Formation of volatile iodinated alkanes in soil: results from laboratory studies

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Abstract

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 paper describes a new source of alkyl iodides from the pedosphere. 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.

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1. 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 a lack of known sources that can account for the total natural emissions (Butler, 2000). Initially, studies focused on the two components methyl bromide and methyl chloride. The tropospheric lifetimes of these compounds (~1 yr) allow significant fluxes to the stratosphere, whereas the shorter lived iodomethane (CH3I) is fully consumed in the troposphere (lifetime less than 10 days). CH3I 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; Rasmussen et al., 1982; Solomon et al., 1994; Stutz et al., 1999; Cotter et al., 2001), volatile organoiodides have gained considerable
scientific interest. A major source of I in the troposphere is the photolysis of alkyl iodides, in processes such as:

\[ \text{CH}_3\text{I} + h\nu \rightarrow \text{CH}_3 + \text{I} \]

Quite significant concentrations of other alkyl iodides, including iodoethane (C\textsubscript{2}H\textsubscript{5}I) and diiodomethane (CH\textsubscript{2}I\textsubscript{2}), have also been found in the lower troposphere (Carpenter et al., 1999). CH\textsubscript{2}I\textsubscript{2} photolyses very quickly (lifetime \( \sim 3\) 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 iodinated compounds are known whereas various natural sources have been identified. Today all the homologous iodine alkanes from C\textsubscript{1} to C\textsubscript{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 Tokarzcyk, 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. 1) 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\textsubscript{2} and H\textsubscript{2}O) 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 sensivity. 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.

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2. Experimental section

**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\textsubscript{3} (65%) were obtained from Sigma-Aldrich, Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}-hydrate was purchased from Fluka and KI was a Merck product. All solutions were prepared with doubly distilled, deionized water.

**Soil samples.** 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\textsubscript{h}) while the peaty soil was taken from the top O-horizon (O\textsubscript{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\textsubscript{org}), total iron and halogens (see Table 1).

**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\textsubscript{3}. After preparation, the vials were sealed and shaken at 30 °C with an incubation period of 5–120 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.
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 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. 2). 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.

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 (60 m × 0.32 mm, film thickness 1 µm) using the following temperature program: initial oven −65 °C, increasing rate 8 °C/min 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. 3). 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.

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).

### 3. Results and discussion

#### 3.1. Soil–water experiments; without additives

To study the natural formation of alkyl iodides, a series of laboratory experiments were conducted using four different humus-rich samples. The peaty soil, with

![Chromatogram of alkyl iodides from a standard solution measured by GC-ECD.](image-url)
a naturally high content of Fe and iodide, showed the highest concentrations of iodomethane (CH₃I), iodoethane (C₂H₅I), 1-iodopropane (1-C₃H₇I), 2-iodopropane (2-C₃H₇I), 1-iodobutane (1-C₄H₉I) and 2-iodobutane (2-C₄H₉I) (Fig. 4a). It is very likely that the monitored alkyl iodides do not give 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 CH₃I (6 pmol g⁻¹ h⁻¹), 2-C₃H₇I and C₂H₅I whereas the release rates for 1-C₃H₇I, 1-C₄H₉I and 2-C₄H₉I were significantly lower. The release rates of alkyl iodides from the two other soil samples were lower and especially for the C₃ and C₄ compounds under the detection limits. Fig. 4b 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 therefore could be the low iodine content of the sample (see Table 1). Fe(II) was monitored, next to the production of alkyl iodides (data not shown), and in the most cases there was a good correlation between Fe(II) formation and the liberation of CH₃I. Further experiments were carried out to test the influence of Fe(III), iodide and pH on the formation of alkyl iodides.

3.2. 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 C₁ to C₄ was observed. Fig. 5 presents the time dependent formation of alkyl iodides with a coniferous forest soil as the organic matter source while in Fig. 6a 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 CH₃I as main product, 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 C₂H₅I and 2-C₃H₇I, have an equivalent or higher share. Table 2 shows the ratios of the produced gas quantities of the main products. The deciding factor for these variations could be the chemical composition of the humus which is discussed in the section ‘proposed reaction schemes’.

The necessity of an oxidizing agent for the formation of alkyl iodides is clearly shown in Fig. 6b. As the grassland soil has an inherent content of iron and iodide, a smaller 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 CH₃I (615 pmol g⁻¹ h⁻¹) production and a 240-fold increase in C₂H₅I (483 pmol g⁻¹ h⁻¹) production. With a 100-fold higher amount of CH₃I and 50-fold higher amount of C₂H₅I 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.

### 3.3. 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. 7). 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

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of most soils is acidic, usually ranging between pH 3 and 6.

3.4. 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 oxihydroxides 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. 8a shows that in the redox-reaction between 2-methoxyphenol and Fe(III) in the presence of iodide, CH₃I is formed (from Keppler et al., 2000 modified). This reaction is specific only for the formation of CH₃I but if using 2-ethoxyphenol or 2-propoxyphenol as organic matter source the corresponding C₂H₅I and 1-C₃H₇I are formed. A completely novel pathway (Fig. 8b) 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 CH₃I, C₂H₅I, 1-C₃H₇I, 2-C₃H₇I, 1-C₄H₉I and 2-C₄H₉I 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 two possible pathways but other possibilities might also exist. Thus it appears that the chemical composition of the organic soil source is responsible for the formation of the different alkyl iodides.

Fig. 7. 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.

Fig. 8. Suggested pathways for the formation of alkyl iodides. Formation of alkyl iodides starting from alkoxyalted phenolic compounds (a). Generation of alkyl iodides by the reaction of catechol and Fe(III) in the presence of iodide (b).
4. Conclusions

Our experiments show that all homologous alkyl iodides from C1 to C4 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. 6a, the forest soil forms 2-C3H7I as the main product, whereas the grassland soil, the peaty soil and humic acid form CH3I as the main product. Considering that humus and iron oxihydroxides 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.

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