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Stable hydrogen-isotope analysis of methyl chloride emitted from heated halophytic plants

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HIGHLIGHTS

- ► We have developed a method to measure D/H ratios of chloromethane (CH_3Cl).
- ► We measure D/H ratios of CH_3Cl released from halophytes.
- ► D/H ratios$_{CH_3Cl}$ released from halophytes are similar over large temperature range.
- ► Good correlation between D/H ratios of CH_3Cl and modelled meteoric water.
- ► Implication for global hydrogen model for atmospheric CH_3Cl.

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ABSTRACT

Stable isotope techniques are increasingly applied to study atmospheric budgets of methyl halides. Here we use compound specific thermal conversion isotope ratio mass spectrometry to measure the stable hydrogen isotope values of methyl chloride ($\delta^2H_{CH_3Cl}$) released thermally from dried leaves of halophyte plants collected from different geographical locations. We developed an automated purification and pre-concentration unit to enable measurement of $\delta^2H_{CH_3Cl}$ from samples (100 ml) when mixing ratios were as low as 1 ppmv. Even though this is considerably higher than normal atmospheric mixing ratios this unit enabled measurement of the δ^2H values of CH_3Cl released during heating of samples at temperatures ranging from 30 to 300 °C. No substantial changes of $\delta^2H_{CH_3Cl}$ values were observed over this temperature range. However, the $\delta^2H_{CH_3Cl}$ values of all plants examined were strongly depleted ($-178 \pm 34‰$) relative to the δ^2H values of their modelled meteoric water, but differ only by 1–50‰ from those observed for their methoxyl groups. Our results indicate that plant methoxyl groups are an important precursor of the methyl group for CH_3Cl thermally emitted from lyophilised and homogenized dry halophyte leaves. Furthermore, the thermal reaction producing CH_3Cl did not show a substantial kinetic hydrogen isotope fractionation between CH_3Cl and precursor methoxyl groups over the temperature range investigated. Moreover, we found a moderate linear correlation ($R^2 = 0.37$) for the relationship between $\delta^2H_{CH_3Cl}$ values released from halophytes and the δ^2H values of modelled precipitation at their geographical locations. As CH_3Cl emissions from terrestrial vegetation, including senescent and dry plants and biomass burning, are considered to provide a substantial fraction of the global emissions our findings are important when establishing a global hydrogen isotope model for atmospheric CH_3Cl.

1. Introduction

Atmospheric methyl halides (halomethanes), such as methyl chloride (CH_3Cl), methyl bromide (CH_3Br) and methyl iodide (CH_3I), are known to play a role in the destruction of stratospheric and tropospheric ozone (Montzka and Reimann, 2011). Although it has recently been established that terrestrial ecosystems play an important role in production, consumption and emission of methyl halides, these remain poorly characterised (Rhew, 2011). Investigation of the formation of methyl halides can be gained through studies employing the measurement of stable isotope ratios ($^{13}C/^{12}C$, $^2H/^1H$). Thus stable isotope techniques are increasingly applied to the study of the atmospheric budgets of methyl halides and have increased our knowledge on their life-cycles (Bill et al., 2002; Bahlmann et al., 2011; Mead et al., 2008; Redeker et al., 2007; Redeker and Kalin, 2012). The best example is CH_3Cl – the

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most abundant halocarbon in the remote atmosphere – where, using a stable carbon isotope mass balance approach, considerable progress has been made in our understanding of its global budget (Keppler et al., 2005; Saito and Yokouchi, 2008; Thompson et al., 2002).

Most atmospheric CH_3Cl is released from terrestrial vegetation (Rhew et al., 2000; Yokouchi et al., 2002; Yoshida, 2004; Gebhardt et al., 2008; Blei et al., 2010) with a fraction suggested to be formed in dead and senescent leaf tissue (Keppler et al., 2005; Blei and Heal, 2011; Derendorp et al., 2012), predominantly through a reaction between the methyl moiety of plant methoxyl groups (OCH_3) and chloride ion (Hamilton et al., 2003; Keppler et al., 2004). The plant structural components lignin and pectin both contain methoxyl groups which can be chlorinated under different environmental conditions. At ambient, and temperatures up to 250 °C only pectin methoxyl groups can react with chloride ion to form CH_3Cl. However at higher temperatures, for example during biomass burning, lignin methoxyl groups also become available for methylation by chloride ion. Both processes are suggested to explain the bulk fraction of CH_3Cl released during biomass burning (Hamilton et al., 2003; Keppler et al., 2005). In addition, CH_3Cl emissions from dry plant matter have been shown to be strongly temperature dependent in the range 20–300 °C (Derendorp et al., 2011, 2012; Hamilton et al., 2003; Yassaa et al., 2009).

Stable carbon isotope modelling studies (Keppler et al., 2005; Saito and Yokouchi, 2008) support the contention that a substantial vegetation source is required to balance the CH_3Cl stable carbon isotope budget. Leaf litter, senescent leaf tissue and living plants are the most depleted known sources of CH_3Cl which can be found in literature with reported $\delta^{13}C$ values ranging from −53 to −135‰ (Bill et al., 2002; Harper et al., 2003; Keppler et al., 2005; Saito and Yokouchi, 2008; Redeker and Kalin, 2012). These depleted isotope values are necessary to balance the strong kinetic isotope effects found for the major sinks of CH_3Cl in the atmosphere and in soils (Miller et al., 2004; Gola et al., 2005).

A further understanding of the global budget of methyl halides could be achieved by the determination of their stable hydrogen isotope ratios (D/H). However, analytical measurement of D/H ratios (δ^2H values) of methyl halides at atmospheric concentrations (pptv to ppbv level) are still an analytical challenge and to our knowledge no values for biospheric and atmospheric CH_3Cl have been published thus far.

The aim of this study was twofold. Firstly, to develop and optimize an automated purification and pre-concentration unit attached to a continuous flow gas chromatograph–thermal conversion–isotope ratio mass spectrometry (GC–TC–IRMS) that could measure δ^2H values of CH_3Cl when concentrations were in the lower ppm level. Secondly, to measure δ^2H values of thermally generated CH_3Cl, at temperatures between 30 and 300 °C, from several dried halophyte species collected at different geographical locations. These data were compared with the δ^2H values of the corresponding plant methoxyl groups and with modelled meteoric water at the sample collection sites as calculated by the Online Isotope Precipitation Calculator (OIPC; accessible at http://www.waterisotopes.org/), employing the IAEA database and interpolation algorithms developed by Bowen and Wilkinson, 2002; Bowen, 2003; Bowen et al., 2005.

2. Experimental section

2.1. Chemicals

Methyl chloride (CH_3Cl 2.8, 99.8%) was obtained from Air Liquide (Düsseldorf, Germany), ascarite II (CO_2 absorbent, 20–30 mesh), hydriodic acid (puriss. p.a., 55–60%, not stabilized), methyl iodide (99.5%), pectin (apple) and sodium chloride (99.5%) were all sourced from Sigma–Aldrich (Seelze, Germany or Gillingham, UK) whilst sodium hydroxide (1N NaOH) was obtained from Roth (Karlsruhe, Germany).

Pectin was dissolved in water and sodium chloride added, and then following freezing was lyophilised to produce a pectin standard powder containing 17,000 ppm chloride ion.

2.2. Plant samples

Fresh leaf tissue of 9 halophyte species was collected in Uzbekistan, Mauritania or Botswana. All the leaf samples were air-dried followed by lyophilisation. Prior to the experiment the leaf litter samples were ground to pass through a 1 mm sieve. For each halophyte species, the sampling location, family, chloride content and percentage methoxyl content are listed in Table 1.

2.2.1. Determination of the chloride content

The total chlorine content of the halophyte samples (Table 1) was measured using X-ray fluorescence (XRF) as described in Cheburkin and Shotyk (1996) and Derendorp et al., 2012. The percentage coefficient of variation of the methods was 6.65%.

2.2.2. Determination of methoxyl content

The determination of the OCH_3 content of halophytic samples was a modification of the ‘Zeisel method’ (Zeisel, 1885). Ester and ether methoxyl groups were reacted with hydriodic acid to generate CH_3I which were determined by GC–MS (Wishkerman et al., 2008; McRoberts, 2011; Derendorp et al., 2012). The recovery of the used standard methyl D-galactopyranoside was 97.1 ± 1.2% and the percentage coefficient of variation was 1.9%.

2.2.3. Heating experiments

For the determination of δ^2H values of CH_3Cl emitted from pectin and halophytes, samples were heated at varying temperatures between 30 and 300 °C. Heating experiments at lower temperature (30–130 °C) were carried out in 100 ml glass vials

Table 1
Details of the halophyte samples analysed in this study, including their location and chloride and methoxyl group content.

Plant species	Plant family	Sampling location	Geographical location	Chloride [ppm]	Methoxyl groups [%]
Tamarix hispida wild	Tamaricaceae	Uzbekistan	43°30′13.92″N 59°24′27.90″E	46,800 ± 6300	1.31 ± 0.06
Tamarix leptostachys bunge	Tamaricaceae	Uzbekistan	43°59′42.84″N, 58°47′55.92″E	33,540 ± 1320	1.64 ± 0.11
Astragalus sp.	Fabaceae	Uzbekistan	43°59′42.84″N, 58°47′55.92″E	12,000 ± 636	2.11 ± 0.43
Calligonum sp.	Polygonaceae	Uzbekistan	43°59′42.84″N, 58°47′55.92″E	4600 ± 48	1.37 ± 0.03
Haloxylon persicum bunge ex boiss	Amaranthaceae	Uzbekistan	43°49′31.68″N, 59°15′54.06″E	3360 ± 322	1.88 ± 0.11
Spergularia rubra	Caryophyllaceae	Botswana	20°27′27.8″S, 25°55′55.9″E	20,700 ± 2090	2.52 ± 0.12
Cynodon dactylon	Poaceae	Botswana	20°27′27.8″S, 25°55′55.9″E	9330 ± 292	1.46 ± 0.04
Panicum sp.	Poaceae	Botswana	20°27′27.8″S, 25°55′55.9″E	8740 ± 737	2.33 ± 0.19
Aerva persica	Amaranthaceae	Mauritania	18°53′28.1″N, 15°39′47.1″W	9240 ± 436	1.95 ± 0.04