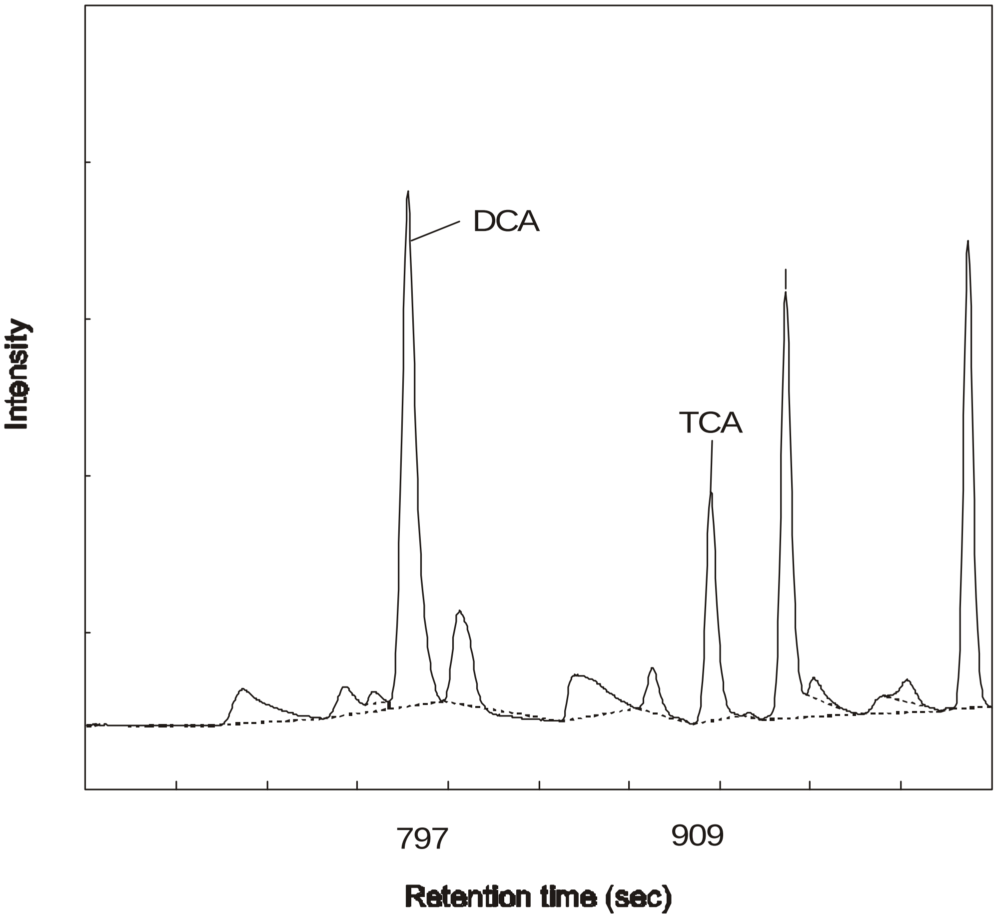

Fig. 3b: Chromatogram of an experiment with catechol, $Fe_2(SO_4)_3$, NaCl and H_2O_2.

3.3 Results and Discussion

For the precipitation/spring water analyses 200 ml sample volume was acidified, extracted, and processed. Rain samples from Bonn were analyzed: 0.82 µg/l DCA and 0.916 µg/l TCA were found. A snow sample from the vicinity of Bonn had 0.437 µg/l DCA and 0.31 µg/l TCA. Spring water from Bröl, Schnörringen and Poche (in the vicinity of Bonn) were measured: the Bröl sample had 0.945 µg/l DCA and 0.1 µg/l TCA, the Schnörringen sample had 1.74 µg/l DCA and 0.15 µg/l TCA and the Poche sample had 1.48 µg/l DCA and 0.1 µg/l TCA.

The formation of CAAs from soil, humic acid and model substances and the influence of oxidizing agents were examined. Varying concentrations of soil and humic acid were added to 200 ml bidistilled water, shaken for an hour and processed. 0.5 g soil, 0.5 g soil with 50 mg $Fe_2(SO_4)_3$, 0.5 g soil with 50 mg $Fe_2(SO_4)_3$ and 50 µl H_2O_2, and 0.5 g soil with 100 mg $Fe_2(SO_4)_3$ and 100 µl H_2O_2 (Fig. 4) was shaken. Humic acid was shaken in varying concentrations from 0.1 to 2 g (Fig. 5). To quantitate the time dependency 1 g humic acid was shaken for 5 minutes, 10 minutes, 40 minutes, 60 minutes and 120 minutes (Fig. 6). To investigate the influence of Fe(III), H_2O_2, and NaCl experiments with 0.5 g humic acid, 0.5 g humic acid and 50 µl H_2O_2, 0.5 g humic acid and 20 mg $Fe_2(SO_4)_3$, 0.5 g humic acid with 20 mg $Fe_2(SO_4)_3$ and 50 µl H_2O_2, 0.5 g humic acid with 100 mg $Fe_2(SO_4)_3$ and 50 µl H_2O_2, humic acid with 100 mg $Fe_2(SO_4)_3$, 50 µl H_2O_2 and 0.5 g NaCl were performed (Fig. 7). To study the effect of Fe(II), H_2O_2, and UV-light experiments with 0.5 g humic acid, with 0.5 g humic acid and 100 µl H_2O_2, with 0.5 g humic acid, 100 µl H_2O_2 and UV-light and with 0.5 g humic acid, 100 µl H_2O_2, and 100 mg $FeCl_2 \cdot 4\ H_2O$ were performed (Fig. 8). In the experiments with model compounds 0.5 mmol model compound was added to 100 mg $FeCl_2 \cdot 4\ H_2O$ and 0.5 g NaCl or 100 mg $Fe_2(SO_4)_3$, and 0.5 g NaCl. (Fig. 10, 11). In the experiments with varying concentrations of resorcinol concentrations from 5 - 55 mg resorcinol were used (Fig. 13).

3.3.1 Soil and Fluka humic acid suspended in water form CAAs

The soil, which we used for our first set of experiments, formed CAAs, and this formation was increased when oxidizing agents were present (Fig. 4). Assuming that humic acid in soil is responsible for these reactions, we then used commercially available (Fluka) humic acid.

The experiments with humic acid in water show that there was no need to add an oxidizing agent or halide source to produce DCA and TCA (Fig. 5). There is a positive correlation between haloacetic acid formation and humic acid content. DCA was always formed in higher concentrations than TCA, the ratio of DCA/TCA ranging between 1 - 3. Monochloroacetic acid (MCA) could not be measured, as it was below the detection limit (< 1 µg).

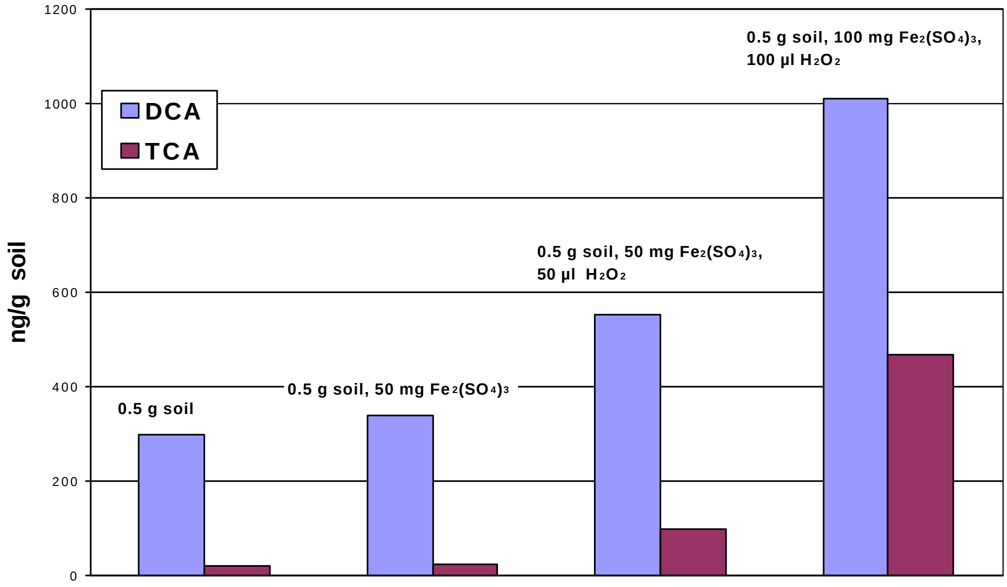

Fig. 4: Formation of DCA and TCA from soil of the Rotwasser reserve with 0.5 g NaCl.

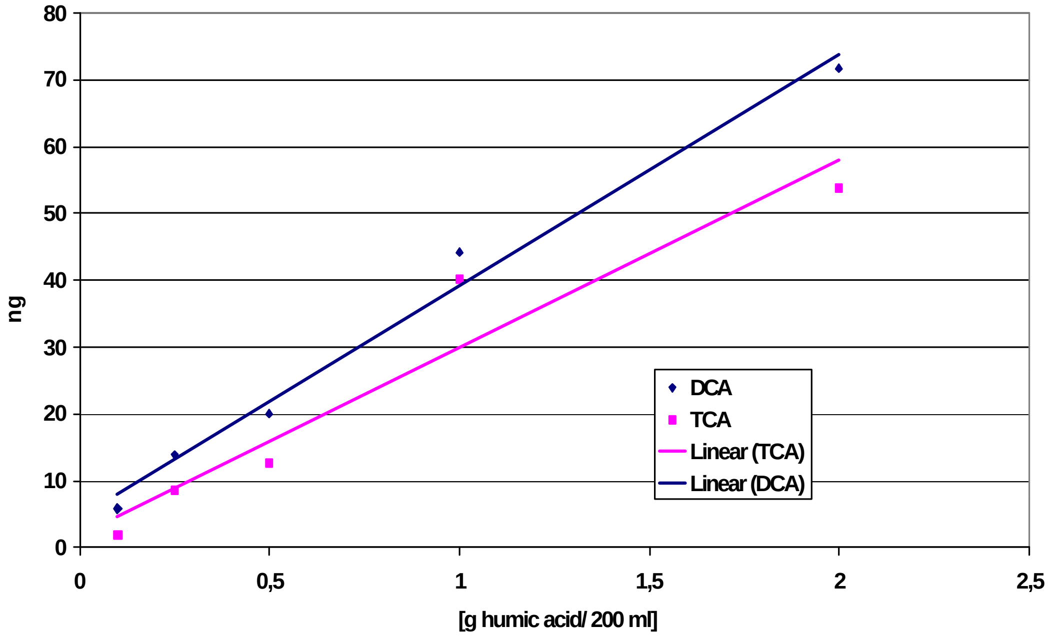

Fig. 5: Formation of DCA and TCA as a function of amount of humic acid.

This linear relationship of humic acid and CAAs formed could be explained by two effects: either by *in vitro* production or by contamination of the humic acid with DCA and TCA. DCA and TCA are omnipresent in the environment and have been shown to contaminate samples in significant amounts. If the commercially available humic acid is contaminated by DCA and TCA, either through exposure to air or from the production process, it is evident that their amounts would increase proportionately by increasing the humic acid concentration. On the other hand, there is also evidence for an *in vitro* production of DCA and TCA: an experiment with 1 g humic acid which was not shaken for an hour but directly acidified was performed, and indeed only about half of the amount of DCA and TCA, compared to the experiment in which the solution was shaken for an hour, was found. Some time-dependent measurements of DCA, using 1 g humic acid with varying time periods of shaking (5 min, 10 min, 40 min) showed an increase of DCA formation in the first 10 minutes (Fig. 6). Another hint to the *in vitro* production is given by recent studies of Keppler et al. (2002). They demonstrated the *in vitro* formation of chloromethane, chloroethane, and vinylchloride from the same humic acid which was used in this study. Thus, it seems that although some of the CAAs found might be due to humic acid contamination, there is indeed evidence of genuine *in vitro* formation as well.

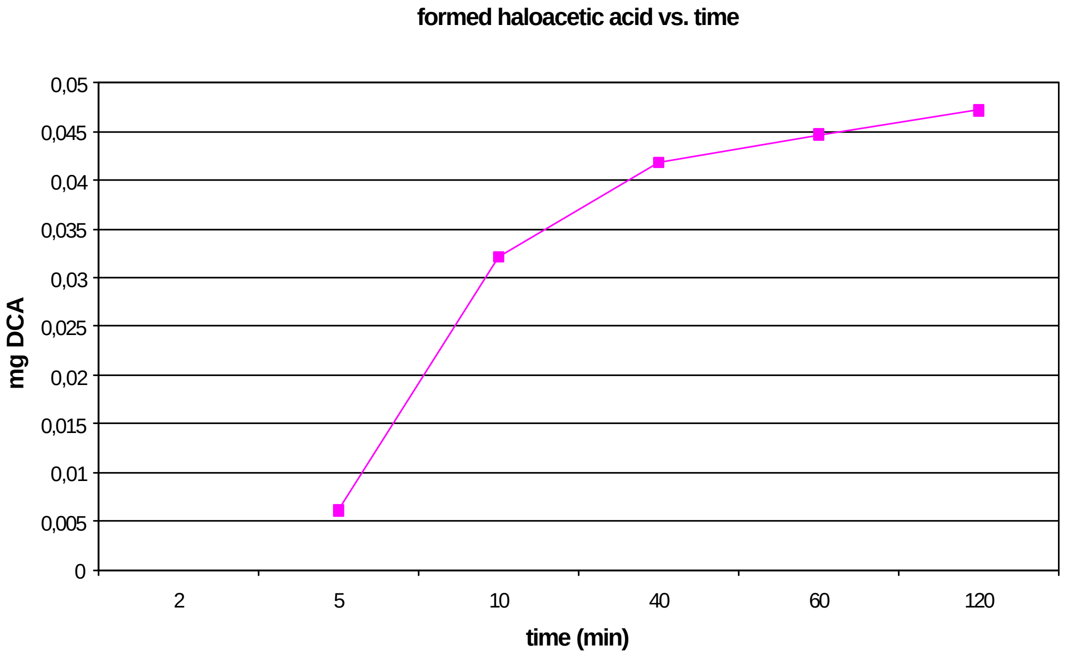

Fig. 6: The formation of DCA as a function of time.

As far as the mode of formation of DCA and TCA is concerned, an explanation could be that the humic acid contained Fe (total iron: 0.9%) and chloride (1.5%) from the manufacturing process. Iron and chloride can react with the organic matter to form CAAs. The fact that the supplement of Fe(III) in the following experiments did not lead to a considerable increase in chloroacetic acid formation might be explained as follows: there are probably complexation sites in the humic acid, all of which were occupied by iron. When additional Fe(III) was supplemented these cations competed for these complexation sites, leading to a saturation in the following experiments.

The Fe(III) reacts as an oxidant in a redox process with the humic acid and during this process organic compounds could be chlorinated, resulting in the production of short-chained carboxylic halogenated acids. A possible reaction mechanism is discussed below.

3.3.2 Influence of H_2O_2, Fe(III) and Fe(II) on formation of chloroacetic acid

Experiments were carried out to test the influence of Fe(III), Fe(II), H_2O_2 and chloride (Fig. 4, Fig. 7, and Fig. 8). The addition of either H_2O_2 or Fe(III) *alone* to the humic acid or soil had no significant effect on haloacetic acid formation (Fig. 4 and Fig. 7). However, when the oxidizing agents H_2O_2 and Fe(III) were combined, a significant increase in haloacetic acid formation was observed with experiments using natural forest soil samples (Fig. 4). An addition of NaCl leads to a minor increase of DCA and a distinct increase of TCA (Fig. 6). Again, DCA was formed in higher concentrations than TCA, and the ratio of DCA/TCA shifted to higher values (4.5) when using $Fe_2(SO_4)_3$ and H_2O_2. Those concentrations increased further with higher amounts of H_2O_2 and $Fe_2(SO_4)_3$, suggesting that Fe(III) was reduced to Fe(II) by redox-sensitive organic material and that probably a Fenton reaction (Fe(II) + H_2O_2 -> Fe(III) + OH^- + $OH^\cdot$) was taking place, generating hydroxyl radicals and leading to a non-specific chlorination of organic compounds when chloride is available in the system (Fig. 7). Hydroxyl radicals and chloride form an equilibrium system with the hypochlorous acid anion as well as with the chloride anion (Herrmann et al., 1999). The latter react with each other forming chlorine which induces the so-called "swimming pool chemistry".

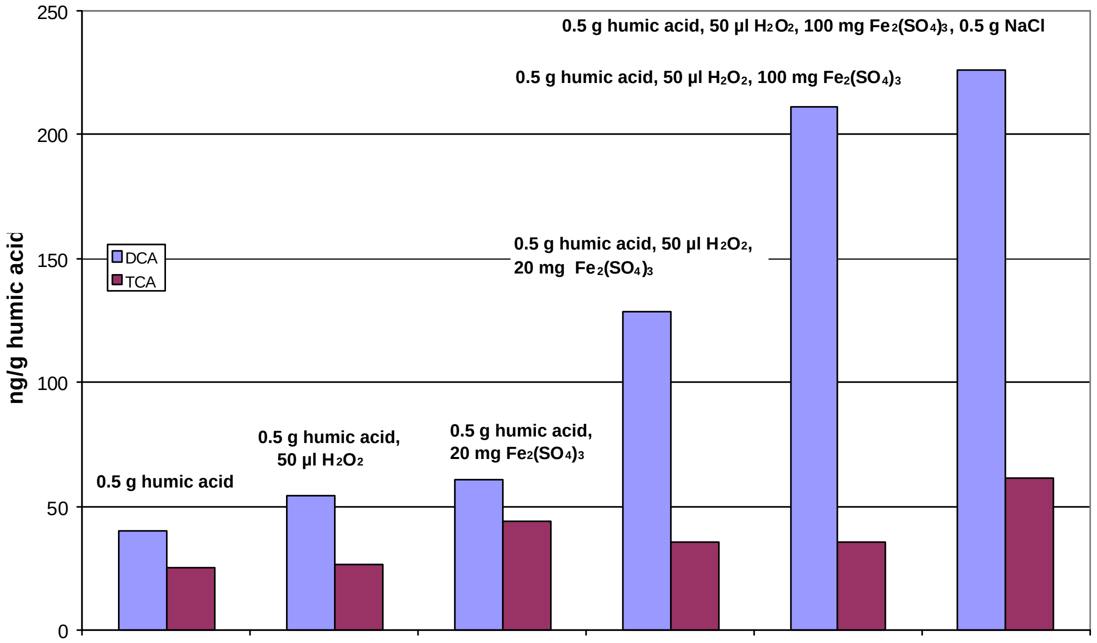

Fig. 7: The formation of DCA and TCA from humic acid increases dose-dependently with the concentration of H_2O_2 and $Fe_2(SO_4)_3$.

The C-Cl bond is probably formed via a radical-related mechanism. To test this hypothesis, we performed experiments with $FeCl_2 \cdot 4\,H_2O$ and H_2O_2 (the Fenton reagent) as well as with H_2O_2 and UV-irradiation (Fig. 8). A drastic increase of both DCA and TCA formation was found in both experiments, which indicates that OH radicals are probably involved in the reaction, either via a Fenton reaction, or the reaction of H_2O_2 with UV-irradiation.

An alternative explanation for the observed effect of the addition of Fe(III) could be the formation of a humic acid/Fe(III)-complex that acts similar to a heme group in the chloroperoxidase-mediated production of hypochlorous acid (Hoekstra, in press).

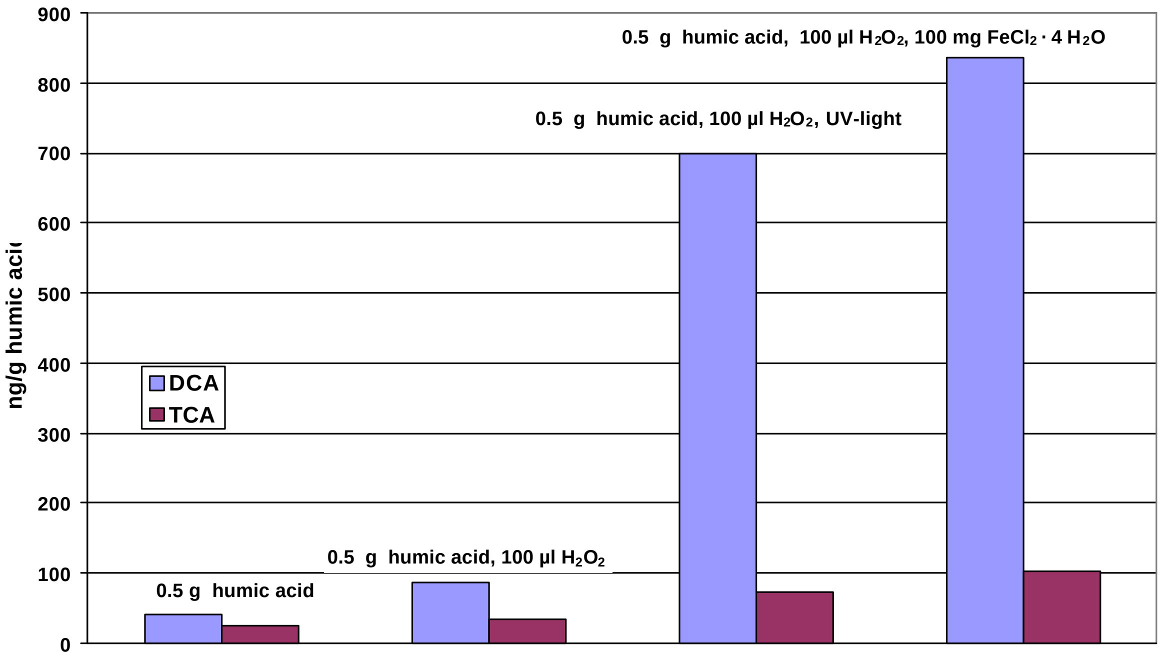

Fig. 8: The formation of DCA and TCA from humic acid is increased with H_2O_2, $FeCl_2$, 4 H_2O and UV-light.

A groundwater sample from Payrbach, Semmering/Austria, was analyzed which partly supported our hypothesis. It was an interesting sample as it contained precipitations which had percolated through an iron-rich layer, dissolving some of the iron through the natural background acidity of the precipitation, which also contained some chloride. As it moved through a former mine gallery, oxidation processes, probably by bacteria, took place. Humic material was present which originated from a forest located above. Thus, a reaction similar to one in our experiments could take place. Actually, 2.10 µg/l DCA and 0.13 µg/l TCA were found, which is slightly elevated for groundwater. This could also be due to the forest soil above.

3.3.3 Model substances: moieties of humic acids form HAAs

The structure of humic substances in nature is only partly known. To reduce the complexity of natural systems, we carried out additional experiments with phenolic model substances (Fig. 9), such as catechol, resorcinol, hydroquinone, guaiacol, ethoxyphenol, phloroglucinol and phenoxyacetic acid, which can be considered as monomeric units of the macromolecule humic acid. These were tested with either

$FeCl_2 \cdot 4\,H_2O$ and H_2O_2 or $Fe_2(SO_4)_3$ and H_2O_2, to assess the effect of hydroxyl radical formation on the production of HAAs.

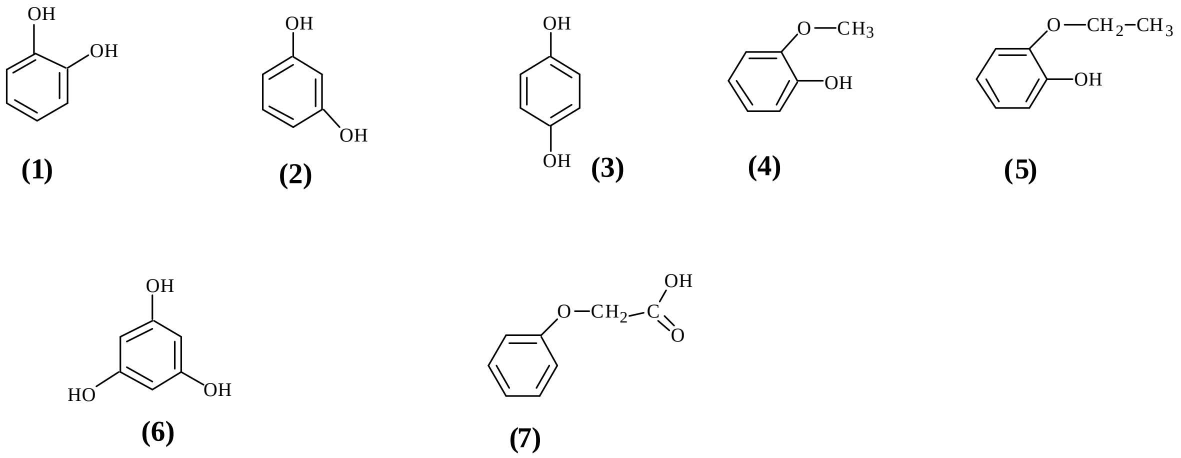

Fig. 9: Model substances used for the experiments: (1) catechol (2) resorcinol (3) hydroquinone (4) guaiacol (5) ethoxyphenol (6) phloroglucinol (7) phenoxyacetic acid

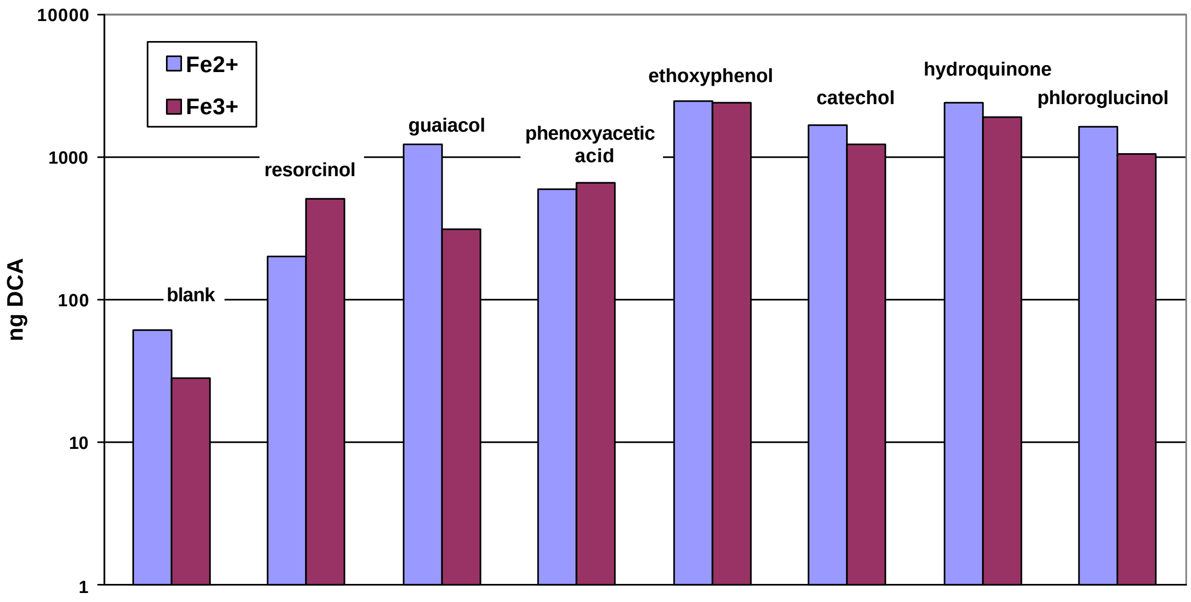

Fig. 10: Amounts of DCA formed from model substances; the relative standard deviation (RSD) ranged from 2.3% to 11.4%-

In all experiments NaCl was supplemented as a source of chloride ions and 0.5 mmol model substances was used. DCA and TCA were formed, with higher values for DCA than TCA (Fig. 10 and 11).

In the case of phenoxyacetic acid, when experiments with $Fe_2(SO_4)_3$ and H_2O_2 were performed, a large amount of MCA was formed (~ 11 µg in reactions with $Fe_2(SO_4)_3/H_2O_2$); phenoxyacetic acid and $FeCl_2 \cdot 4\,H_2O$ did not produce significant amounts of TCA compared to the blank: the blank value with $Fe_2(SO_4)_3$ (100 mg $Fe_2(SO_4)_3$, 0.5 g NaCl and 100 µl H_2O_2) was 28 ng DCA and 11 ng TCA and for $FeCl_2 \cdot 4\,H_2O$ (100 mg $FeCl_2 \cdot 4\,H_2O$, 0.5 g NaCl and 100 µl H_2O_2) was 61 ng DCA and 10 ng TCA. In experiments using only bidest. water, which was extracted and derivatized, a low background level was found (15 ng DCA and 2 ng TCA).

With ethoxyphenol there was a high formation of HAAs, as it already contains ethyl (C_2) units which are easily oxidized and halogenated, without the necessity of a cleavage of an aromatic ring system. But our experiments with other phenolic compounds showed a HAA formation even in the case of those compounds without an ethyl unit, suggesting that phenolic moieties react via a cleavage of the aromatic ring.

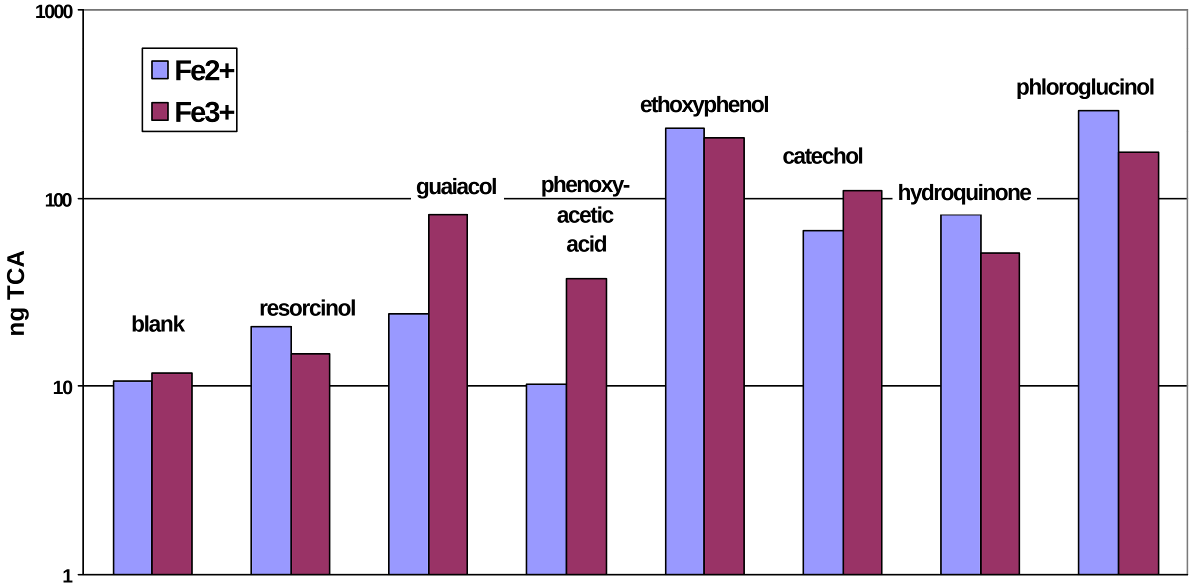

Fig. 11: Amounts of TCA formed from model substances; the relative standard deviation (RSD) ranged from 2.06% to 13.1%.

A possible ring cleavage was also shown by Hoekstra (1999b) for phenolic compounds with hydroxyl groups in meta-position (Fig. 12), which is a well-known reaction scheme elucidated during the chlorination of resorcinol in aqueous solutions.

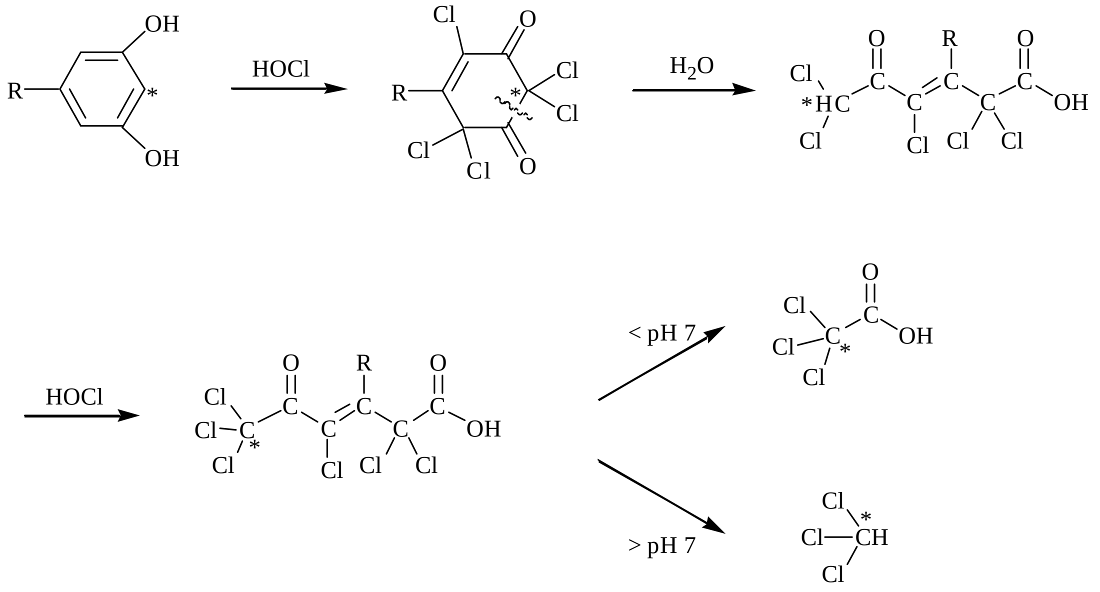

Fig. 12: Reaction path of resorcinolic substances. This reaction scheme is based on that of Hoekstra (1999b).

Recently, Pracht et al. (2001) investigated the abiotic mineralization of phenolic model substances with Fe(III). The liberation of CO_2 points to a cleavage of the aromatic ring. The two keto groups of the quinone-like structure are oxidized and partly expelled as CO_2. A similar process seems to take place here with an additional halogenation in the presence of halide ions, forming DCA and TCA. Interestingly, in the case of resorcinol (Fig. 13), higher concentrations resulted in *lower* halogenated acid formation, possibly because side reactions, e.g. polymerisation reactions, were taking place. The highest DCA and TCA concentrations were found when applying 20 mg resorcinol. This could also be the case with other compounds. Indeed, phloroglucinol also forms more DCA and TCA at lower concentrations; at a concentration of 55 mg, the concentration used for our comparison of the phenolic compounds, it forms more DCA and TCA than resorcinol, possibly because it has three hydroxyl groups in meta-position, and resorcinol only possesses two hydroxyl groups in meta-position.

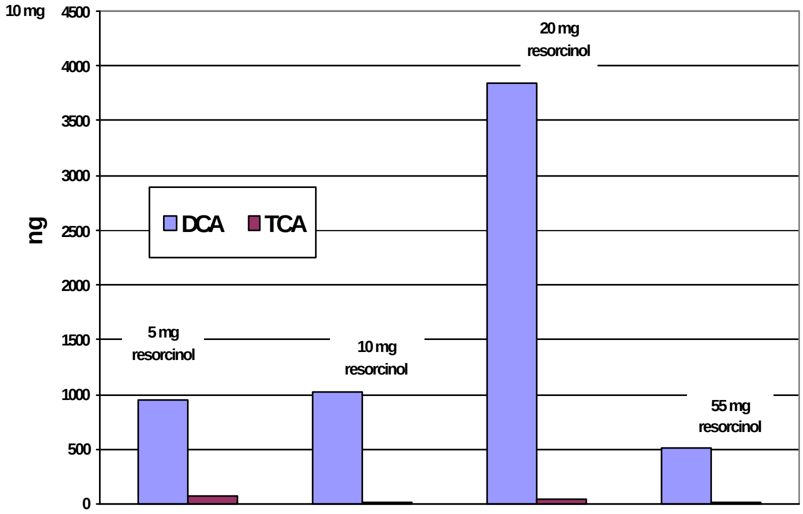

Fig. 13: Effect of resorcinol concentration on the formation of DCA and TCA.

3.4 Conclusions

Our experiments show that DCA and TCA are also formed abiotically from soil and humic acids. The reactions performed with a multitude of phenolic substances, which are common structural components of natural organic matter, supports the abiotic formation of DCA and TCA.

There is no need for either a microbial contribution or a photochemical reaction. Ethoxyphenol is degraded relatively rapidly, as it already has an ethyl unit. For the other phenolic substances a cleavage of the aromatic ring has to take place before C_2-units are available.

The oxidizing mixtures $Fe_2(SO_4)_3/H_2O_2$ and $FeCl_2 \cdot 4\ H_2O/H_2O_2$ lead to an enormous increase in haloacetate formation. Those concentrations increased further with higher amounts of H_2O_2 and Fe(III), suggesting that Fe(III) was reduced to Fe(II) by redox-sensitive organic material and that probably a Fenton reaction (Fe(II)+ H_2O_2 -> Fe(III) + OH^- + $OH^\cdot$) was taking place. Thus hydroxyl radicals were generated, which are able to oxidize chloride to elemental chlorine when chloride is available in the system and leading to a non-specific chlorination of organic compounds. The C-Cl bond is probably formed via a radical-related mechanism. The importance of this new abiotic pathway of haloacetic acid formation for the environment becomes most evident when it is realized that humus, iron and chloride are very widespread in soil. Nevertheless, a transfer of our laboratory experiments to model complex natural systems with varying environmental conditions is difficult.

Additional studies with laboratory experiments and field work on natural soils are necessary to make general assumptions about these processes.

4 OH RADICAL FORMATION IN SOIL

4.1 Summary

Humic substances are heterogeneous organic polymers that are widespread in our environment. Around three billion tons of humus are stored in soil and additionally in aqueous systems where they are involved in a great number of chemical and physical reactions. This work demonstrates the natural generation of hydroxyl radicals ($OH^{\cdot}$), which are powerful oxidants, in an aqueous system containing humic substances. Sunlight or addition of Fe(II), Fe(III) or H_2O_2 are not required to produce hydroxyl radicals. The OH radicals were detected using the 2-deoxy-D-ribose (2-DR) method followed by UV-Vis detection. The *in vitro* production of OH radicals was monitored in three different soil samples (with high humus and varying iron contents) and also in an iron-containing humic acid. The OH radical concentration in the aqueous medium increased linearly with the added amount of soil material or humic acid. The organic-rich samples showed hydroxyl radical formation at certain pH values but for the humic acid an increased radical formation was observed only with lower pH. We suggest that there is a continuous production of OH radicals in soils depending on the particular soil composition. The natural formation of OH radicals in soils may explain a multitude of chemical processes, e.g. natural halogenation and dehalogenation processes.

4.2 Introduction

The hydroxyl radical is a very potent and non-selective oxidizing species. In biological systems, OH radicals are often unwanted and highly toxic, as they can cause damage through oxidation, e.g. lipid peroxidation and DNA damage (Nappi and Vass, 1997). On the other hand, they are generated in soil and aquatic systems to decompose organic pollutants such as herbicides (e.g. 2,4-D (2,4-dichlorophenoxy-acetic acid, 2,4,5-T (2,4,5-trichloroacetic acid) or atrazine). In this context the formation of OH radicals by reaction of Fe(II) and H_2O_2 has been utilized in many studies (e.g. Lindsey and Tarr, 2000a; Lindsey and Tarr, 2000b). The chemical generation of OH radicals via the classical Fenton reaction is given by equation 3:

$$Fe(II) + H_2O_2 \longrightarrow Fe(III) + OH^- + HO^\cdot \qquad (3)$$

In natural aquatic environments one possible way to produce OH radicals is photochemical reactions. In surface water where the UV-intensity is high, they may play an important role in organic degradation processes. However, little is known about the occurrence and formation of OH radicals in soils. Although there are several ways (eq. 4 - 7) to generate H_2O_2 in soil, there is no direct evidence that hydroxyl radical production takes place. The oxidation of Fe(II) by O_2, producing H_2O_2 can be described by the metal catalyzed Haber-Weiss reaction (Haber and Weiss, 1934, Weiss, 1935;):

$$Fe(II) + O_2 \longrightarrow Fe(III) + O_2^{\cdot -} \qquad (4)$$

$$Fe(II) + O_2^{\cdot -} + 2\,H^+ \longrightarrow Fe(III) + H_2O_2 \qquad (5)$$

Another pathway forming H_2O_2 comes through the oxidation of hydroquinone (HQ) or catechol by oxygen (Halliwell and Gutteridge, 1981).

$$HQ + O_2 \longrightarrow SQ^\cdot \text{ (semiquinone)} + O_2^{\cdot -} + H^+ \qquad (6)$$

$$Fe(II) + O_2^{\cdot -} + 2\,H^+ \longrightarrow Fe(III) + H_2O_2 \qquad (7)$$

The fact that there is no direct evidence for the OH radical generation might be because the concentrations of hydroxyl radicals are below the detection limit of the ESR-technique which is used for direct measurement. Therefore, only indirect methods are useful for OH-measurements in aqueous solutions (e.g. Paciolla et al., 1999).

Soils mainly consist of inorganic components and humic substances (HS). Since HS have a variety of functional groups, including phenols and quinones, they are involved in many redox processes. One of the most important inorganic oxidants is iron, due to its abundance and redox-sensitivity. It is the fourth most abundant element in the earth's crust and is present in all natural systems. Thus it plays a key role within redox systems in natural environments (Van Cappellen and Wang, 1996). Iron has two important oxidation states, the reduced and soluble form: Fe(II) (except under sulfidic conditions), and the oxidized and less soluble form: Fe(III), which occurs mostly as oxyhydroxides. Fe(III) can be reduced by microbially catalyzed reactions or in an abiotic reaction with humic acid.

$$\text{Humic substances (red.)} + \text{Fe(III)} \longrightarrow \text{Humic substances (ox.)} + \text{Fe(II)} \quad (8)$$

In most soils the prerequisites for eq. (4) - (7) are present and Fe(II) is produced under oxic conditions. This implies that a Fenton reaction might occur. Investigations of the formation of hydroxyl radicals in iron-containing solutions were published by Yurkova et al. (1999). They described the formation of OH radicals in oxygen-rich Fe(II)/EDTA-solutions that are comparable to our system because Fe(II) and oxygen are also both present. Soil is a highly dynamic and complex system where a multitude of biological, biomediated and abiotic processes are interacting. One important process could be the generation of OH radicals under oxic conditions.

The aim of this study was to verify the non-enzymatic production of OH radicals in soils. Different soils and a commercially available humic acid were used for laboratory studies to prove this hypothesis.

4.3 Experimental section

4.3.1 Materials

Soil samples were collected between September 1998 and May 1999, at three different sampling sites on the basis of their history: soil no.1, a grassland soil of Western Patagonia/Chile (52°48’36’’S/72°55’45’’W); soil no.2, a peaty soil from the natural reserve Rotwasser Odenwald/Germany (49°36’39’’N/8°53’11’’E); and no.3, a forest soil from Hawaii (Big Island) (19°27’30’’S/155°15’40’’W). Using a clean spade, four samples (500 - 1000 g) were collected from the top soil (O- and A-horizon) in a square 1x1 m. The four samples were combined in a polyethylene plastic bag and transported to the laboratory. The soil samples were freeze-dried, milled (0.24 mm mesh) and stored in a freezer (-24°C) until chemical analyses or laboratory experiments were conducted. Soil samples and the humic acid were analyzed for pH, organic carbon (C_{org}), ash content, iron and further soil parameters. The humic acid was obtained from Fluka. For the 2-deoxy-D-ribose method the following chemicals are needed: 2-deoxy-D-ribose, thiobarbituric acid and trichloroacetic acid. All chemicals were purchased from Fluka. The water used in all experiments was freshly prepared by reverse osmosis (Millipore, USA). For the spectral measurements a spectrometer (Beckman, USA) was used.

4.3.2 2-Deoxy-D-ribose method

To detect OH radicals we used the 2-deoxy-D-ribose (2-DR) method with UV-Vis detection. There is some controversy whether the 2-DR-method can quantitate chemically generated OH radicals, because, for example, ferryl and cupryl radicals may interfere with OH radicals in the 2-DR-oxidation. At this time, however, there is no experimental evidence to prove the generation of ferryl radicals in the Fenton reaction. Therefore, with the obvious limitations of all physico-chemical methods, the 2-DR-method was used for OH radical quantitation (Biaglow et al., 1997).

4.3.2.1 Principle of the 2-DR method

The 2-DR method is a highly sensitive indirect method for the detection of OH radicals in aqueous media (Biaglow et al., 1997; Dahle et al., 1962; Winterbourn, 1991). It is based on the formation of malondialdehyde from the sugar 2-deoxy-D-ribose and its subsequent reaction with thiobarbituric acid (Fig. 14). This reaction forms a pink product that can either be analyzed fluorimetrically (λ_{ex} = 531 nm, λ_{em} = 553 nm) or Vis-spectroscopically with an absorbance maximum at 531 nm (ε = 1.49×10^5 l mol^{-1} cm^{-1}). Malondialdehyde, which is necessary for the formation of the pink product is a major product formed by the reaction between 2-DR and OH radicals. The constitutions of all other products that are formed have not been characterized yet.

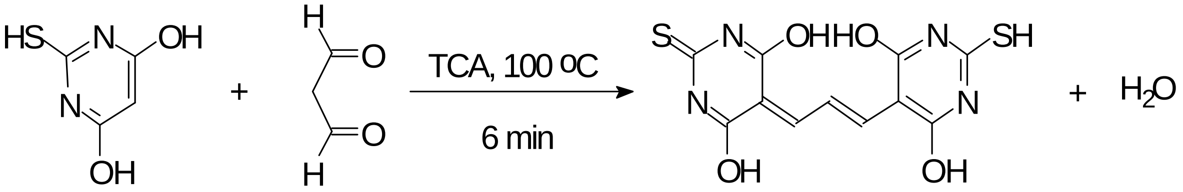

Fig. 14: Scheme of product formation by a reaction between malondialdehyde and thiobarbituric acid.

4.3.2.2 Procedure

The 2-DR method allows the detection of radicals within short times and is highly specific for OH radicals. Furthermore, it has a low limit of detection (L.O.D.). In some sonolytical experiments with pure water the L.O.D. was determined to be approximately $4\text{x}10^{-11}$ mol l^{-1} .

Three different solutions were prepared for our experiments. The first solution contained 2-deoxy-D-ribose (2-DR, c = 4 mmol l^{1}), the second contained trichloroacetic acid (TCA, c = 2.8% w/v), and the third solution contained thiobarbituric acid (TBA, c = 1% w/v).

The general procedure of this method performed in all experiments was as follows:
To a well stirred 2-DR solution (50 ml) a weighed amount of humic acid or soil was slowly added, this mixture was stirred for a defined time, after which the solution was centrifuged for 1 min at 5000 rpm in the case of humic acid to separate undissolved humic acid from the 2-DR solution. 1.5 ml was taken from the supernatant and mixed with 250 µl of TBA solution and 250 µL of TCA solution. The reaction mixture was then heated at 100°C for a total time of 6 minutes. Heating was not continued over 6 min because of the formation of a by-product with a maximum absorbance at 450 nm, which could interfere with the absorbance at 531 nm at higher concentrations (Winterbourn, 1991). When the mixture was cooled the absorbance

was measured in 1 cm cuvettes at 531 nm against appropriate blanks containing 2-DR, TBA, and TCA in concentrations and volumes given above (see Fig. 15, 16).

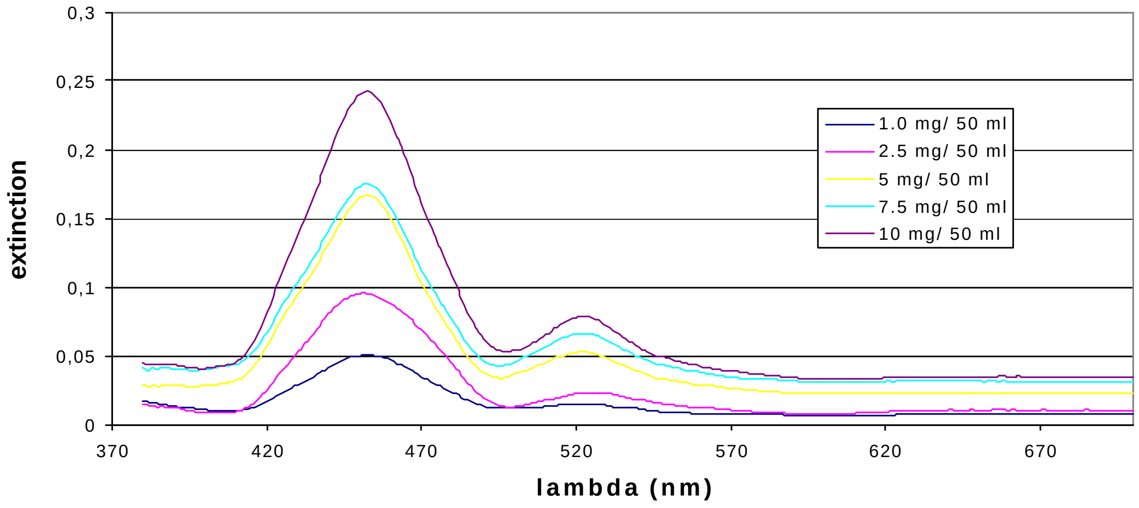

Fig.15: Extinction of a Hawaii soil at 1.3 pH.

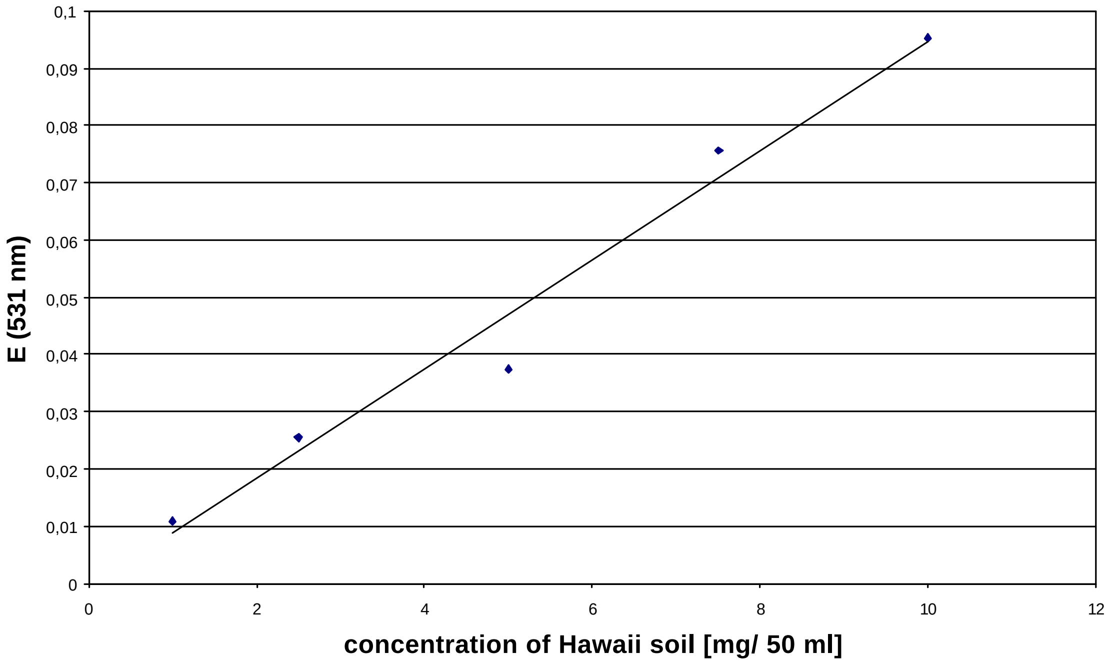

Fig. 16: Concentration of a Hawaii soil vs. extinction at 5.7 pH.

4.3.3 Influence of iron

Zhu and Sorensen (1998) reported the interference of iron on the formation of the pink product of the 2-DR method. They found that Fe(III) and TBA in solution at pH 7.4 form a product with the same spectral properties as the original 2-DR-assay described in this article. Since we worked with solutions that contain different amounts of iron, the influence of iron on the results of the 2-DR-method was studied first to avoid artefacts. The results of Zhou and Sorenson (1998) could not be confirmed by using the original 2-DR-assay with a solution containing an additional 10 mg Fe(III) (Fig. 17). In this figure the solution with and without TCA are clearly distinguished. The shapes of the spectra are totally different. With TCA the characteristic absorptions at 450 and 531 nm are missing from the spectra.

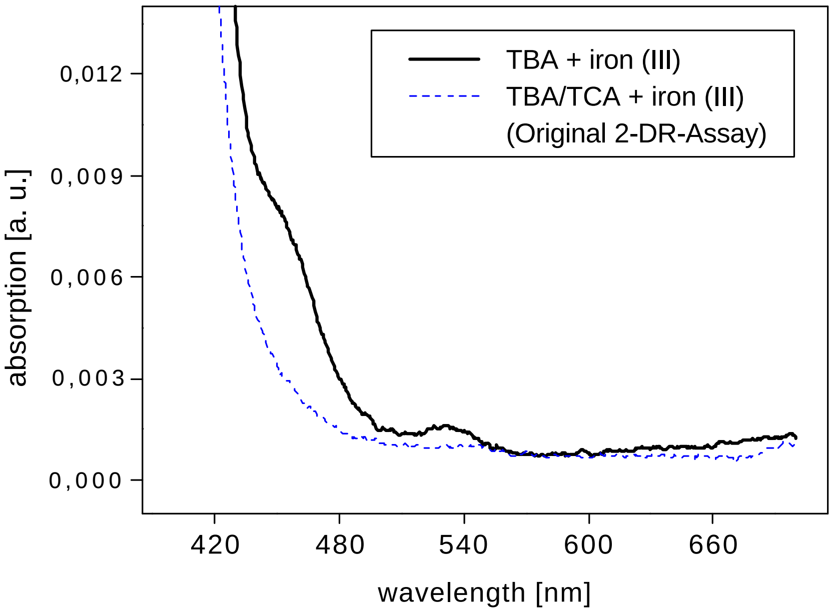

Fig. 17: Comparison of experiments with TBA and iron(II) analogues (Zhou and Sorenson, 1998) compared to the original 2-DR-assay described in this work. The difference between the experiments is clearly discernible. The absorbances at 450 nm and 531 nm that are characteristic for the detection of hydroxyl radicals are not present in the original solution (lightpath = 10 mm).

Thus there is some influence of iron on the absolute absorption of the solution. This has to be taken into account when evaluating the absorbance. The best way to judge the presence of OH radicals is the shape of the recorded spectra. In all solutions studied we found the typical shape of a genuine OH radical assay with absorbance bands at 450 nm and 531 nm. We took absorbance at 531 nm to indicate the formation of “real” OH radicals.

4.4 Results and Discussion

The formation of OH radicals in solutions containing humic acid or soil was investigated by changing several parameters. Equations (4) and (5) [page 60], indicate that the iron and oxygen contents influence the OH radical formation. Important parameters are the O_2 concentration and the pH value. Humic substances contain different amounts of iron, depending on their origin (see Table 3). The radical formation was analyzed as a function of humic acid/soil content in the solution.

Table 3. Organic Carbon, pH and Fe in different organic rich samples

Soil	C_{org} % dry wt	pH	Fe % dry wt
Peaty soil (Odenwald)	34.7	4.1	11.1
Forest soil (Hawaii)	14.2	5.6	1.7
Humic acid (Fluka)	40.3	5.1	0.91
Grassland soil (Patagonia)	46.9	4.9	0.26

4.4.1 Influence of humic acid content on the OH radical formation

It was expected that radical formation would vary as the humic acid or soil concentration in the solution changes. The higher the content of humic acid or soil which is added, the higher the radical concentration should be, because the iron concentration responsible for the radical formation also increases. The results of quantitative analysis confirmed an influence of the content of humic acid and soil on radical formation (Fig. 18 and 19).

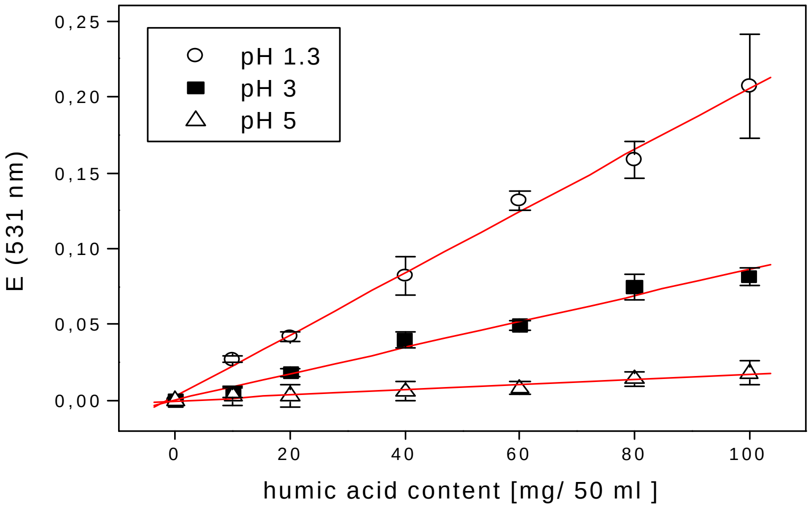

Fig. 18: Formation of OH radicals at different pH values in solutions containing different amounts of humic acid (HA). The reaction time in all experiments was 15 min. The error bars represent the standard deviation (n = 3).

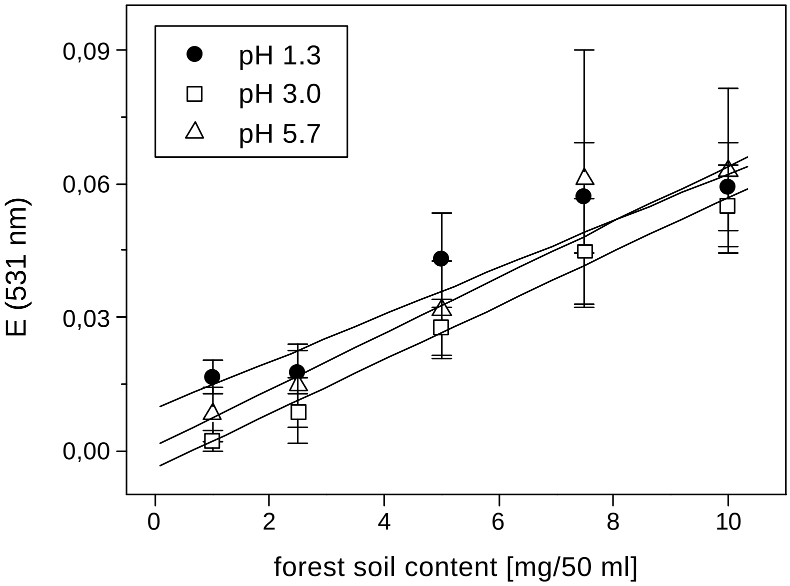

Fig. 19: Formation of OH radicals at different pH values in solutions containing different amounts of forest soil. The reaction time in all experiments was 15 min. The error bars represent the standard deviation (n = 3).

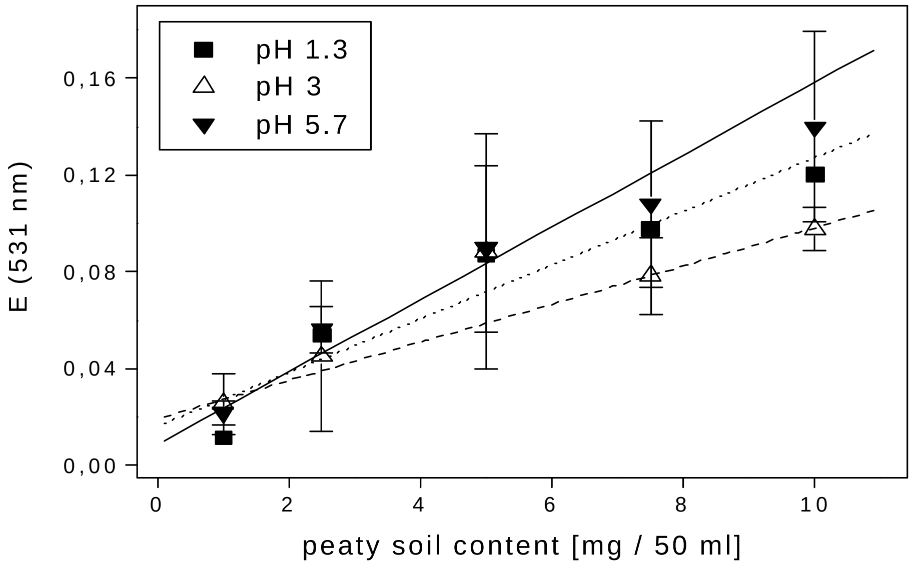

Fig. 20: Formation of OH radicals at different pH values in solutions containing different amounts of peaty soil. The reaction time in all experiments was 15 min. The error bars represent the standard deviation (n = 3).

Here the measured radical formation increased linearly with the amount of humic acid or soil. Concentrations higher than 10 mg/50 ml for soil probes or 100 mg/50 ml for commercial humic acid, respectively, were not performed because limited amounts of soil samples were available and for humic acid the separation of the supernatant liquid and undissolved humic acid by centrifugation did not give a satisfactory result. In all cases except for the grassland soil, good linear results were obtained, suggesting that the radical formation is a linear function of added humic acid and soil. The formation of OH radicals from the grassland soil was below the detection limit, probably because the iron content (see Table 3) was too low.

4.4.2 *Influence of pH on OH radical formation*

Equation 5 [page 60] explains why the OH radical formation should depend on the pH-value of the solution. The more acidic the solution is, the more eq. (5) is shifted to the right with formation of more hydrogen peroxide. Moreover, in the next step Fe(III) and hydrogen peroxide produce hydroxyl radicals by the Fenton-like reaction.

If the radical production depends on the humic acid content in solution it could be expected that the signals should drop at low pH because in an acidic solution (pH < 3) humic acid molecules are almost undissolved. That means that there are no “free” molecules of humic acid. This would lead to the effect that OH radicals that are formed in the inner part of this cluster will react directly with functional groups inside this cluster. As a consequence they could never reach the capturing molecule 2-DR outside the cluster. This means if OH radicals are actually formed by an unknown way directly from humic acid, the measured signal should be higher compared to a solution having a lower pH-value. The experiments carried out with solutions of different pH-values demonstrated an opposite behavior (Fig. 17 and 18). Here the radical concentration was found to be higher the lower the pH value was. These results suggest that radical formation is not a direct function of humic acid. As a consequence based on the results of Halliwell and Gutteridge (1981) it was assumed that only the iron content in the humic acid solution influences the radical formation, and that there was no influence of humic acid molecules. Soil samples showed no dependence of pH-value (Fig.19 and 20).

4.4.3 *Time dependence of OH radical formation*

The results of the time dependence of the OH radical formation in water are shown in Fig. 21. Although the radical formation continues for 90 minutes after the addition of humic acid, nearly 80 percent of the final signal of the 2-DR-method is formed within the first 5 minutes. It is not clearly understood why the formation took place very fast within the first 5 minutes and afterwards no additional OH radical formation was observed.

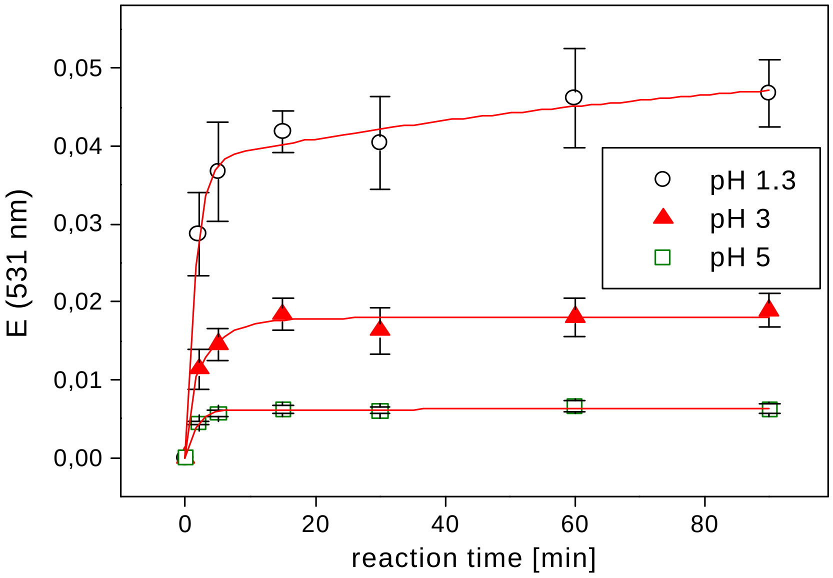

Fig. 21: Formation of OH radicals after different time intervals in an aqueous solution containing commercial humic acid. For the experiments 20 mg humic acid were dissolved in an aquatic 2-DR solution. Error bars represent the standard deviation (n = 3).

One possible explanation could be the metal catalyzed Haber-Weiss reaction. Oxygen is necessary for this reaction. When the oxygen in the solution is nearly completely consumed, the Haber-Weiss reaction will stop and no further radical formation will take place. To verify this hypothesis, the oxygen concentration was measured during the experiments. It was found that the oxygen is nearly consumed after 10 minutes. This result is in good agreement with the assumption that oxygen directly influences the radical formation in solutions of Fe(II) and oxygen.

4.4.4 *Influence of oxygen on the OH radical formation*

In order to confirm the results of the previous experiments, further studies with 2-DR solutions containing different amounts of oxygen were performed (Fig. 22 and 23).

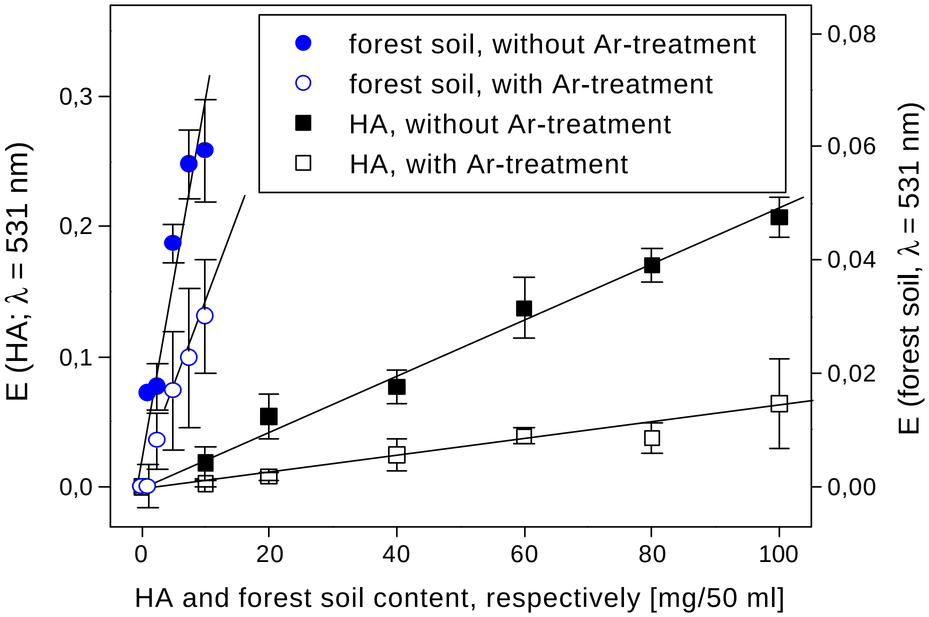

Fig. 22: Humic acid and forest soil with and without Ar-treatment. The error bars represent the standard deviation (n = 3).

For this purpose three different oxygen concentrations were prepared: 0, 3.5, and 8.5 mg l^{-1}, respectively, and in all experiments different amounts of commercially available humic acid were used. Additional experiments were performed with and without an Ar atmosphere (Fig. 22) with technical humic acid and forest soil. Due to its high iron content (1.7%) the radical formation in the forest soil is higher than in the commercially available humic acid. Oxygen is necessary for the formation of malondialdehyde as indicated by Schulte-Frohlinde and von Sonntag (1985). Oxygen was included in both solutions of TBA and TCA since they were not pretreated. So the formation of malondialdehyde and subsequently of the pink chromogen can take place during heating of an Fe-containing solution even when no oxygen is included in the 2-DR solution. This is one explanation why an absorption can be observed in Fig. 23 for the experiment without oxygen.

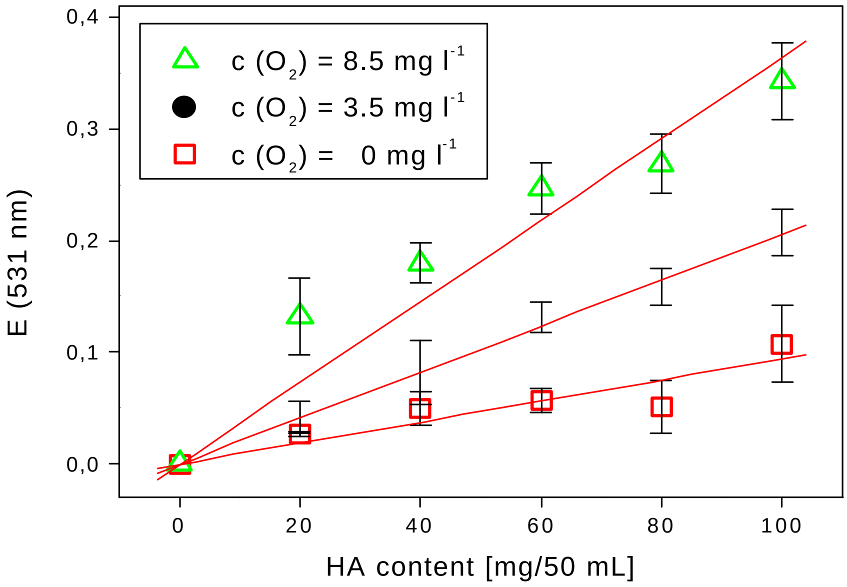

Fig. 23: Demonstration of the influence of oxygen content in the 2-DR solution on the formation of hydroxyl radicals as a function of the humic acid content. All measurements were done in triplicate, the error bars represent 1 standard deviation.

The second reason can be found in the results of Zhou and Sorenson (1998). When the concentration of oxygen in the solution increases, the total signal of the 2-DR method increases as well. Increasing the concentration of oxygen in the solution leads to a higher slope of the regression line. These results support the influence of oxygen on the radical formation as discussed above.

4.4.5 Estimation of the OH radical concentration in the solution

Ultrasonic experiments were performed to find the concentration of hydroxyl radicals formed in the experiments with the humic acid. The relationship between the absorption of the 2-DR-method and the actual concentration of hydroxyl radicals (given in mg ml^{-1}) determined by Fricke dosimetry (data not shown) was

$c(\cdot OH)\ [mg\ ml^{-1}] = 4.08\times10^{-6}\cdot E$ (531 nm) (1 cm cuvette) (9).

Equation (8) [page 61] was used to estimate the approximate concentration of the hydroxyl radicals formed after a total reaction time of 90 minutes as well as the reaction rate for the first 2 minutes (Table 4).

Table 4: Reaction rate of OH radicals in a suspension containing humic acid or soil samples (at pH 1.3 within the first 2 minutes).

Soil Type	**Fe [%]**	**$c(\cdot OH)$ [µmol l^{-1} min^{-1}] (2 min)**	**$c(\cdot OH)$ [mol l^{-1}]^{a} (90 min)**
Peaty soil	11.1	2.65	$1.8\cdot10^{-7}$
Forest soil	1.7	1.75	$1.2\cdot10^{-7}$
Humic acid	0.91	0.86	$5\cdot10^{-8}$
Grassland soil	0.26	Not detected	Not detected
Ref. Exp.	4	6.52	$9.3\cdot10^{-7}$

[a] hydroxyl radicals formed after 90 min

The results were compared to an experiment with pure Fe(II) (2 mg/50 ml) and oxygen (saturated solution). It was found that the OH-formation takes place with a reaction rate of approximately 1 mmol l^{-1} min^{-1} in the case of soil samples and humic acid. The concentration of hydroxyl radicals formed in all investigated systems was about 10^{-7} mmol ml^{-1} (Figs. 15 and 16), here E (531 nm) is not higher than 0.2. So it can be also explained why ESR (electron spin resonance) experiments with metal loaded humic acids by Paciolla et al. (1999) do not show any signal without the addition of DMSO (dimethyl sulfoxide) to form more stable CH_3 radicals.

The results in the present studies provide new information concerning hydroxyl radical formation in soil and water. Since the hydroxyl radical is highly reactive and nonselective, it can react with a wide range of compounds in water and soil. Indeed, this process could be involved in some recently discovered phenomena such as the abiotic formation of halocarbons in soil (Keppler et al., 2000; Fahimi et al., 2001) and the Fe(III) induced mineralization of phenolic compounds (Pracht et al., 2001). However, additional work is needed, including laboratory and field measurements, to further explore the mechanisms of free radicals stemming from geochemical processes in water and soil.

5 FORMATION OF VOLATILE IODINATED ALKANES IN SOIL

5.1 *Summary*

Volatile iodinated organic compounds play an important role in the tropospheric photochemical system, but the current knowledge of the known sources and sinks of these alkyl iodides is still incomplete. This chapter describes a new source of alkyl iodides from soil. Different organic-rich soils and humic acid were investigated for their release of volatile organoiodides. Six volatile organoiodides (iodomethane, iodoethane, 1-iodopropane, 2-iodopropane, 1-iodobutane and 2-iodobutane) were identified and their release rates were determined. We assume an abiotic reaction mechanism induced by the oxidation of organic matter by iron(III). The influence of iron(III), iodide and pH on the formation of alkyl iodides was investigated. Additionally, different organic substances regarded as monomeric constituents of humus were examined for the production of alkyl iodides. Two possible reaction pathways for the chemical formation of alkyl iodides are discussed. As humic acids and iron(III) are widespread in the terrestrial environment, and the concentration of iodide in soil is strongly enriched (compared to seawater), this soil source of naturally occurring organoiodides is suggested to contribute significantly to the input of iodine into the troposphere.

5.2 *Introduction*

Volatile halogenated organic compounds (VHOC) have attracted increasing attention due to their importance in photochemically induced atmospheric processes. The global atmospheric input of man-made VHOC, whose sources are well known, can be estimated from their industrial production rate (Montzka et al., 1996). Halogenated compounds of natural origin, such as methyl halides can also contribute significantly to the levels of VHOC in the atmosphere. Although many sources of methyl halides have already been identified (Winterton, 2000), there is still a lack of known sources that can account for the total natural emissions (Butler et al., 1999). Initially, studies focused on the two components methyl bromide and methyl chloride. The tropospheric lifetimes of these compounds (1.3 years in the case of methyl chloride and 2 years in the case of methyl bromide) allow significant fluxes to the stratosphere, whereas the shorter lived iodomethane (CH_3I) is almost fully consumed in the troposphere (lifetime 2 - 6 days (Chameides and Davis, 1980)). CH_3I was first observed in the atmosphere in the pptv range by Lovelock et al. (1973). Since it has become clear that iodine radicals participate in tropospheric photochemistry (Chameides and Davis, 1980; Solomon et al., 1994a; Rasmussen et al., 1982; Cotter et al., 2001, Stutz et al., 1999), volatile organoiodides have gained considerable scientific interest. A major source of I in the troposphere is the photolysis of alkyl iodides.

Quite significant concentrations of other alkyl iodides, including iodoethane (C_2H_5I) and diiodomethane (CH_2I_2), have also been found in the lower troposphere (Carpenter et al., 1999). CH_2I_2 photolyzes very quickly (lifetime ~ 3 min), therefore the only small concentration found in lower troposphere could induce a considerable source strength.

However, volatile iodinated organic compounds are also believed to play a significant role in the global iodine cycle (Chameides and Davis, 1980; Manley, 1994). No major anthropogenic sources of organic iodinated compounds are known, although some of them might be used as halon replacements in the future, whereas various natural sources have been identified. Today all the homologous iodine alkanes from C_1 to C_4 of biological origin are well-known (Giese et al., 1999), but current knowledge of the known sources, sinks and global burdens of these alkyl iodides is still incomplete.

The oceans have been considered to be the main source of iodinated compounds (Class and Ballschmiter, 1988; Moore and Tokarczyk, 1993; Schall and Heumann, 1993), where organisms like micro- and macroalgae can liberate large amounts of iodinated compounds (Laturnus, 1996). Furthermore, some terrestrial sources, like rice fields (Redeker et al., 2000), peat bogs (Dimmer et al., 2001), wood-degrading fungi (Harper, 1985) and volcanic emissions (Jordan et al., 2000) have been identified as sources of alkyl iodides. Recently, a completely new source of halogenated hydrocarbons was discovered which is based on an abiotic redox mechanism in soils (Keppler et al., 2000). A conceptual model (see Fig. 24) describes the novel source of alkyl iodides in the terrestrial environment but the mechanism remains uncertain. In connection herewith it could be shown that certain phenolic substances are completely mineralized (forming CO_2 and H_2O) in the presence of an oxidizing agent, such as Fe(III) (Pracht et al., 2001). Under these conditions it was found that after addition of iodide ions, alkyl iodides were formed (Keppler, 2000).

Humus is a main constituent of soil and contains a great number of aromatic, primarily phenolic groups, thus qualifying as a potential candidate for the mentioned redox processes. One of the most important inorganic oxidants is iron due to the combination of its abundance and its redox-sensitivity. It is the fourth most abundant element in the earth's crust and is present in all natural systems. The aim of the present study was to investigate (qualitatively and quantitatively) the influence of iodide ions on the formation of volatile alkyl halides under oxidizing conditions using different samples containing humic substances and to establish the mechanism of alkyl iodide formation in soils.

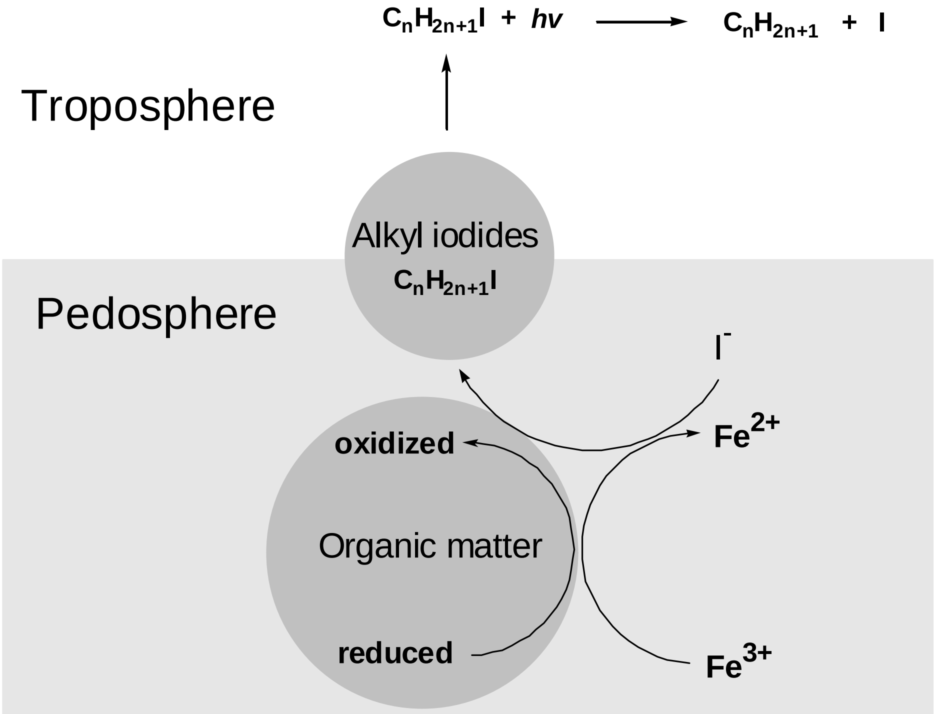

Fig. 24: A conceptual model of alkyl iodide production in soil (from Keppler et al., 2000 modified)

5.3 Experimental Section

5.3.1 Materials

Iodomethane (99,9%), iodoethane (99%), 1-iodopropane (99%), 2-iodopropane (99%), 1-iodobutane (99%), 2-iodobutane (99%), methanol (p.a.), humic acid sodium salt and HNO_3 (65%) were obtained from Sigma-Aldrich, $Fe_2(SO_4)_3$-hydrate was purchased from Fluka and KI was a Merck product. All solutions were prepared with doubly distilled, deionized water.

Organic-rich soils were collected in September 2000 from a rural area located in the Odenwald/Germany (49°36’39’’N/8°53’11’’E). Three different soil samples were collected: grassland, coniferous forest and peatland. The grassland soil and coniferous forest soil were taken from the A-horizon (A_h) while the peaty soil was taken from the top O-horizon (O_h). Soil samples were freeze-dried, milled (0.24 mm mesh) and stored in a freezer (-24°C) until chemical analyses or laboratory experiments were conducted. Soil samples and the humic acid were analyzed for pH, organic carbon (C_{org}), total iron and halogens (see Table 5).

Table 5: Organic carbon (C_{org}), pH, Fe, iodine in different samples containing humic substances

Soil	C_{org} % dry wt	pH	Fe % dry wt	I mg kg^{-1} dry wt
Grassland soil	7.2	4.9	0.74	4.1
Coniferous forest soil	14.2	3.1	0.42	6.7
Peaty soil	34,7	4.1	11.1	65.5
Humic acid	40.3	9.6	0.79	<3.7

5.3.2 Procedure

The investigations were carried out in 20 ml vials (reaction bottles). 1 g humic acid, coniferous forest soil, grassland soil and peaty soil were suspended in distilled water and filled up to 10 ml sample volume. Depending on the experiment, varying quantities of Fe(III) and iodide were added to the medium. Fe(III) was added as iron sulfate and the iodide as potassium iodide. Different pH-values (for humic acid) were achieved by the addition of HNO_3. After preparation, the vials were sealed and shaken at 30°C with an incubation period of 5 to 120 min. To analyze the alkyl iodides, 1 ml of the gaseous phase of the headspace was transferred to the capillary column of the gas chromatograph (GC). Blanks were analyzed according to the same procedure but without addition of soil or humic acid.

5.3.3 Analyses

Alkyl iodides were determined by gas chromatography with electron capture detection (GC/ECD). The GC used was a Fisons HRGC 8265 equipped with an ^{63}Ni-ECD. Separation of alkyl iodides was carried out on a SPB-624 column from Supelco (75 m, 0.53 mm ID; 3.0 µm film thickness). Nitrogen was used as a carrier gas. The initial oven temperature was 35°C for 20 min, then raised to 100°C at a rate of 4°C/min and held for 10 min. The injection volume was 1 ml at a split ratio of 1:1. Retention times of standard dilutions of commercially available iodinated compounds were used for peak identification (Fig. 25). Quantification of the six alkyl iodides was achieved by external calibration standards. Calibration was against samples of the headspace above standard solutions equilibrated at 30°C. Each measurement was repeated three times (n = 3) and the relative standard deviation of all measurements was in the range of 2 - 37% (RSD). The detection limits of the compounds were in the range of 0.04 pmol/20 ml vial for iodomethane and 0.25 pmol/20 ml vial for 2-iodobutane.

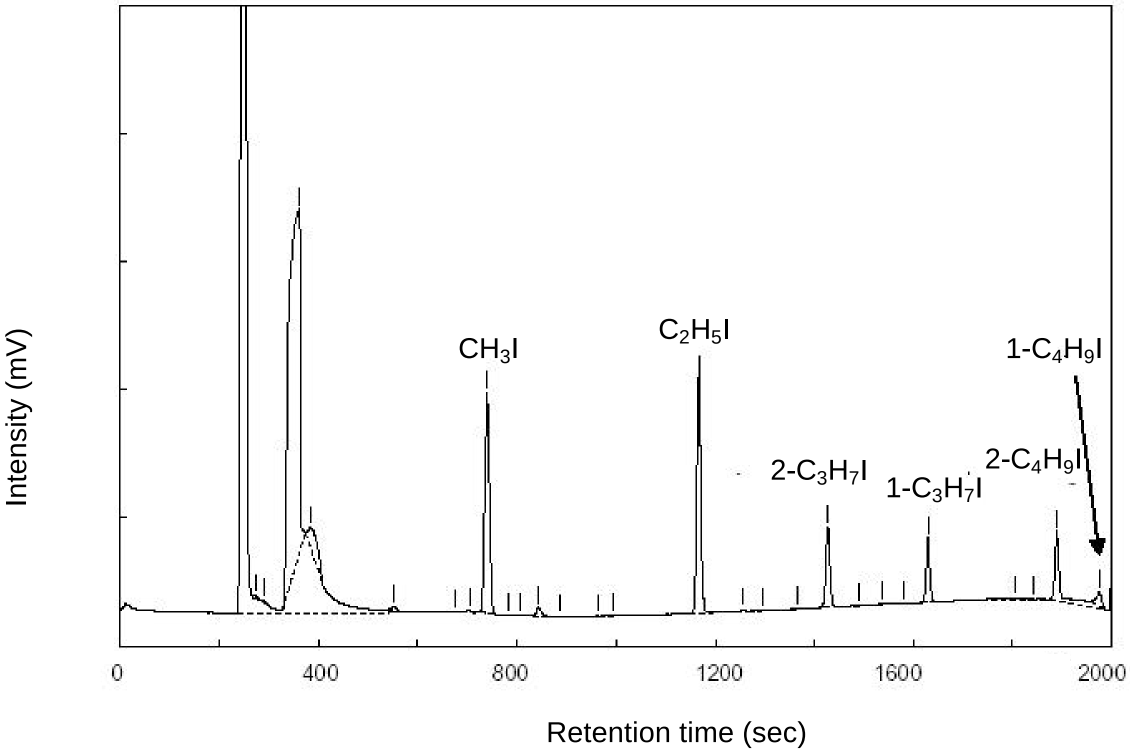

Fig. 25: Chromatogram of alkyl iodides from a standard solution measured by GC-ECD.

To verify the formation of alkyl iodides, a part of the samples was analyzed by GC/MS technique. Gas chromatographic separation was carried out on a DB1 column (60mx0.32 mm, film thickness 1 µm) using the following temperature program: initial oven - 65°C, increasing rate 8°C min^{-1} to 175°C, 5 min isothermal. Mass spectrometric detection was performed over a scan range of 48 - 200 amu. Alkyl iodides were identified from their retention time and mass spectrum (Fig. 26). In general, lower detection limits were obtained with the GC/MS system. Especially for the longer chained alkyl iodides, monitoring was sometimes difficult and values often below detection limit.

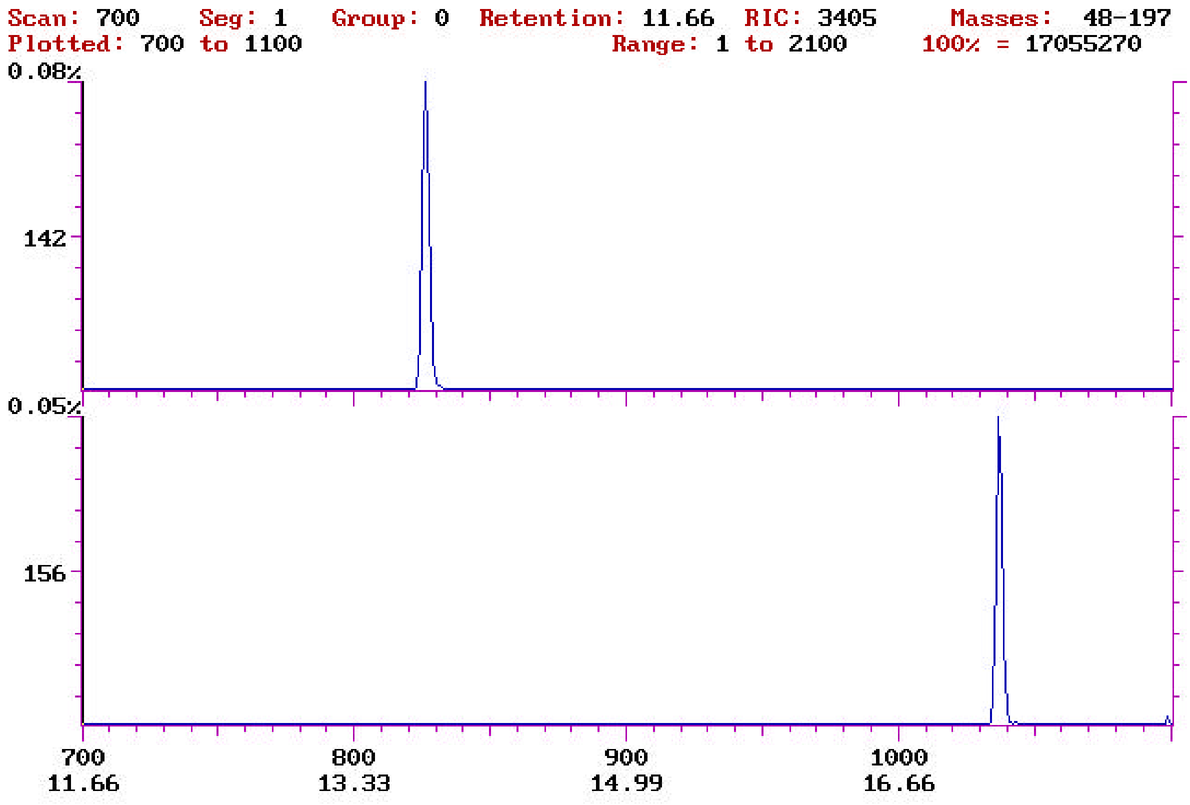

Fig. 26: GC-MS analysis of soil sample, showing the formation of iodomethane and iodoethane. Chromatograms show the response to the molecular ion m/z 142 and m/z 156 (scan 700 - 1100)

Total organic carbon of the soil samples was measured using a C/S analyzer 225 from LECO.

Fe(II) concentration was analyzed as a ferrous iron-phenanthroline complex with a Dr. Lange photometer, CADAS 100, at 510 nm. The iodine content in the samples was measured by instrumental neutron activation analysis (INAA).

5.4 Results and Discussion

5.4.1 Soil-water experiments: without additives

To study the natural formation of alkyl iodides, a series of laboratory experiments was conducted using four different humus-rich samples. The peaty soil, with a naturally high content of Fe and iodide, showed the highest concentrations of iodomethane

(CH_3I), iodoethane (C_2H_5I), 1-iodopropane ($1\text{-}C_3H_7I$), 2-iodopropane ($2\text{-}C_3H_7I$), 1-iodo-butane ($1\text{-}C_4H_9I$) and 2-iodobutane ($2\text{-}C_4H_9I$) (Fig. 27a). It is very likely that the monitored alkyl iodides do not show the full set of produced volatile iodinated compounds in the soil sample, but we focused only on these six compounds. The highest release rates were found for CH_3I (6 pmol g^{-1} h^{-1}), $2\text{-}C_3H_7I$ and C_2H_5I whereas the release rates for $1\text{-}C_3H_7I$, $1\text{-}C_4H_9I$ and $2\text{-}C_4H_9I$ were significantly lower. The release rates of alkyl iodides from the two other soil samples were lower and especially for the C_3 and C_4 compounds below the detection limits.

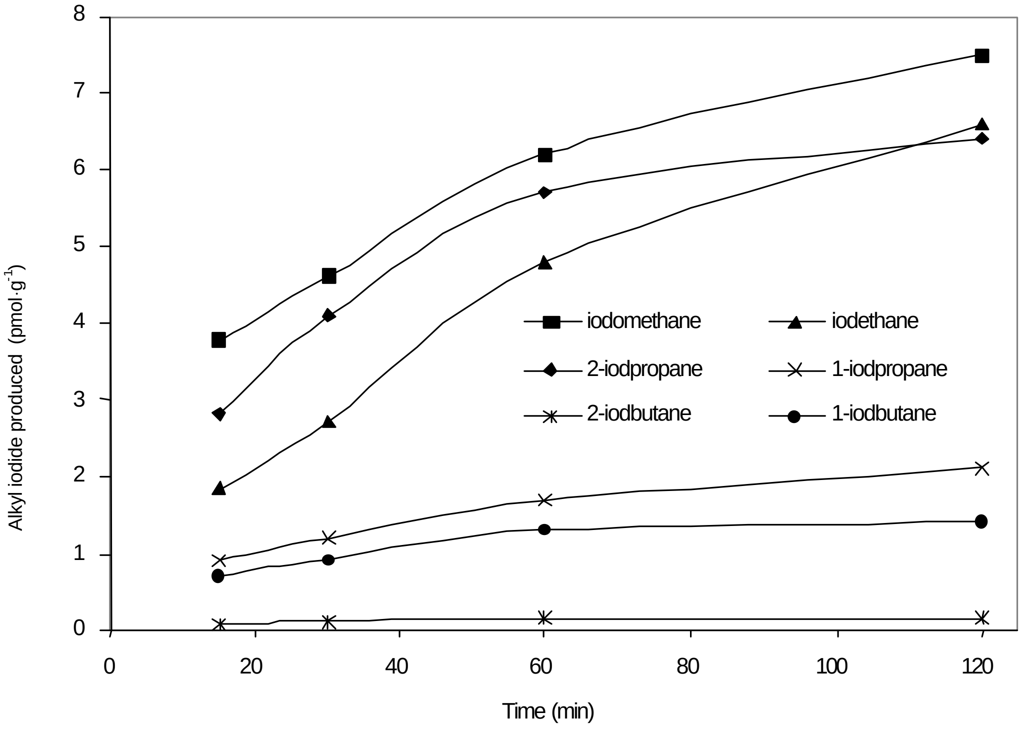

Fig. 27a: Formation of alkyl iodides by organic-rich soils in relation to time. Production of six volatile iodinated compounds from a peaty soil.

Fig. 27b shows the comparison of produced iodomethane from the three different soil samples. The values for commercially available humic acid were below detection limit: a reason for this could be the low iodine content of the sample (see Table 5). Fe(II) was monitored, next to the production of alkyl iodides (data not shown), and in most cases there was a good correlation between Fe(II) formation and the liberation of CH_3I. Further experiments were carried out to test the influence of Fe(III), iodide and pH on the formation of alkyl iodides.

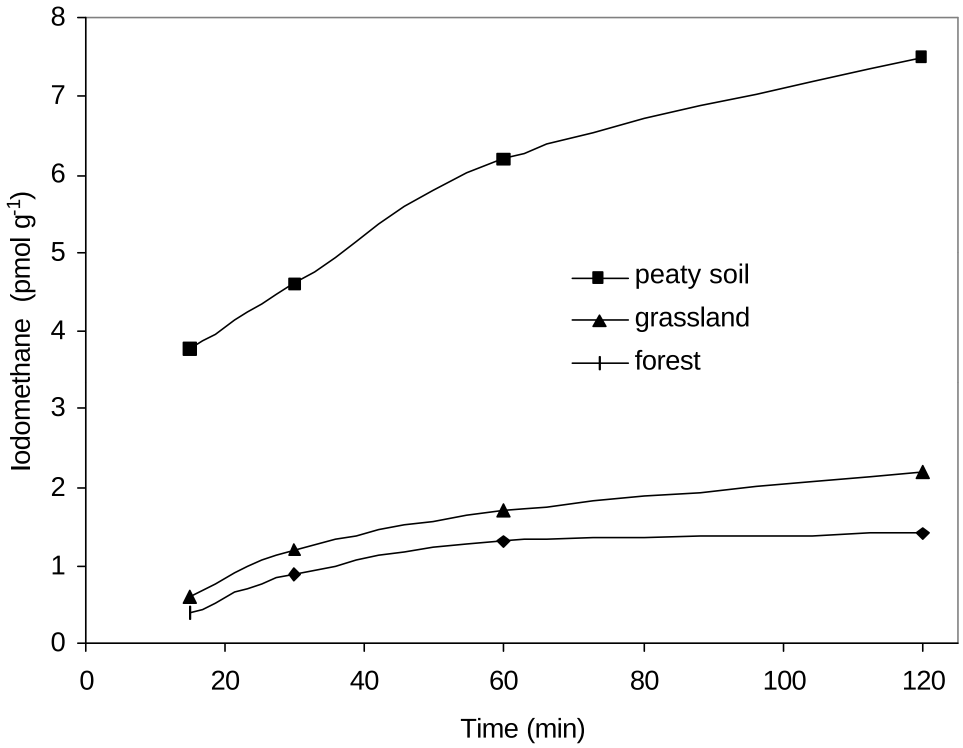

Fig. 27b: Formation of alkyl iodides by organic-rich soils in relation to time. Comparison of produced iodomethane from three different soil samples.

5.4.2 *Influence of Fe(III) and iodide*

After the addition of Fe(III) and iodide to each of the samples, an enormous production of the possible isomers of the homologous iodoalkanes from C_1 to C_4 was observed.

Fig. 28 presents the time-dependent formation of alkyl iodides with a coniferous forest soil as the organic matter source while in Fig. 29a the production of alkyl iodides from different samples is compared. It is noteworthy that the ratios of the produced alkyl iodides of the three samples varies considerably. Humic acid produces CH_3I as main product, while the longer chained compounds are produced in relatively low quantities. The results of the forest soil and grassland soil show that, in comparison to the humic acid, the compounds of higher molecular weight, especially C_2H_5I and 2-C_3H_7I, have an equivalent or higher share. Table 6 shows the ratios of the produced gas quantities of the main products. The crucial factor for these variations could be the chemical composition of the humus which is discussed in the section *'proposed reaction schemes'*.

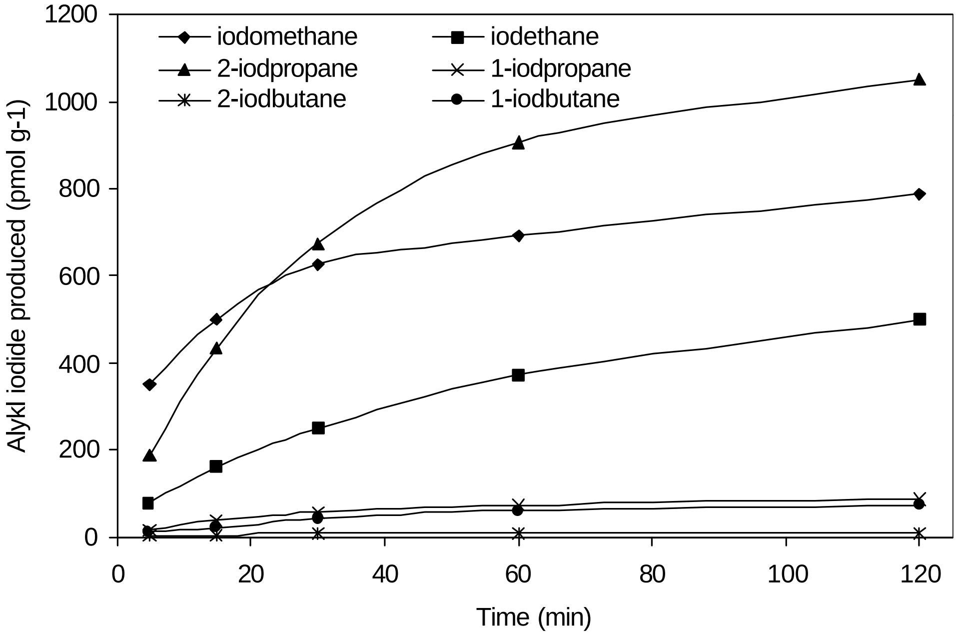

Fig. 28: Enhanced emission of alkyl iodides by adding 100 µmol Fe(III) and iodide to a grassland soil sample (1 g).

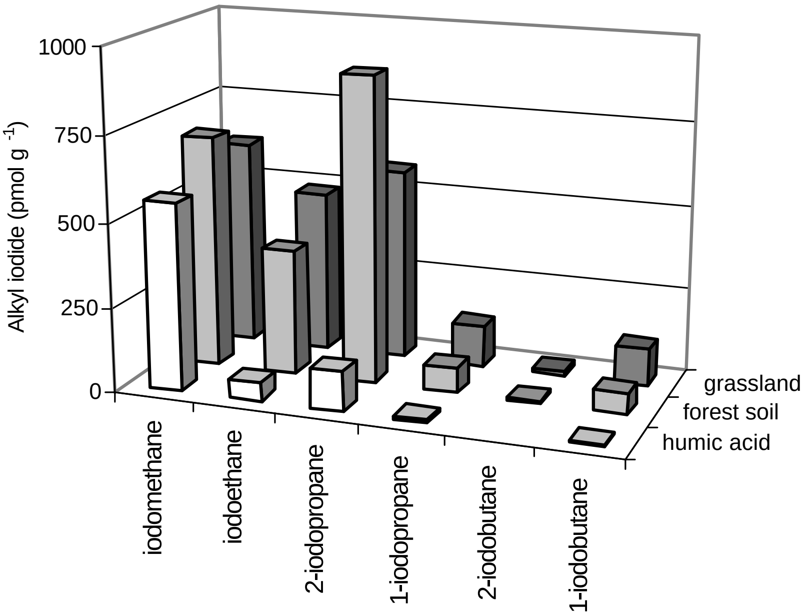

Fig. 29a: Production of alkyl iodides by humic acid, grassland soil and coniferous forest soil.

Table 6: Molar ratio of the main products produced by different organic-rich samples after adding Fe(III) and iodide.

	Iodomethane	Iodoethane	2-Iodopropane
Humic acid	10	1	2
Coniferous forest soil	2	1	2.5
Grassland soil	1.3	1	1.2

The necessity of an oxidizing agent for the formation of alkyl iodides is clearly shown in Fig. 29b. As the grassland soil has an inherent content of iron and iodide, a minimal production of alkyl iodides is observed even without addition of Fe(III) or iodide. An equimolar addition of Fe(III) and iodide ions (100 µmol) leads to a considerable increase in the alkyl iodide production. In comparison to a sample without the addition of Fe(III) and iodide, the grassland soil has a 300 fold increase in CH_3I (615 pmol g^{-1} h^{-1}) production and a 240 fold increase in C_2H_5I (483 pmol g^{-1} h^{-1}) production. With a 100 fold higher amount of CH_3I and 50 fold higher amount of C_2H_5I of the measured gas quantities the humic acid shows somewhat more moderate values (data not shown).

In general, there is a simple correlation between the production of organoiodides and the added amounts of Fe(III) or iodide: the release rates of produced alkyl iodides increased by raising the concentrations of Fe(III) or iodide.

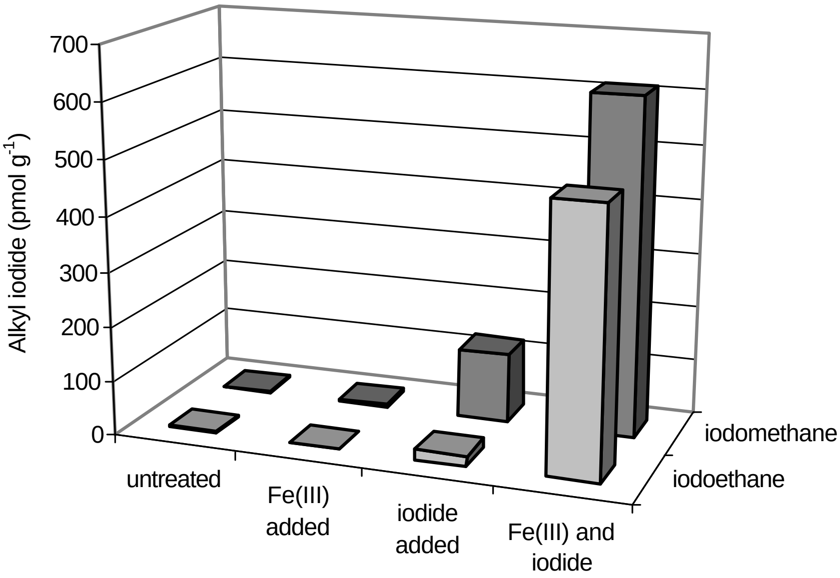

Fig. 29b: 1 g sample suspended in bidistilled water containing 100 µmol Fe(III) and 100 µmol iodide; incubation time 1 h. Influence of Fe(III) and iodide on the release rates of iodomethane and iodoethane using a grassland soil as organic matter source.

5.4.3 Influence of pH

An important factor influencing the quantity of the alkyl iodide production is the pH value. The soil samples were tested for alkyl iodide formation by using pH values in the range of 1.2 - 8.8. In general, it could be shown that abiotic formation of volatile iodinated compounds is favored in an acidic medium: iodomethane production increases with decreasing pH (Fig. 30). The most likely explanation for this behavior is that under acidic conditions Fe(III) reduction is much faster. This is an important aspect in applying the abiotic reaction model to natural soils. It is well known that the pH value of most soils is acidic, usually ranging between pH 3 and 6.

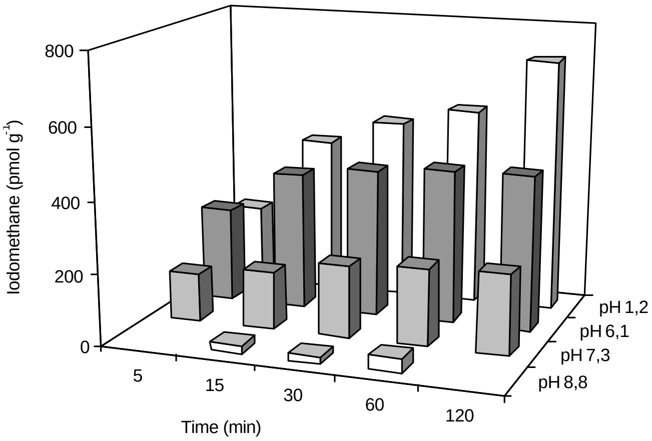

Fig. 30: Effect of pH on the formation of alkyl iodides. 1 g humic acid suspended in bidistilled water containing 100 µmol Fe(III) and 100 µmol iodide.

5.4.4 *Proposed reaction schemes*

As humic substances are heterogeneous aliphatic and aromatic polymers with a variety of functional groups, they can be involved in many chemical and physical processes. To date, the structure of humic substances is unknown, only proposed building blocks exist. Therefore, we assumed that the redox-sensitive phenolic groups of the organic matter in soil such as catechol and guaiacol, and inorganic soil components such as iron oxyhydroxides may play a key role within the organic-inorganic redox systems in natural environments. We have found two chemical pathways leading to the formation of alkyl iodides. Guaiacol (2-methoxyphenol) and catechol (1,2-hydroquinone), which are monomeric units of humus were found to produce alkyl iodides in a reaction with Fe(III) and iodide. Fig. 31a shows that in the redox reaction between 2-methoxyphenol and Fe(III) in the presence of iodide, CH_3I is formed (from Keppler et al., 2000 modified).

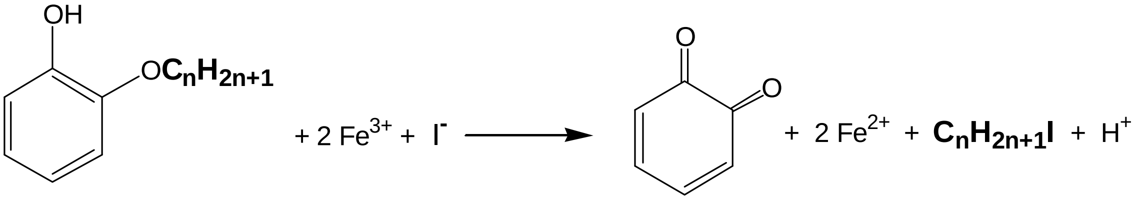

Fig. 31a: Suggested pathways for the formation of alkyl iodides. Formation of alkyl iodides starting from alkoxylated phenolic compounds.

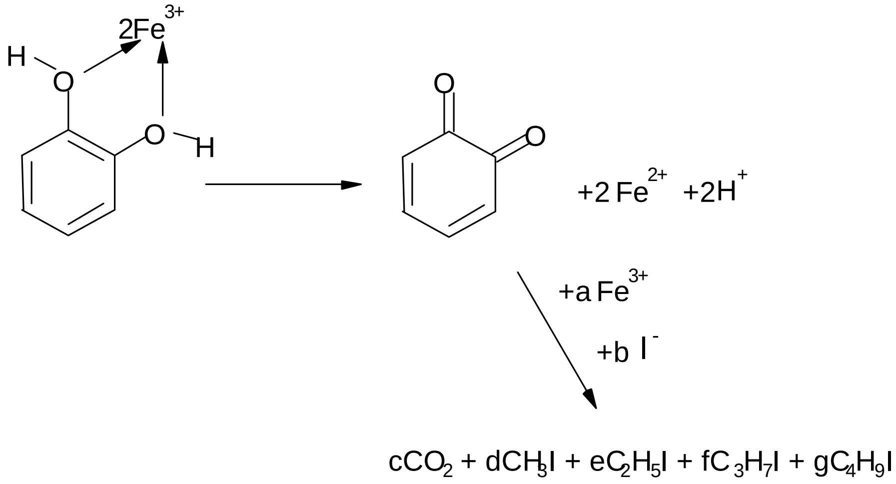

Fig. 31b: Suggested pathways for the formation of alkyl iodides: Generation of alkyl iodides by the reaction of catechol and Fe(III) in the presence of iodide.

A completely novel pathway (Fig. 31b) producing alkyl iodides may be the abiotic ring cleavage of 1,2-hydroquinone catalyzed by Fe(III). In the presence of iodide the six alkyl iodides CH_3I, C_2H_5I, 1-C_3H_7I, 2-C_3H_7I, 1-C_4H_9I and 2-C_4H_9I are formed (Keppler, 2000). Both chemical pathways show how volatile organoiodides can be formed during redox processes between natural organic substances and inorganic soil components. However, these are only two possible pathways, with other possibilities that might also exist. Nevertheless it is apparent that the chemical composition of the organic soil source is responsible for the formation of the different alkyl iodides.

5.5 Conclusions

Our experiments show that all homologous alkyl iodides from C_1 to C_4 are formed in organic and mineral rich soils, depending on factors such as pH, iodide and iron content. It is however difficult to transfer these laboratory experiments to nature and to calculate the global contribution to emissions, as the mineral, organic and salt content of soils and sediments are dependant of the ambient environmental conditions and thus vary considerably. Moreover, the exact structural composition of organic constituents in soils are not known: only the basic compounds are established. This is due to the complex nature of the humic substances: in 1 kg of humic substance only about two identical humic acid molecules can be expected. The different samples analyzed in this study clearly show this effect. As indicated in Fig. 29a, the forest soil forms 2-C_3H_7I as the main product, whereas the grassland soil, the peaty soil and humic acid form CH_3I as the main product. Considering that humus and iron oxyhydroxides are widespread in soil, and iodide can be converted easily into volatile organic compounds, the impact of this newly discovered field of the redox-induced formation of alkyl iodides becomes evident - not only for the tropospheric fluxes but also for the biogeochemical cycling of the element iodine. To calculate the annual fluxes of alkyl iodides from continental areas into the troposphere a broad range of field studies are required.

6 SUMMARY

Natural organohalogens in soils and sediments have been investigated from many different aspects: natural product chemists have looked for new antibiotics from fungi and microorganisms, water chemists have found unexpectedly high concentrations of chlorinated solvents in groundwater, biologists have elucidated biogeochemical metabolic pathways of soil organisms, environmental scientists have applied a new analytical technique (the AOX parameter = adsorbable organic halogen) for depth profiling in soils and sediments. Much of this research has been driven by the need to understand the impact of anthropogenic (man-made) organohalogens, e.g. chloropesticides. These chemicals are directly or indirectly emitted into the environment, but, surprisingly, environmental chemists have found naturally produced organics which are identical or similar to man-made ones. This has stimulated an intensive research into the mechanisms of natural formation of organohalogens.

This study investigates the natural abiotic formation of haloacetic acids (HAAs) in soils, the mechanism of which probably involves the generation of hydroxyl radicals, the production of these hydroxyl radicals in soil systems, and the generation of volatile iodinated alkanes in soil.

HAAs are important for the environment due to their phytotoxicity. They are often investigated in connection with forest dieback. Trichloroacetic acid (TCA) was used as a herbicide in Germany since the end of the 1940s, but now it is prohibited in the European Community exept in Ireland and Italy. Next to the usage as a herbicide, HAAs also enter the environment anthropogenically through precursors that are transformed into HAAs in the troposphere, e.g. 1,1,1-trichloroethane and tetrachloroethene, which originate from their use as industrial solvents and degreasers. Further sources of HAAs are combustion processes and the chlorination of water. It has recently been shown that HAAs are also formed naturally in soil. TCA is found ubiquitously in precipitations and is accumulated in conifer needles. Especially in mountainous areas with high precipitation levels and enhanced fog events (which contains elevated amounts of TCA) the TCA input can be relatively high. Particularly in forested areas in which needles and leaves take up additional dry deposition of HAAs, which is washed off in rain events, and where decaying needles represent a further source of TCA, quite high concentrations of HAAs can be found. In the Black Forest, the PNEC (predicted no effect concentration) of TCA in the soil, 2.4 µg/kg, was compared with the predicted environmental concentration (PEC): the ratio is by far > 1, and this poses a clear risk to the terrestrial ecosystem.

The enzyme chloroperoxidase (CPO) can halogenate natural substrates, its activity has been identified in coniferous forest soils. In experiments with CPO, humic acids and other organic acids which are important for metabolic processes (e.g. acetic acid, malic acid, lactic acid, citric acid) were incubated with H_2O_2, which is generated from microorganisms and fungi, and NaCl, which is added as a halide source were incubated to assess natural production. All incubations resulted in TCA formation, indicating a natural formation. Even in experiments in which CPO was absent HAAs were formed; pointing to an abiotic formation.

We investigated this process to determine a mechanism of this abiotic formation in the soil. Soil samples from a pristine area, the Rotwasser reserve in the Odenwald, commercially available humic acid, and phenolic model substances were used in experiments to generate CAAs. It is shown that CAAs are formed from humic material with a linear relationship between the amount of humic acid used and CAAs formed, whereby more DCA than TCA is generated. Some time-dependent measurements of DCA, using 1 g humic acid with varying times of shaking (5 min., 10 min., 40 min.,) showed an increase of DCA formation in the first 10 minutes. In our studies the addition of $FeCl_2 \cdot 4\ H_2O$, $Fe_2(SO_4)_3$ and H_2O_2, especially the combination of iron and H_2O_2, leads to an increased yield. NaCl was added as source of chloride, an increased amount did not lead to an increased amount of DCA, although the yield of TCA was somewhat elevated.

We further examined the relationship between the structure and reactivity of phenolic substances, which can be considered as monomeric units of humic acids. Ethoxyphenol with built-in ethyl groups forms large amounts of DCA and TCA. The experiments with phenoxyacetic acid yielded large amounts of monochloroacetic acid (MCA). With other phenolic substances a ring cleavage was observed. Our investigations indicate that chloroacetates are formed abiotically from humic material and soils in addition to their known biotic mode of formation. As an increase of iron and H_2O_2 leads to an increase in haloacetic acid formation, one could conclude that a Fenton reaction ($Fe(II) + H_2O_2 -> Fe(III) + OH^- + OH^\cdot$) was possibly taking place, generating hydroxyl radicals which are able to oxidize chloride to elemental chlorine when chloride is available in the system and leading to a non-specific chlorination of organic compounds.

The incubation of soil with ^{37}Cl-enriched chloride with subsequent mass spectrometry of TCA would test the natural formation of TCA in soil. Degradation rates of TCA at environmentally significant concentrations in soils also have to be determined; most of the studies done so far have used concentrations which were sensible when TCA was used as a herbicide, but too high compared to present environmental concentrations in terrestrial ecosystems. Concerted measurements in rain water, needles, soil and groundwater at forested sites over a sufficient period would generate the data needed to more precisely determine TCA's flux through the system and to carry out a further, more exact mass balance calculation than the ones that have been published so far. Indeed, previous investigations have produced uncertain results, because the TCA concentrations in different media were obtained from *different* sampling sites. The main problem of the proposed test strategy is that a large number of parameters (e.g. environmental concentrations, local degradation rates) have to be determined precisely, and even with an expensive research project it is doubtful whether all parameters can be determined with sufficient precision.

Additional model experiments with manganese which is relatively common in soils and of which some species have oxidation potential should be performed to check its influence on the formation of HAAs. It often occurs as MnO_2 and some experiments should be conducted with this compound. It should also be tested if the Fenton reaction really has an influence on our system and whether the formation of hydroxyl radicals triggers the production of HAAs.

The next segment of this work deals with the generation of hydroxyl radicals ($OH^{\cdot}$) in an aqueous system containing humic substances. In presence of humic acid or soils sunlight or addition of iron or H_2O_2 are not required to produce hydroxyl radicals. The OH radical was detected using the 2-deoxy-D-ribose (2-DR) method followed by UV-Vis detection. The *in vitro* production of OH radicals was monitored in three different soil samples (with high humus and different iron content) and also in an iron-containing humic acid. The hydroxyl radical concentration in the aqueous medium increased linearly with the added amount of soil or humic acid. We suggest that there is a continuous production of hydroxyl radicals in soils depending on their particular composition. The natural formation of hydroxyl radicals in soils may explain a multitude of chemical processes, e.g. natural halogenation and dehalogenation processes.

Laboratory and field measurements are needed to further explore the mechanisms of free radicals originating from geochemical processes in water and soil. Extensive ESR measurements could help quantify the OH radical production. Further investigations of the reactions of the nonselective hydroxyl radical with a wide range of compounds found in water and soil could be interesting, e.g. the abiotic formation of HAAs and halocarbons in soil.

Volatile halogenated organic compounds (VHOC), such as methyl halides, have received increasing attention due to their importance in photochemically induced atmospheric processes. Initially, research on VHOC focussed on chlorinated and brominated compounds, as they could reach the stratosphere and become involved in stratospheric chemistry due to their long lifetimes (1.3 years in the case of methyl chloride and 2 years in the case of methyl bromide). Only recently volatile iodinated organic compounds have become important, as it has been revealed that they can produce iodine radicals that may participate in tropospheric chemistry and can react with ozone in the lower stratophere (Solomon et al., 1994b). The iodinated organic compounds are also believed to play an important role in the global iodine cycle. Although they are ubiquitous in the environment, their dominant source is the ocean. Marine macroalgae and phytoplankton take up iodide and iodate from the seawater and transform it into different iodine compounds. The current knowledge concerning the sources and sinks of alkyl iodides is incomplete and still under investigation.

The fourth segment of my work deals with the investigation of a new source of alkyl iodides from the soil. Different organic-rich soils and humic acid were investigated for their release of volatile organoiodides. Six volatile organoiodides, iodomethane, iodoethane, 1-iodopropane, 2-iodopropane, 1-iodobutane and 2-iodobutane were identified and their release rates were determined. We assume an abiotic reaction mechanism induced by the oxidation of organic matter by iron(III). The influence of iron(III), iodide and pH on the formation of alkyl iodides was studied. Additionally, different organic model substances regarded as monomeric moieties of humus were examined for the production of alkyl halides. Two possible reaction pathways for the chemical formation of alkyl iodides is discussed. As humic acids and iron(III) are widespread in the terrestrial environment, and the concentration of iodide in soil is strongly enriched (compared to seawater), this soil source of naturally occurring organoiodides is suggested to contribute significantly to the input of iodine into the troposphere.

The construction of a mass balance calculation for alkyl iodides would be of interest. To calculate the annual fluxes of alkyl iodides from continental areas into the troposphere a broad range of field studies are required.

In summary, the results of this study indicate that organohalogen compounds, both the polar phytotoxic HAAs and volatile iodinated organic compounds, which are important for the iodine cycle and tropospheric chemistry, are formed by abiotic soil processes. Their formation is dependent on environmental conditions, e.g. the iron content of the soil is important for these coupled oxidation/halogenation reactions of organic matter. Interestingly, in both cases of polar HAAs and nonpolar alkyl iodides the two possible reaction mechanisms are similar, consisting on one side of the cleavage of an alkyl group, and on the other side of the fragmentation of an aromatic ring structure.

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