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Stable hydrogen-isotope analysis of methyl chloride emitted from leaves using continuous flow gas chromatography-isotope ratio mass spectrometry

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Atmospheric methyl halides (halomethanes), such as chloromethane (CH3Cl), bromomethane (CH3Br) and iodomethane (CH3I), are known to play a role in the destruction of stratospheric and tropospheric ozone. Although it has recently been established that terrestrial ecosystems play an important role in production, consumption and emission of methyl halides, these remain poorly characterized. A potentially powerful tool for investigation of the formation of methyl halides is stable isotope ratios analysis. Thus stable isotope techniques are increasingly applied to the study of atmospheric budgets of methyl halides. Several investigations into the atmospheric budget of methyl halides have increased our knowledge about their life-cycles. The best example is CH3Cl 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 & Yokouchi, 2008).
However, analytical measurements of stable carbon isotope values of methyl halides at atmospheric concentrations (pptv to ppbv level) are still an analytical challenge. Furthermore, to our knowledge no stable hydrogen isotope data of biospheric CH3Cl have been published thus far.
Here we use continuous flow GC-P-IRMS attached to a pre-concentration unit to measure stable hydrogen isotope values of biospheric CH3Cl. We have developed an automated purification and pre-concentration unit that can measure these values for methyl halides at low ppmv concentrations. Even though this is considerably higher than normal atmospheric concentration, using this system we can measure the hydrogen stable isotope signature of CH3Cl released from heating of dry plant matter at temperatures ranging from 30 to 300°C.
We present initial data for CH3Cl obtained from heating of both lyophilised and ground leaves of several halophytes, a group of plants containing high amounts of chloride. In addition, using the "HI-method" (Greule et al., 2009) the isotopic signature of the methoxyl groups from these plant samples has been analysed and comparing these values with those of CH3Cl we suggest that the plant methoxyl groups are the precursor of CH3Cl emitted from dry leaves. This confirms findings reported by Hamilton et al. (2003) and Keppler et al. (2004) where it was indicated that the plant methoxyl pool is an important precursor of atmospheric methyl halides.
Based on this first data together with previous findings from our laboratory we would suggest that the stable hydrogen isotopic signature of CH3Cl released from plants is likely related to the hydrogen isotope values of local precipitation.

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