

Constraining the global bromomethane budget from carbon stable isotopes

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Despite intense research in the last two decades, the global bromomethane (CH_3Br) budget remains unbalanced with the known sinks exceeding the known sources by about 25%. The reaction with OH is the largest sink for CH_3Br . We have determined the kinetic isotope effects for the reactions of CH_3Br with the OH and Cl radical in order to better constrain the global CH_3Br budget from an isotopic perspective.

The isotope fractionation experiments were performed at $20 \pm 1^\circ\text{C}$ in a 3500 L Teflon smog-chamber with initial CH_3Br mixing ratios of about 2 and 10 ppm and perfluorohexane (25 ppb) as internal standard. Atomic chlorine (Cl) was generated via photolysis of molecular chlorine (Cl_2) using a solar simulator with an actinic flux comparable to that of the sun in mid-summer in Germany. OH radicals were generated via the photolysis of ozone (O_3) at 253.7 nm in the presence of water vapor (RH = 70%). The mixing ratios of CH_3Br , and perfluorohexane were monitored by GC-MS with a time resolution of 15 minutes throughout the experiments. From each experiment 10 to 15 sub samples were taken in regular time intervals for subsequent carbon isotope ratio determinations by GC-IRMS performed at two independent laboratories in parallel.

We found a kinetic isotope effect (KIE) of $17.6 \pm 3.3\text{‰}$ for the reaction of CH_3Br with OH and a KIE of $9.8 \pm 1.4\text{‰}$ for the reaction with Cl*. We used these fractionation factors along with new data on the isotopic composition of CH_3Br in the troposphere ($-34 \pm 7\text{‰}$) and the surface ocean ($-26 \pm 7\text{‰}$) along with reported source signatures, to constrain the unknown source from an isotopic perspective. The largest uncertainty in estimating the isotopic composition of the unknown source arises from the soil sink. Microbial degradation in soils is the second largest sink and assigned with a large fractionation factors of about 50‰. However, field experiments revealed substantially smaller apparent fractionation factors ranging from 11 to 22‰. In addition, simple model studies suggest that the soil uptake of CH_3Br and hence its isotopic effect is largely controlled by diffusion resulting in an even smaller apparent isotopic fractionation. As a consequence, the estimated source signature for the unknown source is discussed with respect to the assumptions made for the soil sink.