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Carbonyl sulfide sulfur isotopes in the atmosphere and in seawater

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Carbonyl sulfide (COS) is the major long-lived sulfur bearing gas in the atmosphere, and is used to estimate the rates of regional and global photosynthesis. Sulfur isotope measurements ($^{34}S/^{32}S$ ratio, $\delta^{34}S$) of COS may offer a way for improved determinations of atmospheric COS sources. However, measuring the COS $\delta^{34}S$ at the atmospheric concentrations of $\sim$0.5 ppb is challenging. In addition the $\delta^{34}S$ of COS emitted from its main source, the ocean, was never measured before. We have developed a novel method for high-accuracy and high-sensitivity (only 2 liters of air required) $\delta^{34}S$ analysis of atmospheric and oceanic COS. The measurements are conducted by pre-concentrating the air samples and subsequent $\delta^{34}S$ analysis by gas chromatograph (GC) connected to a multicollector inductively coupled plasma mass spectrometer (MC-ICPMS). For seawater analysis, air was first equilibrated with the dissolved gases. Here we present $\delta^{34}S$ results of atmospheric COS from samples collected in Israel and in the Canary Islands. In addition, we present measurements of $\delta^{34}S$ of COS from Mediterranean seawater, together with measurements of DMS (dimethyl sulfide) $\delta^{34}S$, from the same water. Our preliminary results show that the COS and DMS isotopic values hint that DMS oxidation is a major source for atmospheric COS. By using the $\delta^{34}S$ value of atmospheric COS we measured (13.2$\pm$0.6‰ for both location), and by including the expected isotopic signature of COS sources and sinks, we estimated that about half of it originates from the ocean. Further measurements of the sources isotopic signatures, and the fractionation in plant uptake, will improve this estimate.