



Invited review

Anthropogenic contributions to global carbonyl sulfide, carbon disulfide and organosulfides fluxes

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ABSTRACT

Previous studies of the global sulfur cycle have focused almost exclusively on oxidized species and just a few sulfides. This focus is expanded here to include a wider range of reduced sulfur compounds. Inorganic sulfides tend to be bound into sediments, and sulfates are present both in sediments and the oceans. Sulfur can adopt polymeric forms that include S–S bonds. This review examines the global anthropogenic sources of reduced sulfur, updating emission inventories and widening the consideration of industrial sources. It estimates the anthropogenic fluxes of key sulfides to the atmosphere (units Gg S a⁻¹) as: carbonyl sulfide (total 591: mainly from pulp and pigment 171, atmospheric oxidation of carbon disulfide 162, biofuel and coal combustion, 133, natural 898 Gg S a⁻¹), carbon disulfide (total 746: rayon 395, pigment 205, pulp 78, natural 330 Gg S a⁻¹), methanethiol (total 2119: pulp 1680, manure 330, rayon and wastewater 102, natural 6473 Gg S a⁻¹), dimethyl sulfide (total 2197: pulp 1462, manure 660 and rayon 36, natural 31,657 Gg S a⁻¹), dimethyl disulfide (total 1103: manure 660, pulp 273, natural 1081 Gg S a⁻¹). The study compares the magnitude of the natural sources: marine, vegetation and soils, volcanoes and rain water with the key anthropogenic sources: paper industry, rayon-cellulose manufacture, agriculture and pigment production. Industrial sources could be reduced by better pollution control, so their contribution may lessen over time. Anthropogenic emissions dominate the global budget of carbon disulfide, and some aromatic compounds such as thiophene, with emissions of methanethiol and dimethyl disulfide also relatively important. Furthermore, industries related to coal and bitumen are key sources of multi-ringed thiophenes, while food production and various wastes may account for the release of significant amounts of dimethyl disulfide and dimethyl trisulfide.

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1. Introduction

Sulfur has been known from ancient times. Homer's *Odyssey* cleansed his hall with burning sulfur (*Odyssey* Book 22), which was used as fumigant, bleach or incense in the classical world. The first notion of a sulfur cycle is apparent in the work of Lindgren (1923) and was elaborated in books such as Rankama and Sahama's *Geochemistry* (1950). Agricultural scientists of the 19th century were greatly interested in the flux of nitrogen and other elements to the Earth's surface in line with developing an understanding of plant nutrition and a need to improve agricultural yields. By the mid 20th century the problems of urban pollution and acid rain encouraged the construction of detailed sulfur cycles (e.g. Robinson and Robinson, 1970). These were useful in revealing a system that seemed out of balance, and contributed to an awareness of the importance of reduced sulfur and to the discovery of dimethyl sulfide (DMS) in the environment (Lovelock et al. (1972)). The oceans are rich in sulfur, which made a large marine source plausible, but a role for an organosulfide had not been expected, despite a longstanding awareness that living systems produced alkylsulfides, as in the extensive studies of methylation by Challenger and his colleagues (e.g. Bywood and Challenger, 1953).

This led to the study of an ever-widening range of organosulfides among environmental chemists that has continued to the present. The global cycling of the elements has become a common part of science education, perhaps the carbon and nitrogen cycle being most frequently taught, but even the environmental chemistry of organosulfur compounds is seen as instructive for young chemists (Chasteen and Bentley, 2004). Many estimates of sulfur budgets have been published over recent decades (e.g. Andreae, 1990; Brimblecombe, 2004; Brimblecombe and Lein, 1989; Kellogg et al., 1972; Langner and Rodhe, 1991; Nguyen et al., 1983; Robinson and Robinson, 1970; Watts, 2000).

The detection of ambient DMS by Lovelock et al. (1972) represented a very important change to the sulfur cycle as it introduced organosulfides, which have been a significant part of our understanding ever since. Despite this, the global cycling of sulfur has typically focused on just a few sulfides (e.g. Watts, 2000) and inorganic sulfur (Brimblecombe and Lein, 1989). Here we examine the environmental origins for carbonyl sulfide (OCS), carbon disulfide (CS₂) and a wider

range of organosulfides. Many have relatively small fluxes in terms of total sulfur, but can nevertheless be important because they are often isolated in small reservoirs, such as urban run-off, the sea-surface microlayer or coastal sediments. In other cases they have important biogeochemical roles. Additionally Domagal-Goldman et al. (2011) have explored the potential that reduced sulfur gases have for the detection of life on extra-solar planets, although they acknowledge that these compounds may be sensitive to photo-chemical degradation, which might reduce their lifetime and our ability to detect them.

Global geochemical cycles of materials at the surface of the Earth typically focus on systems that are sunlit, oxidizing, and dominated by water. Such systems can reduce the stability of organosulfides, which are soft-bases in a Pearson sense (Pearson, 1963), of low polarity and solubility. Despite this, there is a rich organosulfur chemistry on the Earth. Recognition of large fluxes of DMS from the ocean to the atmosphere has emphasised that organosulfur chemistry is not limited to the Earth's reducing sediments. Sulfur has the ability to adopt polymeric forms that include the S—S bond, or indeed S—S—S and beyond. Polymeric sulfur compounds are found in both their oxidized state (as polythionates, e.g. S_nO₆ where n is 4, 5, or 6 in volcanic crater lakes; see Sriwana et al., 2000) and reduced states as polysulfanes or polysulfides (H₂S_n and S_n²⁻ where n can be eight or possibly more, Gun et al., 2000) and organopolysulfides (e.g. as CH₃S_nCH₃ where n can be 1, 2, 3 or 4). Although nitrogen is found in polymeric compounds, such as hydrazine, these are less common and not widely characterised in the environment.

There have been a number of reviews of the sulfur cycle and with respect to sulfides; Watts (2000) is now more than a decade old. There have been some more recent accounts of OCS (Kettle et al., 2002; Montzka et al., 2007; Campbell et al., 2015; Launois et al., 2015b) and DMS (Gabric et al., 2001; Lana et al., 2011) and work on vegetation and soils (Kesselmeier, 2005), but these have often been concerned with specific compounds. Sulfur in the ocean has been the focus of some specialist reviews (Sievert et al., 2007; Jasinska et al., 2012; Liss et al., 2014). It also seems necessary to expand the range of compounds to include methanethiol (MeSH) and dimethyl disulfide (DMDS), usually discussed only in terms of marine sources, and additionally the rarely mentioned thiophenes, with a particular focus on anthropogenic sources. Industrial releases of organosulfides can be a source of odour

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