



## Assessing the role of trichloroacetyl-containing compounds in the natural formation of chloroform using stable carbon isotopes analysis

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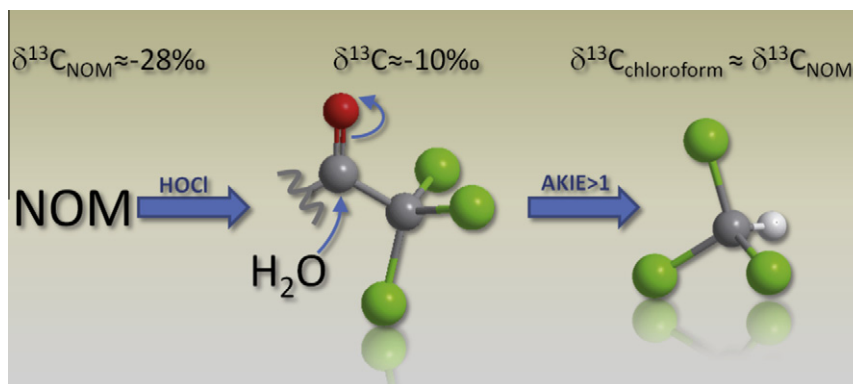
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### HIGHLIGHTS

- ▶ Trichloroacetyl-containing compounds (TCAC) and  $\text{CHCl}_3$  were detected in forest soils.
- ▶ TCAC are much more enriched in  $^{13}\text{C}$  compared to natural  $\text{CHCl}_3$  and NOM.
- ▶ Natural  $\text{CHCl}_3$  has a similar carbon isotope composition as NOM.
- ▶ The formation of  $\text{CHCl}_3$  by hydrolysis of TCAC induced large  $^{13}\text{C}$ -isotope fractionation.
- ▶ Our model confirms that TCAC are likely precursors of natural  $\text{CHCl}_3$  in soils.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Chloroform ( $\text{CHCl}_3$ ) is an environmental contaminant widely distributed around world, as well as a natural compound formed in various aquatic and terrestrial environments. However, the chemical mechanisms leading to the natural formation of chloroform in soils are not completely understood. To assess the role of trichloroacetyl-containing compound (TCAC) in the natural formation of chloroform in forest soils, carbon stable isotope analyses of chloroform and TCAC in field samples and chlorination experiments were carried out. The isotope analysis of field samples have revealed that the  $\delta^{13}\text{C}$  value of natural chloroform ( $\delta^{13}\text{C}_{\text{mean}} = -25.8\text{‰}$ ) is in the same range as the natural organic matter ( $\delta^{13}\text{C}_{\text{mean}} = -27.7\text{‰}$ ), whereas trichloromethyl groups of TCAC are much more enriched in  $^{13}\text{C}$  ( $\delta^{13}\text{C}_{\text{mean}} = -9.8\text{‰}$ ). A similar relationship was also observed for TCAC and chloroform produced by chlorination of natural organic matter with  $\text{NaOCl}$ . The strong depletion of  $^{13}\text{C}$  in chloroform relative to TCAC can be explained by carbon isotope fractionation during TCAC hydrolysis. As shown using a mathematical model, when steady state between formation of TCAC and hydrolysis is reached, the isotope ratio of chloroform is expected to correspond to isotope composition of NOM while TCAC should be enriched in  $^{13}\text{C}$  by about 18.3‰, which is in good agreement with field observations. Hence this study suggests that TCAC are likely precursors of chloroform and at the same time explains why natural chloroform has a similar isotope composition as NOM despite large carbon isotope fractionation during its release.

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### 1. Introduction

Chloroform ( $\text{CHCl}_3$ ) has for a long time been considered as of anthropogenic origin only, classified as a Group B2 probable human carcinogen according to the World Health Organization

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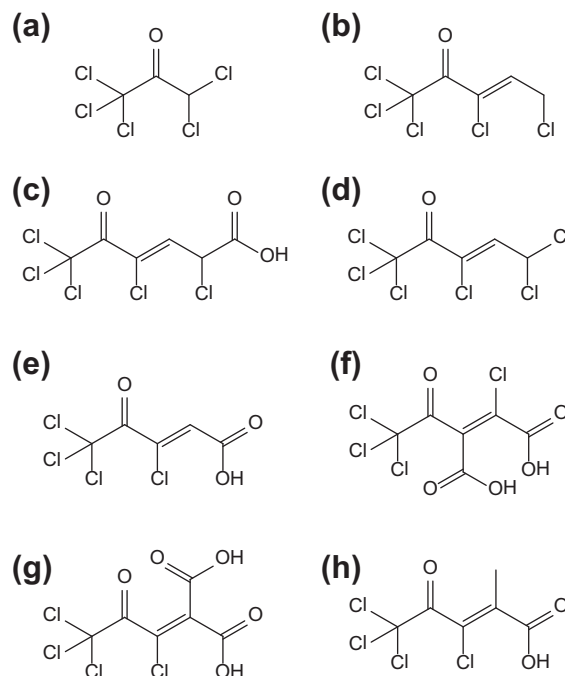
classification scheme (WHO-IARC, 1999). Recently, the presence of chloroform in coniferous forest soil and groundwater has been demonstrated (Haselmann et al., 2000, 2002; Albers et al., 2008a,b). The frequent detection of chloroform in groundwater in absence of other anthropogenic contaminants suggests that chloroform may be formed naturally by biogeochemical processes (Laternus et al., 2002). Numerous studies on natural organohalogenes have suggested that enzymes such as chloroperoxidase (CPO) excreted by fungi could play an important role in biosynthesis of chlorinated organic compounds in soil (Urhahn and Ballschmiter, 1998; Hoekstra et al., 1998a,b; van Pee and Unversucht, 2003). The current hypothesis is that CPO expresses a chlorinating activity by forming HOCl or other oxidized chlorine species (Hoekstra et al., 1998a,b). Recently, Huber et al. (2009) have demonstrated that chloroform can also be formed abiotically, when organic matter is incubated with  $\text{Cl}^-$ ,  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$ .

As CPO is able to chlorinate the natural organic matter (NOM) likely via the formation of an oxidized diffusible intermediate like HOCl (Griffin, 1983), the chemical chlorination with sodium hypochlorite constitutes a good model system to mimic the enzymatic chlorination of NOM. Since NOM has a very complex chemical structure it is impossible to propose a unique reaction mechanism. Therefore, most studies have focused on the chlorination mechanism of simple model compounds such as phenol, substituted phenols, aliphatic  $\beta$ -dicarbonyl acids and glycosides (Rook, 1977; Boyce and Hornig, 1983; Gallard and von Gunten, 2002a,b; Dickenson et al., 2008). The chlorination of substituted aromatic compounds is presumed to take place through a halogenation by oxidized chlorine species on the activated aromatic carbon atoms. This step is followed by hydrolytic cleavage of the aromatic ring; further chlorination of aliphatic intermediates and finally the release of chloroform by hydrolysis. Boyce and Hornig have demonstrated that during the conversion of 1,3-dihydroxyaromatic substrates to chloroform the aromatic ring is broken and several chlorinated aliphatic intermediates are formed (Boyce and Hornig, 1983). Among these intermediates, several trichloroacetyl-containing compounds (TCAC) have been identified by GC/MS (Fig. 1) (Boyce and Hornig, 1983; de Leer et al., 1985).

TCAC can release chloroform either by nucleophilic substitution or by alkaline hydrolysis. Recently, Albers et al. have shown that TCAC are present in forest soils containing natural chloroform and the concentrations of TCAC and chloroform show a similar spatial variability (Albers et al., 2010a,b). They furthermore found the concentration of TCAC in soil profiles to decrease when the pH increases, suggesting natural TCAC to be stable only at acidic conditions.

Compound-specific isotope analysis (CSIA) constitutes a potential tool to assess the mechanisms leading to formation of chloroform during chlorination of organic matter. This technique has recently been used to distinguish natural and anthropogenic sources of contaminants and to gain insights into the mechanisms of degradation of various pollutants (Aelion et al., 2010). Changes of the carbon isotope composition of organic compounds during formation and transformation processes can be attributed to a kinetic isotope effect due to the presence of a heavy isotope in the reacting bond(s), which is characteristic for the underlying reaction mechanism. Recently Arnold et al. (2008), have used CSIA to investigate the apparent  $^{13}\text{C}$  kinetic isotope effect of the formation of chloroform during chlorination of selected model compounds to evaluate the functional group(s) in NOM responsible of chloroform formation. They suggest that compounds containing 1,1,1-trichloropropanone-like functional groups could be intermediates leading to chloroform.

The aims of this study are to characterize the isotope signature of natural chloroform and trichloromethyl groups of the TCAC in order to (i) gain better understanding of the role of TCAC in the for-



**Fig. 1.** Structures of trichloroacetyl-containing compounds formed by chemical chlorination of dihydroxyaromatic model compounds (a–d) (Boyce and Hornig, 1983) and humic acid (e–h) (de Leer et al., 1985).

mation of natural chloroform and (ii) constrain the carbon isotope signature of TCAC and chloroform in the natural environment in view of using isotope data for distinguishing different sources of chloroform. If TCAC is the precursor of chloroform, the isotopic signature of trichloromethyl groups of TCAC should be offset from that of chloroform by an amount that depends on the kinetic isotope effect associated with chloroform release. This study included a field study at forested sites where natural chloroform production is well established (Albers et al., 2010c,2011) and laboratory experiments to investigate the relationship between chloroform and trichloromethyl groups in TCAC in a well-defined closed system. In the field study, the isotope ratio of chloroform present in soil air was compared to the isotope ratio of trichloromethyl groups of TCAC in forest soil. The chlorination experiments were carried out under various pH (pH = 4, 7, 8) conditions as the release of chloroform by hydrolysis is pH dependant using soil material from one of the field sites and humic substances. As for the field study, the carbon isotope ratio of chloroform and trichloromethyl-groups in TCAC was determined. Finally, a mathematical model of the carbon isotopic trends of chloroform and TCAC was established to assess the role of TCAC in the formation of chloroform and to better constrain the isotope signature of natural chloroform.

## 2. Materials and methods

### 2.1. Chemicals

The following chemicals were used as received: sodium hypochlorite (Sigma–Aldrich, available chlorine  $\geq 4\%$ ), phosphoric acid (Fluka, 85%), sodium dihydrogenphosphate monohydrate (Merck, >99%), disodium hydrogenphosphate dodecahydrate (Fluka, >99%), sodium sulfite (Sigma–Aldrich, >98%). Ultrapurified water (18.2 M $\Omega$  cm at 25 °C, Direct-Q UV-3 Millipore) was used to prepare the phosphate buffer solutions. Chloroform from Fluka (99.5%) and Acros Organics (99.8%) were used to prepare concentration and isotope standards. Humic substances used for chlorina-

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