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Chloromethane (CH₃Cl, often named methyl chloride) is an important provider of chlorine to the stratosphere. It accounts for ~16% of the ozone-depleting halogens delivered to the stratosphere [1] and is predicted to grow in importance as the chlorine contribution to the stratosphere from anthropogenic chlorofluorocarbons decline. Today CH₃Cl originates mainly from natural sources with only a minor fraction considered to be of anthropogenic origin. However, until as recently as 2000 most of the CH₃Cl input to the atmosphere was considered to originate from the oceans, but investigations in recent years have clearly demonstrated that natural terrestrial sources such as biomass burning, wood-rotting fungi, salt marshes, tropical vegetation and soil organic matter degradation must dominate the atmospheric budgets of CH₃Cl [2].

Anthropogenic CH₃Cl release to the atmosphere comes from the combustion of coal and biomass with minor emissions from cattle and humans. In addition, it has been reported that emissions from industrial sources might be much higher than previously assumed [3].

The dominant sink for atmospheric CH₃Cl results from the reaction with photochemically-produced hydroxyl radicals [1]. Furthermore, in the marine boundary layer the reaction of CH₃Cl with chlorine radicals represents another sink. Microbial CH₃Cl degradation in soils may be a relevant additional global sink [4] but its impact on the global CH₃Cl budget is still highly uncertain. Moreover, small proportions of tropospheric CH₃Cl are lost to the stratosphere and to cold polar oceans though oceans in total are a net source [1].

In summary many uncertainties still exist regarding strengths of both sources and sinks, as well as the mechanisms of formation and degradation of CH₃Cl. A better understanding of the atmospheric budget of CH₃Cl is therefore required for reliable prediction of future ozone depletion.

A potentially powerful tool in the investigation of the budget of volatile compounds in the atmosphere is the use of stable isotope ratios [5]. Stable isotope analysis, when used in combination with CH₃Cl flux measurements, has the potential to better constrain the atmospheric CH₃Cl budget

as suggested by [6, 7]. The isotopic composition of tropospheric CH₃Cl depends on the isotopic source signatures and the kinetic isotope effects (KIE) of the sinks.

In this presentation recent advances in our understanding of the origin and fate of CH₃Cl in the environment/atmosphere with particular emphasis on the applications of stable isotope techniques/tools including hydrogen, carbon and chlorine will be discussed.

Acknowledgements

The ORCAS group and the German Science Foundation (DFG) are greatly acknowledged.

References

- [1] Carpenter, L.J. *et al.*, Chapter 1: Update on Ozone-Depleting Substances (ODSs) and Other Gases of Interest to the Montreal Protocol, in: Scientific Assessment of Ozone Depletion, *Global Ozone Research and Monitoring Project Report*, World Meteorological Organization (WMO), 21-125, 2014.
- [2] Keppler, F. *et al.*, Mass spectrometric measurement of hydrogen isotope fractionation for the reactions of chloromethane with OH and Cl, *Atmos. Chem. Phys. Discuss.*, 2018, 1-23, 2018.
- [3] Li, S., Park, M.-K., Jo, C.O., Park, S., Emission estimates of methyl chloride from industrial sources in China based on high frequency atmospheric observations, *J. Atmos. Chem.*, 1-17, 2016.
- [4] Jaeger, N. *et al.*, Chloromethane degradation in soils - a combined microbial and two-dimensional stable isotope approach, *J. Environ. Qual.*, doi: 10.2134/jeq2017.09.0358, 2018.
- [5] Brenninkmeijer, C.A.M. *et al.*, Isotope Effects in the Chemistry of Atmospheric Trace Compounds, *Chem. Rev.*, 103, 5125-5162, 2003.
- [6] Keppler, F. *et al.*, New insight into the atmospheric chloromethane budget gained using stable carbon isotope ratios, *Atmos. Chem. Phys.*, 5, 2403-2411, 2005.
- [7] Saito, T., Yokouchi, Y., Stable carbon isotope ratio of methyl chloride emitted from glasshouse-grown tropical plants and its implication for the global methyl chloride budget, *Geophys. Res. Lett.*, 35, 2008.