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Chloride – a precursor in the formation of volatile organochlorines by forest plants?

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Abstract

Two plants, a fern (*Athyrium filix-femina*) and a moss (*Polytrichum commune* Hedw.), both commonly occurring in Northern Temperate forests, were exposed in a laboratory study to a solution of ^{36}Cl-chloride. The uptake of ^{36}Cl-chloride by the plants was investigated and the emission of volatile chlorine 36 by the plants was determined. Furthermore, speciation of the emitted volatile organochlorine compounds (VOCls) was investigated. For the fern and the moss a rapid uptake of ^{36}Cl-chloride was observed within a 1-h exposure period. The uptake rates for the fern and the moss, respectively, were 16 μg ^{36}Cl-chloride g^{-1} fresh weight (FW) h^{-1} and 3.0 μg ^{36}Cl-chloride g^{-1} FW h^{-1}, respectively. The study also suggested that after uptake by the plants ^{36}Cl-chloride is incorporated into VOCls, which were emitted by the plants into the atmosphere. Speciation analysis of the VOCls revealed the emission of chloroform, tetrachloromethane and 1,1,1-trichloroethane.

Keywords: ^{36}Chloride; Volatile Organochlorines; VOCl; Forest; Fern; Moss

1. Introduction

Despite a worldwide ban on chlorine- and bromine-containing ozone-depleting substances (ODS) after the discovery of the ozone hole over Antarctica and Arctica, exactly when the stratospheric ozone layer will completely recover remains uncertain. Recently, extremely large ozone depletion has been detected over the Northern Hemisphere (Randall et al., 2005) exposing large, highly populated areas of the Northern Hemisphere to increasing levels of UV radiation.

Besides an industrial release also a natural emission of ODS, such as volatile chlorinated organic compounds (VOCls), has been discovered. For example, forest soil has been found to be a dominant source for VOCls (Laturnus et al., 2000). However, in general knowledge on the natural sources of VOCls is still scarce. There is, therefore, a strong need to investigate the natural input of VOCls. First, to understand the size of their contribution to the

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atmospheric load of VOCls, and, second, to estimate how climatic changes may effect the natural emission of VOCls, and likely support a further destruction of stratospheric ozone. Thus, the present picture of the recovery of stratospheric ozone might be even more complex than has widely been assumed.

Chloride in natural ecosystem has been under scrutiny recently. Considered for a long time as conservative in the environment, chloride was often used as a tracer in hydrology (Schlesinger and Andrews, 1997). However, recent studies revealed a picture of chloride retention and transformation in soil including ‘‘chloride imbalances’’ probably caused by heterogeneous vertical transport, uptake by vegetation and microorganisms, geochemical sorption and chlorination and soil organic matter (Rodstedth et al., 2003; Öberg et al., 2005; Lovett et al., 2005; Bastviken et al., 2007).

It is known by now that a significant natural formation of VOCls exists, and several marine and terrestrial sources have already been discovered. However, data on the processes underlying the formation of VOCls are still scarce. A general agreement is that the first step in the formation of VOCls is the halogenation of organic matter by either biotic enzymatic controlled mechanisms (van Pee and Unversucht, 2003) or abiotic halogenation processes (e.g. Laturnus et al., 2005). For both mechanisms it is assumed that chloride, abundantly occurring in the marine and terrestrial environment, is oxidized and incorporated into organic matter. How VOCls are actually formed is not yet known. They can be a product from the degradation of larger chlorinated organic molecules or they can be directly formed by chlorination of the respective non-halogenated molecules. Furthermore, it is unknown if chloride or perhaps other forms of chlorine are actually used for the formation of VOCls. Recently, it was discovered that microorganisms occurring in forest soil are taking up chloride (Bastviken et al., 2007) and it is known that plants too are taking up chloride (White and Broadley, 2001). For plants, data on their participation in the formation of VOCls are still scarce although the emission of some VOCls has been reported occasionally (Yokouchi et al., 2002).

The aim of the present study was to investigate if the chloride pool available in forest soil is used by plants as precursor for the formation of VOCls, and, thus, to obtain details on the formation mechanism of VOCls by plants.

2. Material and methods

Two species, a fern (*Athyrium filix-femina*) and a moss (*Polytrichum commune* Hedw.), both common in European ecosystem were used in this study. Whole plants of the fern species were freshly collected in August 2006 in a forest close to the Institute of Experimental Botany in Prague and kept in the laboratory until further studies. Due to the size of the whole fern species (root/stem system and leaves) only leaves cut from the stem were used in this study. In contrast, the moss consisted of gametophytes, which were placed in hydroponic culture 4 weeks prior to the start of the study. During cultivation the conditions were as following: day to light cycle 16:8 h, light source was a high pressure sodium lamp, which provided a photon flux of 105 μmol m^{-2} s^{-1}, day temperature 23°C, night temperature 20°C. Irrigation was done with tap water. No additional nutrients were added to the culture medium. During the incubation period, no tissue damage was observed.

The study consisted of three parts requiring different treatment of the plant samples. The first part was to study the uptake of chloride by the plant species and to investigate the distribution of chloride within the plants and leaves, respectively. The second part of the study focussed on monitoring a possible emission of VOCls by the plants, followed by the third part of the study, which consisted of a speciation of the, if at all, emitted VOCls.

To investigate the uptake and distribution of chloride, radiolabelled ^{36}Cl-chloride was used. Chlorine 36 is a beta emitter (0.710 MeV) with a half-life of 3.01×10^5 years. Fern leaves with a size between 12 and 15 cm length (weight 0.3 ± 0.1 g FW each leave) were fresh cut from the stem prior the start of the incubation. To increase the uptake of water and to avoid blocking of the transpiration system of the leaves by air bubbles entering the petiole during the cut received the petiole of each fern leave a 2 cm vertical cut which was applied with a scalpel under water. For moss, gametophytes with a size between 8 and 10 cm and a weight of 0.2 ± 0.1 g FW were used. No special pre-treatment was applied to the moss prior the incubation. The basal end of the moss gametophytes and the petiole of the fern leaves were placed in 5 mL of a solution containing ^{36}Cl-chloride with an activity of 0.577 μCi mL^{-1} (Amersham Biosciences CIS3 Chlorine 36, specific activity 3 mCi g^{-1} chloride = 1.11×10^8 Bq g^{-1} chloride). The condition during exposure to ^{36}Cl-chloride was identical to the pre-labelling conditions. After a time period of 1, 3, 6 and 24 h the plants were removed from the solution and the activity uptaken by the gametophytes and leaves was monitored by radioluminography (Phosphor Screen Autoradiography). After the samples were placed for 30 min on a phosphor screen consisting of BaFBr (Eu^{2+} doped) in an organic matrix, which is sensitive for the high-energy radiation emitted by the radioactive sample in the gametophytes and leaves, the emitted radiation was determined by a FujiFilm BAS-5000 Autoradiograph with AIDA (Advanced Image Data Analyzer) version 3.28 at a picture resolution of 50 μm pixel.

The incorporation of ^{36}Cl-chloride into VOCls and their emission by the plants was studied by determining the total activity emitted by the plants into the gas phase. Ferns (0.7–0.8 g FW) and moss (1.4–1.6 g FW), respectively, treated in the same way as for the phosphor screen experiment were exposed to a solution of ^{36}Cl-chloride containing an activity of 10 μCi mL^{-1}