



Mechanistic insights into the formation of chloroform from natural organic matter using stable carbon isotope analysis

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Abstract

Chloroform can be naturally formed in terrestrial environments (e.g. forest soils, peatland) by chlorination of natural organic matter (NOM). Recently, it was demonstrated that natural and anthropogenic chloroform have a distinctly different carbon isotope signature that makes it possible to identify its origin in soil and groundwater. In order to evaluate the contribution of different functional groups to chloroform production and factors controlling the isotopic composition of chloroform, carbon isotope trends during chlorination of model compounds, soil organic matter (SOM) and humic acids were evaluated, and apparent kinetic isotope effects (AKIEs) quantified. Phenol and propanone were selected as model compounds representing common functional groups in NOM. Chlorination was induced by hypochlorous acid to mimic natural chlorination. The pH ranged between 4 and 8 to cover typical soil conditions. For each model compound and pH, different AKIEs were observed. For phenol, the AKIE was normal at pH 4 (1.0156 ± 0.0012) and inverse at pH 8 (0.9900 ± 0.0007). For 2-propanol, an opposite pH dependence was observed with an inverse AKIE at pH 4 (0.9935 ± 0.0007) and a normal AKIE at pH 8 (1.0189 ± 0.0016). The variations of the AKIE values suggest that the rate-limiting step of the reaction is either the re-hybridization of the carbon atom involved in chloroform formation or the hydrolysis of trichloroacetyl intermediates depending on the nature of functional group and pH. The chloroform formation from humic acid and SOM gives rise to small isotope variations. A comparison of the isotopic trends of chloroform formed from humic acid and SOM with those found for the model compounds suggest that opposed AKIE associated with the chlorination of phenolic and ketone moieties of NOM partly compensate each other during chlorination of NOM indicating that different types of functional groups contribute to chloroform formation.

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1. INTRODUCTION

Chloroform is an anthropogenic contaminant widely used in the chemical industry as a solvent or as an extracting agent. Chloroform is also a disinfection by-product resulting from the reaction of chlorine with natural organic matter (NOM) present in water (Deborde and von Gunten,

2008). The frequent detection of chloroform in groundwater in absence of other industrial pollutants suggests that chloroform may be also produced naturally by biogeochemical processes (Laternus et al., 2000, 2002). Recently Hunkeler et al. have demonstrated that chloroform present in groundwater beneath some forested areas in Denmark is formed naturally from NOM using carbon stable isotopes analysis (Hunkeler et al., 2012). Moreover Hunkeler et al. have shown that natural chloroform has $\delta^{13}\text{C}$ values in the same range as NOM whereas industrial chloroform is characterized by an isotopic composition similar to methane (Hunkeler et al., 2012). The current hypothesis is that natural chloroform formed in soils is produced by enzyme-catalyzed chlorination of NOM (Asplund et al.,

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1993; Ortiz-Bermudez et al., 2007). It has been demonstrated that in presence of chloride and H_2O_2 , enzymes such as chloroperoxidase from *Caldariomyces fumago* produces hypochlorous acid (HOCl) which is a strong chlorination agent (Griffin, 1983; Murali Manoj, 2006). As the chemical structure of NOM is complex with various functional groups that could potentially be involved in the formation of chloroform, it is impossible to propose a unique formation mechanism. So far most studies that investigate mechanisms of chloroform formation have focused on the chlorination of simple molecular structures such as mono and poly-hydroxybenzenes, ketones, aliphatic β -dicarbonyl acids and some glycosides (Rook, 1977; Boyce and Hornig, 1983; Arnold et al., 2008; Dickenson et al., 2008). Some studies suggested that trichloroacetyl-containing compounds produced during chlorination of model compounds and humic substances might release chloroform by hydrolysis of the trichloroacetyl group (Boyce and Hornig, 1983; Dickenson et al., 2008; Breider et al., 2013). Recently Albers et al. and Breider et al. have detected trichloroacetyl-containing compounds in some forest soils with natural chloroform (Albers et al., 2010; Breider et al., 2013). Such trichloroacetyl-containing compounds could be formed by successive chlorination of aliphatic groups or by chlorination followed by hydrolytic cleavage of the aromatic rings.

Compounds-specific isotope analysis (CSIA) is a powerful tool to determine the origin of contaminants and gain insight into the mechanisms leading to the formation and the degradation of various organic contaminants (Bergamaschi et al., 1999, 2001; Arnold et al., 2008; Aelion et al., 2010; Hunkeler et al., 2012). Many reactions are associated with a kinetic isotope effect (KIE). The KIE is defined as the ratio between the (pseudo) first-order rate constants for molecules containing light (Lk) and heavy (Hk) isotopes, respectively:

$$\text{KIE} = \frac{^Lk}{^Hk} \quad (1)$$

KIEs arise when at the reactive bond(s) a light isotope is substituted by a heavy isotope. A faster reaction of molecules with light isotopes in the reactive position ($\text{KIE} > 1$) is denoted as *normal isotope effect*. In this case, the reactant becomes enriched in heavy isotope over time. An *inverse isotope effect* ($\text{KIE} < 1$) can be observed in the rare cases where the activation energy is lower for the heavy isotope substituted molecules. Such inverse isotope effects may be observed in cases in which the reacting bond(s) are strengthened or formed in the rate limiting step(s) (Ruszczycky and Anderson, 2006; Elsner, 2010). The analysis of isotope enrichment or depletion in reactant(s) or the product(s) can provide information about the reaction mechanism. In multistep processes the apparent kinetic isotope effect (AKIE) reflects the rate limiting step of the overall reaction (Ruszczycky and Anderson, 2006; Elsner, 2010). Recently Arnold et al. have used carbon stable isotopes analysis to evaluate the role of selected NOM functional groups in the chloroform formation process (Arnold et al., 2008). In their study, Arnold et al. have monitored the $\delta^{13}\text{C}$ value of chloroform produced by chlorination of different models compounds and NOM samples,

and used KIE values to identify specific mechanisms of chloroform formation. The qualitative comparison of the AKIE of chloroform produced by chlorination of NOM with those of NOM models compounds suggested that the phenolic moieties may be essentially responsible for chloroform formation (Arnold et al., 2008). However, the significant difference observed between the AKIE measured for the formation of chloroform from phenol ($\text{AKIE} = 0.980 \pm 0.004$; Arnold et al., 2008) and NOM ($\text{AKIE} = 0.9971 \pm 0.0004$; Arnold et al., 2008) may be an indication for the simultaneous implication of other slowly reacting chloroform precursor with normal AKIEs such as ketone-containing functional groups. While the study of Arnold et al. demonstrates the potential of isotope analysis to explore formation pathways, the results of the study are not directly applicable to forest soils as the experiments were carried out at pH 8, while the pH of forest soils ranges between 4 and 7. As the rate limiting step might vary as a function of pH, AKIE values might vary as well.

The aims of the present study are (i) to better understand the mechanisms controlling the formation and the carbon isotopic composition of chloroform produced from forest soils organic matter (SOM) and (ii) to evaluate the effect of pH on the carbon isotopic composition of chloroform. In order to reach these objectives, chloroform was produced in laboratory studies by chemical chlorination of two model compounds, humic acid and SOM. As phenolic and ketone functional groups are among the most abundant reactive NOM moieties (Sutton and Sposito, 2005; Arnold et al., 2008), phenol and propanone were chosen as model compounds. For these experiments, the organic precursors were chlorinated with hypochlorous acid to mimic naturally occurring chlorination. During the chlorination experiments the concentration and the $\delta^{13}\text{C}$ values of the chloroform were monitored. The isotope trends of chloroform formed by chlorination of humic acid and NOM were compared with those measured for the formation of chloroform from model compounds to explore which functional groups in NOM might contribute to chloroform formation.

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 hydrogen phosphate dodecahydrate (Fluka, $>99\%$), sodium sulfite (Sigma–Aldrich, $>98\%$), phenol (Sigma–Aldrich, $>99\%$), propanone (Acros Organics, $>99.97\%$). Ultrapurified water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$ at 25°C , Direct-Q UV-3 Millipore) was used to prepare the solutions. Chloroform from Fluka (99.5%) was used to prepare concentration standards. SOM collected in H and F horizons of a forest soil from Denmark (spruce forest) was used for chlorination experiments. Humic acid also used for chlorination experiments were obtained by alkaline extraction of SOM with aqueous NaOH, followed by precipitation of humic acid at low pH and a desalting steps involving dialysis (Albers et al., 2008).

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