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Photoproduction and sedimentary sources of COS and CS_2 identified by their sulfur isotopic values

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Carbonyl sulfide (COS) is a long-lived trace gas, and an important precursor for stratospheric sulfate aerosols, which reduce solar radiation reaching earth surface. The main sink of COS is the uptake by terrestrial plants, similar to CO_2. Therefore, COS is used as a proxy for CO_2 removal by terrestrial plants (gross primary production, GPP), which regulates earth's climate. Currently, COS budget calculations are associated with large uncertainties. Yet, these calculations are needed for GPP and stratospheric sulfate modelling [1]. Sulfur isotopes measurements ($^{34}S/^{32}S$; $\delta^{34}S$) may be used in an isotopic mass-balance to constrain COS budget assuming each end-member has a unique isotopic value. We have recently presented such isotopic mass-balance for the COS budget based on atmospheric and marine measurements, and plant chamber experiments [2]. However, the largest source for tropospheric COS, the ocean-atmosphere COS flux, is still not well understood. In this work we use S isotopes measurements from the marine environment to distinguish between photo-production in the surface ocean and the sedimentary-production of COS and one of its main precursors, carbon disulfide (CS_2). Our measurements from the Atlantic Ocean, the Mediterranean, North, Wadden, and Red Seas show surface $\delta^{34}S$ values in the range of -4 to 18‰ for COS, and -10 to 20‰ for CS_2. Based on these measurements we calculate the isotopic values of COS and CS_2 that was formed by photo-production in the range of 13 to 15‰ and 6‰ respectively. The isotopic values of sedimentary-production are calculated as -4‰ for COS and -10‰ for CS_2, based on the samples from the sediment rich waters of the Wadden Sea. These new findings help constraining the ocean-atmosphere COS flux, and create an improved COS budget isotopic mass-balance to be incorporated into COS based GPP models and stratospheric sulfate models.

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