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ANTHROPOGENIC CONTRIBUTIONS TO GLOBAL CARBONYL SULFIDE, CARBON DISULFIDE AND ORGANOSULFIDES FLUXES**Chon-Lin Lee^{1, 2, 3} and Peter Brimblecombe^{4, 5*}**

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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 impact 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.

Keywords

Biogeochemical cycles, methanethiol, dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide, thiophene, benzothiophene

1. Introduction

Sulfur has been known from ancient times. Homer's Odysseus 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_nO_6 where n is 4, 5, or 6 in volcanic crater lakes; see Sriwana et al., 2000) and reduced states as polysulfanes or polysulfides (H_2S_n and S_n^{2-} where n can be eight or possibly more, Gun et al, 2000) and organopolysulfides (e.g. as $CH_3S_nCH_3$ 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., 2013; 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; Jasińska 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 complaints, with the paper industry especially notable. Agricultural practices are also an important source of reduced sulfur and spoilage can produce volatile sulfides with strong odours (Obenland et al., 1994).

2. Methodology

The sources of sulfides are discussed in Section 3, while in Section 4 we compare the anthropogenic fluxes to the natural fluxes and put them into the context of the global budgets for the most important sulfur gases. This is followed by a discussion of the removal mechanisms in Section 5. Very often the anthropogenic emission data was not in the form of a global, or even regional flux, so often assumptions were required to bring estimates into a consistent form as presented in the section. Extrapolation to global emissions is particularly

prone to error when estimated from a single factory or agricultural activity. The seemingly simple need to convert data into the same units was not always easily accomplished, especially where measurements were for mixed sulfides. For the most part the data is expressed as the mass of sulfur (e.g. mg S m^{-3} , ng S L^{-1}), not the total mass of the compound, although the few exceptions where it is as the mass of the compound it is denoted by omitting the S (e.g. ng L^{-1}). Occasionally the metric tonne (t, i.e. Mg) is used. Time in flux units was expressed as years, i.e. per annum in the case of global fluxes (typically Gg S a^{-1}), but short term experimental measurements or observations made at a local level are expressed in seconds. A range of important sulfides is discussed in the text, but we tend to give more attention than has been typical to the global cycles of the lesser known sulfides such as methanethiol, dimethyl disulfide, dimethyl trisulfide and the thiophenes. Some sulfides have been abbreviated in our text following popular convention, with the exception of thiophene where there is no obvious and convenient abbreviation:

carbonyl sulfide (OCS)
 carbon disulfide (CS_2)
 methanethiol (MeSH)
 dimethyl sulfide (DMS)
 dimethyl disulfide (DMDS) and occasionally dimethyl trisulfide (DMTS)
 thiophene (no widely adopted abbreviation)
 benzothiophene (BT)
 dibenzothiophene (DBT)
 benzonaphthothiophenes (BNT)
 polychlorinateddibenzothiophenes (PCDTs)

The more complex thiophenes that include BT, DBT and BNT are often grouped as the thia-arenes, although they can also be termed polycyclic aromatic sulfur heterocycles (sometimes abbreviated as PASH). Where the abbreviation refers to a group of compounds, plurality is denoted by a lowercase s, for example as DBTs rather than DBT.

3. Sources

Table 1 gives the fluxes of the anthropogenic sulfides derived as discussed in the sections below.

3.1 Biomass burning

Biomass burning is increasingly recognised as an important source of emissions to the

global atmosphere. It is difficult at times to assess the balance between the natural and anthropogenically induced biomass burning, as some is conducted as an agriculture practice. It is a large source of OCS, and Andreae and Merlet (2001) recommended OCS emission factors for open combustion of biomass: grassland, $0.008 \text{ g S kg}^{-1}$ dry fuel burnt; tropical forest, 0.02 g S kg^{-1} dry fuel burnt; extra-tropical forest, $0.018 \text{ g S kg}^{-1}$ dry fuel burnt; and crop residue, $0.035 \text{ g S kg}^{-1}$ dry fuel burnt. The global annual biomass burning emission flux of OCS was recently estimated to be $70 \text{ (30-110) Gg S a}^{-1}$ (Nguyen et al., 1995) compared with 46 Gg S a^{-1} (Meinardi et al., 2003), $11\text{-}64 \text{ Gg S a}^{-1}$ (Kettle et al., 2002) and $140 \text{ (40-260) Gg S a}^{-1}$ (Chin and Davis, 1993). Research has shown that a fraction of longer lived components of Australian bushfires such as C_2H_2 and OCS may also be transferred to the stratosphere (Notholt et al., 2003; Glatthor et al., 2013). The emissions of OCS from biomass combustion have recently been re-evaluated (Campbell et al., 2015) as $116 \pm 52 \text{ Gg S a}^{-1}$ split between biofuel, agricultural waste and open burning in the ratio 63:26:11. Here we take biomass burning as incorporating the latter two thus amounting to 43 Gg S a^{-1} .

We take CS_2 to be 1/25th of the OCS in line with the measurements of Meinardi et al. (2003). Emissions of OCS, DMDS, DMS and CS_2 have been identified during biomass burning in the Northern Territory of Australia, with OCS and DMDS present as major reduced sulfur gases from the bushfires (Meinardi et al., 2003). The ratios suggest global fluxes for OCS, DMS and DMDS of 43, 6 and 119 Gg S a^{-1} . The high fluxes set for DMDS are particularly interesting and need further measurements, but we have placed them in Table 1. Biomass combustion does not produce significant amounts of PASH (Ross et al., 2002).

3.2 Biofuel combustion

Of the $4.4 \times 10^9 \text{ m}^3$ of wood harvested in 1996, some $1.9 \times 10^9 \text{ m}^3$ were burnt for cooking and heat, although in total the amount burnt may be greater than 60% of the total harvest (FAO, 1999). The combustion of biofuels in residential stoves has been taken to emit $0.04 \text{ g OCS kg}^{-1}$ dry fuel burnt (Andreae and Merlet, 2001). Overall, the biofuel combustion source of OCS was estimated at 46.8 Gg S a^{-1} by Blake et al. (2004) and Watts (2000). The recently re-evaluated emissions of OCS produced during the combustion of biomass from Campbell et al. (2015) place global emissions from the use of biofuels at 73 Gg S a^{-1} . In the absence of an estimate for CS_2 , a ratio of CS_2 :OCS of 1/25 (Meinardi et al., 2003) was used, which would make the CS_2 from biofuel 2.9 Gg S a^{-1} .

Wang et al. (2009) examined VOC species from biofuel-stoves and found: alkanes (containing cycloalkanes), alkenes and alkynes, carbonyls, aromatics (containing aromatic carbonyls), halogenated hydrocarbons, nitrogen containing compounds, and sulfur containing compounds. Measurements available show that wood and sawdust, not surprisingly, emit a much smaller quantity of thia-arenes than bituminous coal (Ross et al., 2002). Pine sawdust

appears to emit much more than wood, with total amounts of the compounds as: BT 0.004 mg S kg⁻¹, methylbenzothiophene 0.007 mg S kg⁻¹, dimethylbenzothiophene 0.013 mg S kg⁻¹, naphthothiophene 0.020 mg S kg⁻¹, methyl dibenzothiophene 0.005 mg S kg⁻¹, while wood emits methyl dibenzothiophene at 0.004 mg S kg⁻¹. Total thia-arenes from sawdust were emitted at 0.338 mg kg⁻¹. Assuming 1.5 billion tonnes of wood are burnt each year and the pine sawdust emission rates were typical, it would suggest the release of almost a gigagram of these thia-arenes each year, but the constituents are unclear, though the DBT from wood may amount to some 0.035 Gg S a⁻¹.

Increasing interest in biofuels for vehicles creates a novel source, although ethanol and methanol as fuels are low in sulfur. Biodiesel also has a low sulfur content, but this is dependent on feedstocks (e.g. He and van Gerpen, 2008). Correa and Arbilla (2008) suggest that methane, ethane, *n*-propane and *n*-butanethiols in a biodiesel diesel mix of 20:80 are reduced by 18.4%, 18.1%, 16.3% and 9.6% respectively. Since biodiesel is virtually free from sulfur this is not surprising, but the results hint that some sulfides may be generated during combustion of the mixed fuel. Similar results were found when running an engine with unmodified sunflower oil, which generated DBT and methyl naphthothiophene. These are only released in small quantities, at 129±28 and 153±32 µg S m⁻³ of burnt fuel and are associated with engine exhaust particles (Lalah and Kaigwara, 2005). As only 13.9 Tg of biodiesel was produced worldwide in 2008 (Atabani, et al., 2012), this source represents mere kilogram quantities of the thiophenes so can hardly be a significant source.

3.3 Pulp and paper industry

The paper industry is considered to be the sixth largest polluter (after the oil, cement, leather, textile and steel industries) and is particularly associated with odour complaints (Latorre et al., 2005). By 2020 paper mills will have an estimated annual production of almost 500 Tg of paper and paperboard (Wyatt, 2007). The industry is potentially very polluting, with both the *Kraft process* and the less important *sulfite process* giving rise to H₂S, MeSH, DMS, DMDS, and other volatile sulfur compounds that account for the industry's characteristic odour. The *Kraft process* opts for a large amount of internal recycling, with the black liquor, other wastes and discarded wood fragments typically burnt in a recovery furnace. Nevertheless, concerns about sustainability, as well as air and water pollution, have been a focus of both the industry and environmental campaigners. In particular DMTS has sometimes been linked to odours have attracted attention to the industry, making this compound of special interest (Brownlee et al., 1995) and it is a potentially important olfactant in other contexts (Hesta et al., 2003). Gun et al. (2000) believe that the dimethyl polysulfides in aqueous systems are produced by the methylation of polysulfides or polysulfanes by

organic methyl donors, such as methionine. They suggest that this is supported by observations that lower dimethyl polysulfides are always found when the higher polysulfides are present in oceans and other aquatic systems, i.e. DMDS is always found when DMTS is reported, and DMTS and DMDS are always found when dimethyl tetrasulfide is reported. The frequent occurrence of polysulfides in sludges (e.g. van der Zee et al., 2007) makes this process of likely importance in wastewaters more generally.

Water from pulp and paper mills gave median concentrations at primary clarifier outlets of 3.5 mg S L^{-1} for total sulfide, $38 \text{ } \mu\text{g S L}^{-1}$ for MeSH, $66 \text{ } \mu\text{g S L}^{-1}$ for DMS, $22 \text{ } \mu\text{g S L}^{-1}$ for DMDS, and $<20 \text{ } \mu\text{g S L}^{-1}$ for DMTS (Cook and Hoy, 2007). Benzothiazoles are used as slimicides in the paper and pulp industry (Meding et al., 1993) and benzothiazole, 2-mercaptobenzothiazole, and 2-(methylthio)benzothiazole were found as degradation products of the fungicide 2-(thiocyanomethylthio)benzothiazole in wastewater (de Vos et al., 1993). Very high concentrations of organosulfides are found in gas from recovery boilers including H_2S , OCS and CS_2 , MeSH, ethanethiol (EtSH), DMS and DMDS (for details see Vainio et al., 2010a). Toda et al. (2010) argue that MeSH is formed in the reactor by methylation of sulfide and is vaporised relatively easily because of its weak acidic dissociation constant (Ka), more than six orders of magnitude smaller than that of H_2S (pKa for MeSH 13.6, for H_2S 7.0 and 12.9). DMS also has a high vapour pressure, but the formation of DMS is likely much slower because of the second methylation. These may be reasons for the importance of MeSH in the exhaust from pulp and paper production.

Polychlorodibenzothiophenes (PCDBTs), polychlorothianthrenes (PCTAs) and polychloro diphenyl sulfides (PCDPSs) were detected in the range of $40\text{-}2700 \text{ } \mu\text{g L}^{-1}$ in pulp mill effluents and in the range of $2\text{-}40 \text{ } \mu\text{g g}^{-1}$ dry weight in the sediments. PCDBTs have previously been analysed in particles filtered from bleached pulp mill effluent samples. Tetrachlorodibenzothiophenes (TeCDBTs) were detected in low concentrations ($1\text{-}60 \text{ } \mu\text{g L}^{-1}$) and 2,3,7,8-TeCDBT was found as the dominating isomer in some effluents. Pentachlorodibenzothiophenes and other higher chlorinated PCDBTs were not detected (Sinkkonen et al., 1994). There is probably some transfer of these chlorinated sulfides into the air.

Bordado and Gomes (2001) and Muezzinoglu (2003) give measured emission concentrations of H_2S (up to $3\,795 \text{ mg S m}^{-3}$), MeSH (up to $17\,067 \text{ mg S m}^{-3}$), DMS (up to $31\,484 \text{ mg S m}^{-3}$); with DMDS (up to 766 mg S m^{-3}) coming from Kraft pulp mill operations. The emission factor for the sum of MeSH, DMS and DMDS was estimated as 8 kg Mg^{-1} of weight of air-dried unbleached pulp (EPA, 1995a). Along with the global wood pulp production of 500 Tg a^{-1} , this allows the global emissions to be estimated, but typically control of the black liquor by oxidation can much reduce the sulfides. Here we take sulfur emissions (of MeSH, DMS and DMDS) to be 5 kg Mg^{-1} , although improvements in pollution control will no doubt reduce this further.

The relative strength of sulfides was reported as 202, 164, 1730, 1777, 3051 and 437 mg S m⁻³ in a furnace of a recovery boiler for the compounds OCS, CS₂, MeSH, EtSH, DMS and DMDS respectively (Vainio et al., 2010b), allowing global fluxes to be approximated as 97, 78, 830, 855, 1470 and 210 Gg S a⁻¹, respectively. Emission from this source alone was close to that of global anthropogenic OCS flux of 120 Gg S a⁻¹ estimated by Watts (2000), in which the pulp and paper industry was ignored. The dimethyl trisulfide (DMTS) and thiophene concentrations also seem high above mill lagoons where the median relative strengths of DMDS:DMTS:thiophene in the gas phase are 1:15:4 (Lange and Christiansen, 2004). However, it may be that only 2% of the DMDS arises from the mill wastewater compared with other sources (Catalan et al., 2009). Thus we place DMTS and thiophene as 63 and 17 Gg a⁻¹. The magnitude of global emissions from these industries is large, so environmental concern over the emissions seems justified.

3.4 Rayon/cellulosic industry

The cellulosic industry uses CS₂ as a solvent and some 251 g are released during the production of one kilogram of rayon, but options for control were troublesome (EPA, 1995b). There have been some improvements in the case of staple production (down to 70 g kg⁻¹), which has grown to be the dominant output element of the production (Campbell et al., 2015). Although there has been some reduction in demand for rayon in recent years, growth has been stronger since 2009, when global production of cellulosic fibres stood at 3.8 Mt (HB, 2013). Newer fabrics, such as Lyocell, that do not require CS₂ “failed to live up to [their] early promise” (Advameg, 2013). There are also releases from the cellophane and rubber industries. Taking 5 Tg a⁻¹ as the global production of rayon (GIA, 2011) and an emission factor of 79 g S kg⁻¹ gives an annual emission of CS₂ of 395 Gg S a⁻¹ in reasonable agreement with the 340 Gg S a⁻¹ from Watts (2000). Using the relative concentration ratios (0.09 for DMS:CS₂ and 0.13 for 2-propanethiol:CS₂) measured in the ambient air around a chemical fibre manufacturing facility (Lin, 2001), rough estimates of the global emission (Gg S a⁻¹) of DMS and 2-propanethiol can also be made, as shown in Table 1.

3.5 Agriculture: rice paddies and manure

Agricultural practices are an important source of reduced sulfur, although these are not always easy to distinguish. Crops themselves emit reduced sulfur compounds, but these are part of the emissions from vegetation. Spoilage can produce volatile sulfides with strong odours (Obenland et al., 1994), but much of this source will be included in food processing and waste.

The manure emission factor for DMS was measured as 13.8±10.3 μg (DMS) cow⁻¹ s⁻¹

from a dairy farm (Filipy et al., 2006). Using a global cattle population of 1.91×10^9 (Bouwman and van der Hoek, 1997), global DMS emission from cattle could be estimated as $430 \pm 321 \text{ Gg S a}^{-1}$. As 65% of global $\text{NH}_3\text{-N}$ emission from animal excreta was allocated as contributions from cattle, including buffalo (Bouwman and van der Hoek, 1997), assuming that the $\text{NH}_3\text{-N}$ and DMS emission was proportional, global DMS emission from all livestock can be calculated as $660 \pm 493 \text{ Gg S a}^{-1}$. Manure is also a source of MeSH with maximum concentrations of about half that of DMS (Muezzinoglu, 2003). Taking the ratio as relative emission strength, global MeSH emissions from animals can be calculated to be 330 Gg S a^{-1} .

The studies of cattle emissions and those from poultry suggest a wide range of sulfides can be released. These are associated with strong odours; polysulfides can be abundant from chicken manure (Poels et al., 1987; Smet and van Langenhove, 1998), and in the case of emissions from poultry broilers both DMDS and DMTS concentrations were higher than DMS: H_2S 6.7, OCS 1.0, CS_2 28.1, MeSH 2.1, DMS 12.6, DMDS 29.4, DMTS $170.2 \mu\text{g m}^{-3}$ (Trabue et al., 2008). With just a few isolated measurements it is hard to estimate the global emissions of DMDS and DMTS (and indeed CS_2), but taking a conservative approach here their total is set at the same value as DMS (i.e. each at 330 Gg S a^{-1}) as an indicator of a potentially large source that needs to be resolved with further research. The global emissions are given in Table 1.

Watts (2000) placed the emissions of OCS and CS_2 from wetlands as 30 Gg S a^{-1} and 20 Gg S a^{-1} , but these flux rates were assigned large errors. Here, as we separate natural and anthropogenic sources, it has been necessary to distinguish salt marshes from agricultural sources such as rice paddies. Rice paddies can emit volatile sulfur compounds, such as H_2S , OCS, CS_2 , DMS and DMDS (Kanda and Minami, 1992; Nouchi et al., 1997; Redeker et al., 2003; Yang et al., 1996; Yang et al., 1998), among which CS_2 and DMS are the most important (Kanda and Minami, 1992; Redeker et al., 2003). However, Yi et al. (2008) found that paddy fields could also be a net sink for OCS and a source of DMS, with an uptake rate of $0.39 \pm 0.19 \text{ ng S m}^{-2} \text{ s}^{-1}$ for OCS and an emission rate of $0.83 \pm 0.11 \text{ ng S m}^{-2} \text{ s}^{-1}$ for DMS. The OCS fluxes varied significantly between non-planted dry and waterlogged soils, with an uptake rate of $0.36 \pm 0.23 \text{ ng S m}^{-2} \text{ s}^{-1}$ for non-planted dry soils, an emission rate of $0.29 \pm 0.17 \text{ ng S m}^{-2} \text{ s}^{-1}$ for non-planted waterlogged soils and an uptake rate of $0.93 \pm 0.82 \text{ ng S m}^{-2} \text{ s}^{-1}$ for planted waterlogged soil. However, for DMS the variation between non-planted dry and waterlogged soils was not significant, thus both the planted and non-planted waterlogged soils acted as sources, with an emission rate of $1.63 \pm 1.2 \text{ ng S m}^{-2} \text{ s}^{-1}$ for the planted waterlogged soil, which was significantly higher than that for the non-planted waterlogged soil ($0.12 \pm 0.9 \text{ ng S m}^{-2} \text{ s}^{-1}$).

Assuming rice paddies globally cover $1.54 \times 10^6 \text{ km}^2$ (FAO, 2002), DMS emission rates from Yang et al. (1998) suggest annual fluxes ranging from $4.8\text{-}10 \text{ Gg S a}^{-1}$. However, using the emission factor from Yi et al. (2008) suggests 40 Gg S a^{-1} . The ratios of aerobic emissions

of OCS, CS₂, MeSH, DMS and DMDS from Chinese rice paddies were estimated at: 0.2, 14.2, 0.4, 13.2 and 0.3 $\mu\text{g S g}^{-1}$ soil (Yang et al., 1998). So taking an intermediate DMS flux of 25 Gg S a⁻¹ would place the global emissions of OCS, CS₂, MeSH and DMDS from rice paddies at 0.38, 26.9, 0.76 and 0.57 Gg S a⁻¹.

3.6 Pigment industry

Pigments such as carbon black and titania both give rise to sulfides during production. About 5.3 g S as OCS and 25.3 g S as CS₂ are produced for every kilogram of carbon black produced (Blake et al., 2004) and additionally about 14.7 g OCS kg⁻¹ derives from the production of titanium white, TiO₂. Some 8 Tg of carbon black is manufactured each year (ICBA, 2006), which suggests the emission of 43 Gg S a⁻¹ OCS and 205 Gg S a⁻¹ CS₂. Annual production of titanium dioxide amounts to 4 Tg, so OCS from this source amounts to 31 Gg S a⁻¹. The total emissions from the pigment industry are given in Table 1.

3.7 Food processing and waste

The food processing industry can generate a wide variety of sulfur compounds. These are popularly associated with the unpleasant odours generated during the cooking process in rendering plants. They are largely attributable to the presence of VOSCs (volatile organic sulfidic compounds), amines, acids, alcohols and aldehydes (Chélu and Nominé, 1984; Prokop and Bohn, 1985; van Langenhove, 1982). Average concentrations of 39 mg S m⁻³ H₂S (peak concentrations up to 1040 mg S m⁻³) and 39 $\mu\text{g S m}^{-3}$ MeSH (peak concentrations up to 260 mg S m⁻³) with ranges 5.2-15.6 mg S m⁻³ for DMDS and 0.78-7.8 mg S m⁻³ for DMTS, were measured in the non-condensable gaseous effluent from continuous rendering cookers. Emission of sulfur and nitrogen compounds were estimated as 3 to 280 mg t (treated material)⁻¹ s⁻¹ in a rendering factory, mainly as H₂S, MeSH, EtSH and NH₃.

The offensive odours in some foods also arise from DMS and volatile organic sulfur compounds. The aerobic decomposition of food wastes gave a total of 410 mg kg⁻¹ (dry weight), which included VOSCs, with DMDS the most abundant accounting for about 76%, while others such as DMS, methyl 2-propenyl disulfide, OCS and methyl 1-propenyl sulfide shared 13.5%, 4.8%, 2.2% and 1.3% respectively among a total of fifteen VOSCs released (Wu et al., 2010). Decaying food can also be a source and as with aerobic decomposition DMDS is the most abundant, with DMS and CS₂ notably smaller (Zhang et al., 2013). Some 1.3 billion tonnes of food is wasted each year (Gustavson et al., 2011). Taking this to be 90% water allows estimates of the global flux, which is dominated by the disulfides at some 29 Gg S a⁻¹. This calculation does not add anything for rendering, which may yield substantial amounts of MeSH, as noted above.

DMS is important in flavouring some beverages (Segurel et al., 2004; Shaw et al., 1980). Varlet and Fernandez (2010) reviewed the occurrence, odorant properties and formation mechanisms of sulfur-containing volatile compounds in seafood. MeSH, DMS and DMDS were important components of seafood odour while DMTS was a marker of spoilage (Duflos et al., 2006). Benzothiazole, 2-methylbenzothiazole and 2-mercaptobenzothiazole are occasionally found (Vitzthum et al., 1975; Anjou and von Sydow, 1967).

3.8 Gas industry

Natural gas always contains H₂S, OCS, and thiols (Ryzhikov et al. 2011; Ghaedian et al., 2012). Gases with more than 5.2 mg S m⁻³ sulfides are said to be sour, so these are removed during processing. It is important that gas has an odour to allow leaks to be detected, so additives such as EtSH, tetrahydrothiophene and t-butanethiol are commonly used, although they can be a problem in some industrial applications, so they may need to be removed (de Wild et al., 2006).

Thia-arenes such as benzo[b]naphthothiophenes have been identified in emissions from natural gas home appliances. Together, aza-arenes (nitrogen containing heterocycles) and thia-arenes are present at a mass concentration of roughly 10%, as high as that of the PAHs or oxy-PAHs. Thia-arene emission rates were estimated as: 163.4-568.0 pg kJ⁻¹, with benzo[b]naphthothiophenes: 103.5-325.4 pg kJ⁻¹, assuming the heating value of the natural gas to be 52.6 kJ g⁻¹ with a density of 0.77 kg m⁻³ (Cass, 1993). Taking the global annual natural gas production to be 455x10⁹ m³ in 2009 (EIA, 2011) and assuming the home appliance emission factor can be applied to global emission rates, the global emission of thia-arenes and benzo[b]naphthothiophenes are estimated as 5 (3.0 – 10.5) and 3 (1.90 – 6.0) t S a⁻¹, respectively.

Global emission from the micro-seepage of methane has been estimated to exceed 10 Tg a⁻¹ (Etiope and Klusman, 2010). Assuming gas composition with H₂S/OCS of 450 (Tu et al, 2010), H₂S/CH₄ of 0.031 (NGO, 2004-2011) and H₂S/organic sulfur of 50, places the global microseepage of organic sulfur as 6.2 Gg S a⁻¹ and OCS at 0.7 Gg S a⁻¹. More specifically, based on Vol'tsov et al. (1986), we assume 78% is methanethiol, 13.6% dialkyl sulfides (with a trace of others such as the alkylcycloalkyl sulfides) and 1.6% disulfides (diethyl disulfide, dipropyl disulfides, etc.) with respect to the total organosulfur. The emissions of MeSH, dialkyl sulfides and dialkyl disulfides could be as high as 4.8, 0.84 and 0.1 Gg S a⁻¹, and estimated global emissions are given in Table 1.

3.9 Wastewater

A wide range of volatile sulfides is found in wastewater, and these are often a problem

because of the strong odours from sewage treatment. Some industries are likely to be particularly significant contributors, and a number have already been discussed in previous sections. It is also likely that tanning and wool scouring waters are a source of sulfur compounds, particularly OCS and CS₂ as they are prevalent in the emissions from wool grease, and odour problems from organosulfides can be an issue for the wool industry (Lisovac and Shooter, 2003).

VOSCs are generated in wastewaters with limited dissolved oxygen. Several VOSCs typically found in wastewater treatment plants are MeSH, DMS, CS₂, DMDS, DMTS and OCS (Cheng et al., 2005; Cook and Hoy, 2007). Langenhove et al. (1985) found a wide range of sulfur compounds in wastewater samples: MeSH, 2-propanethiol, t-butanethiol, DMS, methyl 2-propyl sulfide, ethyl propenyl sulfide, diethyl sulfide, methyl propyl sulfide, ethyl propyl sulfide, methyl pentyl sulfide, methyl phenyl sulfide, methyl benzyl sulfide, DMDS, methyl ethyl disulfide, methyl propyl disulfide, DMTS, thiophene, 2-methylthiophene, 3-methylthiophene, 2-ethylthiophene, 2,5-dimethylthiophene, 3-ethylthiophene, 2-propylthiophene, 2-methylthiothiophene, 3-methylthiothiophene and 2-ethylthiothiophene. Among these, DMS was found to be dominant in most cases (Cheng et al., 2005; Cook and Hoy, 2007). Its concentration may reach 1260 µg L⁻¹, followed by MeSH, OCS and CS₂ (Cheng et al., 2005; Devai and DeLaune, 1999). Studies of the volatile organic sulfur emissions that cause urban odours suggest these include MeSH, EtSH, 2-propanethiol, 2-butanethiol, DMS, DMDS, thiophene, diphenyl sulfide and H₂S. These were studied in the air at selected urban sites where an odour nuisance was recognised (e.g. Gerards, 1994; Mansfield et al., 1992; Muezzinoglu, 2003; Smet and van Langenhove, 1998). Volatile organic sulfides that cause odour were studied at Philadelphia's Northeast Water Pollution Control Plant, showing that DMS dominated the VOCS pool whenever VOSC concentration rose above the background level (<50 mg L⁻¹). MeSH was generally less than 10% of VOSCs and DMDS represented about 1%, although CS₂ was not detected (Cheng et al., 2005). The biological reduction of dimethylsulfoxide, a common solvent, in sewage can be a source of DMS during waste treatment (Glindemann et al., 2006).

Liquid phase measurements at a wastewater treatment plant in Baton Rouge, Louisiana (Devai and DeLaune, 1999) found CS₂, among other sulfides, but at highly variable concentrations (0.006 to 5.70 µg S L⁻¹). The concentrations of CS₂, MeSH, DMS and DMDS in wastewater from Hwang et al. (1995) were combined with measurements from Sheng et al. (2008) to get a sense of typical aqueous concentrations, which we set at 0.09, 2.7, 170, 14.7 and 70 µg S L⁻¹ for OCS, CS₂, MeSH, DMS and DMDS respectively.

Taking as typical 200 L as the per capita water use around the world (UNDP, 2006), with a factor of 0.8 for the sewage producing fraction, global sewage volumes could be estimated at 4.1x10¹⁴ L a⁻¹ (population of 7.03 billion). If an additional 10% is released as industrial wastewater, the estimated total wastewater is 4.51x10¹⁴ L a⁻¹. The emissions of OCS, CS₂,

MeSH, DMS and DMDS can be estimated as 0.022, 1.03, 51.1, 3.42 and 21.4 Gg S a⁻¹. This gives emission fluxes that appear rather small in comparison with the pulp and paper industries, for example. However, the importance of DMDS in emissions from sewage continues to emerge in more recent papers (Holub et al., 2014).

3.10 Aluminium industry

Aluminium production is an important source of OCS, with an emission factor of some 2.1 g S kg⁻¹ of aluminium produced (Harnisch et al., 1995), suggesting a significant contribution to global release (Blake et al., 2004). However, recent studies suggest that the early emission factors were often too high, so here we used the work of Campbell et al. (2015) and set global emissions at 30±7 Gg S a⁻¹. The estimate for CS₂ of 4 Gg S a⁻¹ from Kjellstrom (1998) is used here.

Tetra-, penta- and hexacyclic aromatic sulfur heterocyclic compounds (thia-arenes) were found in aluminium melting facilities where indoor air samples contained 53 components as thia-arenes, with the total concentration in air found to be 12 µg m⁻³ (Becker et al., 1998). As thia-arenes account for 2.5-10% (0.45-3.1% for PCDTs) of PAH emission (Becker et al., 1999) it is possible to estimate the global emission, because 5.6 g PAH is released per tonne of aluminium produced (Näf et al., 1994). Thus the global thia-arenes, where some 58% is benzo[b]naphthothiophenes (BNT) can be calculated with emission up to 0.023 and 0.013 Gg a⁻¹ respectively (as weight of compound). If thia-arenes have an average MW of 234 (i.e. BNT), then upper estimates of the emissions of thia-arenes and BNT become 0.003 and 0.0018 Gg S a⁻¹. Chlorinated sulfur compounds are also found, typically tri-, tetra- and pentachloro DBTs (Aittola et al., 1996; Sinkkonen et al., 1994), particularly at aluminium reclamation plants. If we assume a molecular weight of 322 and emissions relative to PAHs estimated by Becker et al. (1999), we get upper estimates of 0.0016 Gg S a⁻¹.

3.11 Coal combustion and use

Coal typically has a high sulfur content and it has long been of concern as a fuel because of sulfur emissions. The odour of coal smoke is very characteristic and related to its sulfur content: “Burning or burnt, it has this harsh chemical/earthy smell...” (TOD, 2007). Coal emits OCS at 2.6 × 10⁻³ g S kg⁻¹ coal burnt at a power plant (Chin and Davis, 1993; Khalil and Rasmussen, 1984, as cited in Blake et al., 2004) and 2.7 × 10⁻³ g S kg⁻¹ coal burnt in a coal stove (Mu et al., 2002). Estimates of emission rate for eight different types of coal combustors yields a CS₂ emission factor of 5.5 × 10⁻⁵ g S kg⁻¹ coal burnt (Blake et al., 2004). Coal yields OCS and CS₂ at 60 (Campbell et al., 2015) and 0.33 Gg S a⁻¹ respectively, and assuming for CS₂ that the global coal use is about 7.2 Pg a⁻¹ (WCA, 2010a). However, the

plumes from Chinese power plants in Shanghai seem to have as much sulfur appearing as CS₂ as is present as SO₂ (Yu et al., 2004), so if this were true more widely than coal burning emissions of CS₂ could be underestimated.

About 15% of coal is diverted to make coke, mostly for the steel industry, which uses about 70% of the coke (WCA, 2010b), with the rest being taken here as used in gasification, thus giving rise to only small sulfide emissions to the atmosphere. Coke production gives emission factors that are rather larger than for coal combustion i.e.: OCS 0.01208, CS₂ 0.01907, thiophenes 0.019 and BT 0.0043 g S kg⁻¹. This leads to global emissions of OCS, CS₂, thiophenes and BT calculated at 9, 14, 14 and 3 Gg S a⁻¹ respectively. Significant releases occur as thiophenes: thiophene, alkylated thiophenes and alkylated BTs. BT is often, though not always, the major sulfur containing aromatic compound (Thuss et al., 2000).

Polish bituminous coal (Wujak coal; total sulfur at 0.56%) appears to emit much more than wood with total amounts of the compounds as: BT 0.44 mg S kg⁻¹, methylbenzothiophene 0.31 mg S kg⁻¹, dimethylbenzothiophene 0.16 mg S kg⁻¹, methyldibenzothiophene 0.50 mg S kg⁻¹, dibenzothiophene 0.43 mg S kg⁻¹ and dimethyldibenzothiophene 0.25 mg S kg⁻¹ with total thia-arenes at 12.62 mg kg⁻¹

Global PAH emissions from domestic coal combustion are estimated to be 19.6 Gg a⁻¹ (Zhang and Tao, 2009). If we assume that thia-arenes typically amount to 10% of the mass of PAH, it suggests that about 2 Gg a⁻¹ appears as sulfur heterocycles, so taking the molecular weight of DBT as representative, it would make the emissions about 0.3 Gg S a⁻¹. It is probable that the single ringed BTs have similar emissions on the basis of the comparative amounts found from Polish coal. Emissions of thiophene, BT, BTs and DBTs are estimated as 0.32, 0.07, 0.09 and 0.2 Gg S a⁻¹. Thiophene was estimated by assuming the emission ratio for coke, and coal is the same as for the BT's. In addition, as the emission of naphtho[2,1-b]thiophene was about 7% of the total thia-arenes emitted (Thuss et al., 2000), the global naphtho[2,1-b]thiophene emission would be about 0.02 Gg S a⁻¹.

3.12 Bitumen production and use

The fumes from asphalt and bitumen production and use release thia-arenes at a higher concentration than the average PAH of similar molecular weight, whereas in coal-tar fumes thia-arenes have a much lower concentration than the corresponding PAHs.

Benzo[b]thiophenes, DBT, benzo[b]naphtha[2.1-d]thiophenes derive from indoor mastic laying. Thia-arene emission rates in the fine aerosol emissions from hot roofing tar pot fumes are: 2303 µg S g⁻¹ (including dimethyldibenzothiophenes: 175 (1170); dimethylbenzo[b]thiophenes: 41 (245); DBT: 45 (45); methyldibenzothiophenes: 101 (630) µg S g⁻¹ (µg g⁻¹); compared with 3370 µg g⁻¹ for PAHs (Rogge et al., 1997). About 15% of bituminous material is consumed for roofing purposes. Most bitumen (85%) is used in road

making where the total asphalt production was 1.6 Pg in 2007. Asphalt paving is about 5% bitumen. Assuming current use of asphalt pavement amounts to 2 Pg a⁻¹ then some 100 Tg of bitumen would be required for roads along with an additional amount (18 Tg) each year in roofing (EAPA, 2011). This gives a global asphalt/bitumen annual production rate of 118 Tg, little different from the estimate of 107 Tg taken from Freedonia (2006) places the annual emission of these thia-arenes at 7 Gg S a⁻¹. Thiophene and thia-arenes represent an important part of the nonmethane volatile organic compound (NMVOC) emitted from hot stored bitumen. Deygout (2011) found that thiophenes and disulfides ranged between 7 and 13.5 % of the NMVOC emission from hot stored bitumen. Recent observations (Boczkaj et al, 2014) would suggest a substantial release of CS₂. Estimated global emissions are given in Table 1, and list bitumen as potentially the largest source of thia-arenes.

3.13 Vehicles and ships

Fried (1992) measured OCS/CO mass ratios in automobile exhausts as 5.8×10^{-6} for gasoline vehicles, and a significantly higher value of 1.99×10^{-4} for diesel vehicles, which suggests emissions in the range of 0.8-8 Gg S a⁻¹. This estimate has been slightly adjusted to 2 (0.5-4) Gg S a⁻¹ by Chin and Davis (1993) and 6 ± 4 Gg S a⁻¹ by Watts (2000). No newer estimates are available and considering that an increase in vehicle numbers is counteracted by a decrease in fuel sulfur content, 6 Gg S a⁻¹ was used here; while 0.3 Gg S a⁻¹ for CS₂ from Chin and Davis (1993) was adopted. There are no observations of reduction of sulfur compounds to organosulfides (such as thiophenes) or OCS or CS₂ in catalytic converters on mobile vehicles. Removal of sulfides from feedstocks has seen renewed interest lately. Processes for removing H₂S are not normally effective in removing OCS, and these may even produce OCS through a reaction of H₂S with CO₂ (Pessayre et al., 2007; Rhodes et al., 2000). The automotive three-way catalytic converter lowers emissions of VOC and NO_x, but was found to preferentially produce H₂S and OCS over SO₂ (Watts and Roberts, 1999). The production of sulfides is apparent when an engine runs rich.

Diesel vehicles can be a source of substituted aromatic compounds, although increasingly regulations insist on a low sulfur content for fuels adopted. Emission factors are available for gasoline and diesel vehicles for BNT 0.08 ± 0.10 μg S km⁻¹ and 0.94 ± 0.96 μg S km⁻¹, respectively (Staehelin et al., 1998). Emissions of DBT from light duty vehicles were: <0.017 μg S km⁻¹ for gasoline with three way catalytic converters; 0.17 μg S km⁻¹ for diesel with oxidizing catalytic converters and for heavy-duty trucks and $0.52-1.74$ μg S km⁻¹ for diesel without catalytic converters (Bostrom et al., 2002). By comparison the mean emission factors for benzo[a]pyrene were 2.92 and 2.47 μg km⁻¹ for 95-LFG and PLG powered engines (Mi et al., 1996). Larger thiophene molecules are found on diesel particles, with small amounts of BNT present in diesel vehicle exhaust at a few ng S m⁻³, compared with

tens of thousands for the naphthalenes (Zielinska et al., 2004).

The PAH mass fraction determined in fine particulate exhaust emitted from catalyst-equipped automobiles is about 0.5% compared with 0.1% for heavy duty diesel trucks. Some heavier thia-arenes (e.g. BNT) are not present in typical diesel fuels, but they are found in diesel particulate matter, with total concentrations of 9.9 and 2.1 $\mu\text{g S g}^{-1}$ for DBTs and BNTs, respectively (Liang et al., 2006). These emission factors lead to estimates for their annual (year 2000) emissions at 7.87 and 4.06 t S of DBTs and BNTs respectively from diesel vehicles in China alone (Saikawa et al., 2011). Using the global value for vehicle kilometres driven as 3.86×10^{12} km at 2005 (Melaina and Webster, 2011), and assuming half comes from diesel vehicles we can estimate the global vehicle emissions as DBTs 47 t S a^{-1} and BNTs 24 t S a^{-1} .

Higher sulfur content is found in heavy fuel oil (near 2% S) used in ship diesel engines than in automotive vehicles, which means organosulfide emissions are likely to be higher e.g. benzothiazole is on the list of ship particulate pollutants (Moldanová et al., 2009; Popovicheva et al., 2009). There is much pressure on the shipping industry to use low sulfur fuels in future.

The OCS and CS₂ fluxes from land transport are set at 6 and 0.3 Gg S a^{-1} . The equivalent emissions are not available from shipping, but we have taken these emissions to vary with total sulfur (as SO₂). The total sulfur from land transport is 0.96-1.83 Tg S a^{-1} (Uherek et al., 2010) and shipping 5.5 Tg S a^{-1} (Eyring et al., 2010). Assuming a ratio of 1:5 gives shipping emissions for OCS and CS₂ as 30 and 1.5 Gg S a^{-1} . As calculated above, the global value for diesel vehicle kilometres is 1.93×10^{12} km a^{-1} for 2005 (Melaina and Webster, 2011), and assuming fuel economy for commercial low sulfur diesel (0.04% S) was 0.4 L km^{-1} (Tente et al., 2011; Wang et al., 2000), 0.31 Tg S a^{-1} has been estimated for the total vehicle sulfur emission, compared with 6.7 Tg S a^{-1} from international shipping. The annual global emissions of DBTs and BNT could then be estimated as 1.0 and 0.5 Gg S a^{-1} , but may reduce as ships begin to use higher quality fuels.

3.14 Tyres

More than two decades ago Pos and Berresheim (1993) suggested that global OCS emissions from automobile tyre wear could be as much as 40 (36-44) Gg S a^{-1} and could dominate urban sources, as well as be a major global source. This would be much larger than emissions from combustion. Unfortunately there appears to have been little further evaluation of this potentially large source. The flux determined in Pos and Berresheim's (1993) experiments showed that tyre fines on the roadside had lost 57% of the sulfur as CS₂ and the rest as OCS. Here the emissions were then scaled up assuming that vehicles deposited 1.17 kg a^{-1} rubber each year (following Pos and Berresheim, 1993) and that the 1.6% sulfur in the

rubber (Susa and Haydary, 2013) was ultimately released as these two sulfides. Taking 1.18 billion vehicles to be currently in use (OICA, 2013) suggests global emissions of 9.5 Gg S a^{-1} and 12.6 Gg S a^{-1} as OCS and CS_2 . This calculation takes a lower value of the sulfur content of tyres than Pos and Berresheim's (1993) 2%, in line with a wider range of polymers in contemporary tyres. However, their approach also assumed all vehicles had identical tyre wear, so here we have adopted an approach based on tyre use. It assumes that 10% of the tyre is would be deposited on the road surface as fines, an estimate based on retreading, which starts with a tyre that contains 90% of the original material. Taking the predicted annual global production for 2015 to be 1.7 billion tyres (GIA, 2010) of average weight of 10 kg, suggests a release of the two sulfides at 11.7 Gg S a^{-1} and 15.5 Gg S a^{-1} as OCS and CS_2 . This is smaller than the earlier estimates of Pos and Berresheim (1993), but in reasonable agreement with our values determined from their vehicle-use method. Here we will adopt 11.7 Gg S a^{-1} and 15.5 Gg S a^{-1} as the global emissions OCS and CS_2 , but note that tyre use may continue to grow although possibly counterbalanced by lower sulfur content in the materials used.

Runoff waters from city streets contain oil, tyre fragments and other pollutants. Tyre wear also deposit a range of sulfur heterocyclic compounds. Benzothiazoles and its derivatives are used as accelerators in vulcanization and are loosely bound in the rubber matrix. Because of this, benzisothiazoles predominate in urban run-off, while thiophene was found after tyres were burnt. Benzothiophenes derivatives appear as 3-methyl-1,2-benzisothiazole, 2(3H)-benzothiazolone, 2-mercaptobenzothiazole, 2,2-dithiobisbenzothiazole, 2-(methylthio)benzothiazole and 2-(4-morpholinodithio)benzothiazole etc. (Sarasa et al., 2006; Zeng et al., 2004).

Scrap tyres represent slightly more than 12% of all solid waste and raise special disposal and reuse problems because of their size, shape, and physicochemical nature. Globally about a billion tyres are scrapped each year (Kyari et al., 2005). Tyre wastes contain a high amount of energy, so energy recovery has often been a strategy; for example, tyres are more energetic than bituminous coal, a classical energy source (Conesa et al., 2004). However, tyres contain much sulfur, and in the US some 42% of these scrap tyres were used for fuel (Karell and Blumenthal, 2001). The open burning of tyres gives a wide range of sulfur compounds: thiophene, methyl thiophenes, benzothiophenes and their methyl/dimethyl/trimethyl derivatives and benzo[b]naphtho-2,3-d thiophene and methyl derivatives (Chen et al., 2007; Fullana et al., 2000). Scrap tyre combustion has emission factors of: OCS 80 mg S kg^{-1} , and MeSH 53 mg S kg^{-1} (Hu et al, 2014), with thiophene 23 mg S kg^{-1} , BT 5.5- 10 mg S kg^{-1} , methylthiophene 2 mg S kg^{-1} , and benzisothiazole 40 mg S kg^{-1} (Reisman, 1997). There are no doubt emissions of CS_2 and DBT, but the factors were not available. About a billion tyres (10 Tg) are likely to be scrapped each year, so assuming globally that 40% are burnt, as is typical in the US, the annual emissions for OCS, MeSH, thiophene, methylthiophene, BT and

benzothiazole would amount to: 0.32, 0.212, 0.09, 0.0075, 0.025 and 0.16 Gg S a⁻¹ as presented in Table 1.

3.15 Landfill waste

Landfills provide a reducing environment and can produce a wide range of sulfides. The average emission rates from landfills were set at 0.116 g OCS t⁻¹ and 0.178 g CS₂ t⁻¹ by Blake et al. (2004). Muezzinoglu (2003) determined emission fluxes from sources in the city of Izmir, Turkey in summer of 2001 from a creek as: DMS 0.73-3.67 μg S m⁻² s⁻¹; 2-propanethiol nd-1.26 μg S m⁻² s⁻¹; 2-butanethiol nd-0.53 μg S m⁻² s⁻¹; thiophene 0.002-0.02 μg S m⁻² s⁻¹; diphenyl sulfide nd-0.01 μg S m⁻² s⁻¹ (nd: not detectable), while from wastewater treatment these were: DMS 1.78-3.67 μg S m⁻² s⁻¹; 2-propanethiol nd-0.3 μg S m⁻² s⁻¹; 2-butanethiol nd; thiophene 0.005 μg S m⁻² s⁻¹; diphenyl sulfide nd. The concentrations of a range of compounds in soil gas from ten Florida construction and demolition landfills were measured as up to: OCS 79300, MeSH 213200, DMS 2730, EtSH 260, CS₂ 236600, isopropanethiol 3640, butanethiol 260, thiophene 130 and 2- and 3-methylthiophene, 520 μg S m⁻³ (USDHHS, 2007). At Penrose, California MeSH, EtSH, DMS and DMDS were measured at 6.5, 6.5, 10.4 and 0.052 mg S m⁻³ and at Anoka, Minnesota MeSH and DMS were measured at 2.7 and 6.4 mg S m⁻³ (Sanderson, 1998). Landfill emission fluxes of MeSH, DMS, CS₂ and DMDS from a young facility were estimated to be 579, 401, 281 and 245 g S km⁻² a⁻¹, respectively, and 0.041, 0.322, 0.973 and 0.362 g S km⁻² a⁻¹, respectively for an old facility (Kim, 2006).

By using the emission factors OCS and CS₂ (0.062 and 0.15 g S per Mg of waste) suggested by Blake et al. (2004) and buried landfill at 0.5 kg day⁻¹ solid waste as a global per capita average (Doorn and Barlaz, 1995) yields a total burial of 1.3 Pg a⁻¹. This can be combined with the OCS and CS₂ emission factors to give 0.079 Gg S a⁻¹ and 0.19 Gg S a⁻¹. Although the observations in the preceding paragraph give a sense of the relative amount of gases, they cannot be directly converted to fluxes. Here we have used the widely varying values to set the ratio of the sulfides to OCS to estimate OCS:MeSH:EtSH:DMS:DMDS:thiophene as 1: 2.3:2.1:2.1:3.3:0.1:0.005 with respect to sulfur. The ratio also allows a rough estimate of the global emissions for MeSH, EtSH, DMS, DMDS and thiophene as 0.17, 0.17, 0.26, 0.008 and 0.0004 Gg S a⁻¹, which are given along with all the fluxes in Table 1.

3.16 Waste incineration

Waste incineration produces a range of compounds, but many waste materials such as tyres, wood etc. are covered under other headings. However, the concern over PAHs and

halogenated compounds in furnaces, particularly the polychlorodibenzodioxins and furan (PCDD/Fs) has created an interest in the associated thia-arenes particularly the polychlorodibenzothiophenes (PCDTs). Total emissions of PAHs from municipal waste are about 800 mg t^{-1} , and assuming about 2% is as thia-arenes (with MW 184), taking global waste production of 4.37 Pg a^{-1} (WB, 1999) and assuming half is burnt gives $0.004 \text{ Gg S a}^{-1}$.

3.17 Brickmaking

Bricks are produced globally at some 1.4 Pg a^{-1} , mostly using very primitive brick kiln technology, with less than 10% under modern production methods. It is a highly polluting industry (Baum, 2010) where a range of sulfides are produced with CS_2 up to 0.02 g S t^{-1} (EPA, 1997). Assuming this high value applies to total brick production, the annual emissions from this source would amount to 0.03 Gg S a^{-1} . In some cases tyres are used as fuel, but these emissions are taken to be captured in a previous section.

3.18 Atmospheric oxidation

Oxidation processes in the atmosphere make an important contribution to OCS via the homogeneous oxidation of CS_2 , and DMS (Watts, 2000). Most of this secondary OCS derives from the oxidation of atmospheric CS_2 which yields 0.83 parts OCS and 1.17 SO_2 (Stickel et al., 1993). The oxidation is relatively slow which leads to a CS_2 residence time of about six days, so in the case of marine CS_2 , 90% of the marine (i.e. natural CS_2) are taken here to be oxidized in the atmosphere (i.e. only 10% deposits), because oceans so predominate the Earth's surface. In the case of terrestrial CS_2 some 50% will be oxidized (the rest deposited to the surface), which aligns with the estimates of Watts (2000). As the anthropogenic emission of CS_2 amount to 747 Gg S a^{-1} the flux of OCS that derives from its oxidation is 162 Gg S a^{-1} . This flux arise largely from terrestrial emissions although has to omit that which arises from marshes, vegetation and volcanoes ($\sim 36 \text{ Gg S a}^{-1}$). The flux of OCS from DMS oxidation is difficult to establish because the yield is sensitive to the presence of NO, but here we have followed Patroescu et al. (1999) and set it to 0.002. Anthropogenic sources of DMS are estimated at about 2120 Gg S a^{-1} , which yields some 4.6 Gg S a^{-1} OCS through oxidation, which neglects the oxidative flux from marshes and vegetation ($\sim 7 \text{ Gg S a}^{-1}$).

There is a small oxidative flux from rainwater where the photochemical production of OCS has been estimated at $4.84 \text{ pg S L}^{-1} \text{ s}^{-1}$ (Mu et al., 2004). This production arises from the oxidation of soluble organosulfides, and has been measured over land. Assuming 10^{17} L of water falls on land annually (Wu, 2008), with peak daytime production of OCS yielding about 26.7 ng S L^{-1} (Mu et al., 2004), the upper limit to global photochemical production of OCS in precipitation could be estimated as 2.7 Gg S a^{-1} . Although this is based on the solitary

observations of Mu et al. (2004) it suggests that this source is likely to be much smaller than the 130 Gg S a⁻¹ estimated by Watts (2000). We have assumed only continental rain (e.g. Matsumoto and Uematsu, 2005) will have precursors, but it remains unclear the extent to which this small flux derives from anthropogenic or natural sources.

4. Sulfide emission fluxes

The anthropogenic fluxes of key sulfides: OCS, CS₂, MeSH, DMS, DMDS, and thiophenes are arranged in sub-sections along with a brief description of the natural sources, so that the global fluxes of these compounds can be presented in Fig. 1 to give a sense of their comparative magnitude. The magnitude of the natural fluxes used here are summarised in the lower part of Table 1 and details of the origin of these values given in the sections below.

4.1 OCS

OCS is the most abundant reduced sulfur gas in the atmosphere. This is a product of its long residence time of 5.7 a (Ulshöfer and Andreae, 1997). The anthropogenic flux of OCS including the relevant oxidative sources and pulp and paper industry, biofuel combustion, coal combustion, biomass burning etc sums to 598 Gg S a⁻¹ as presented in Table 1. These can be compared with natural sources of OCS, mainly composed of saline and ocean water, volcanoes, as well as atmospheric oxidation of naturally derived CS₂ and DMS.

Photochemical and non-photochemical production of OCS from marine organic matter has been estimated recently as 800 Gg S a⁻¹ (Launois et al., 2015a). Whelan et al. (2013) made a number of observations of OCS from a coastal salt marsh in the Gulf of Mexico. Assuming these representative of all swamps and marshes globally, the OCS fluxes would amount to 87 Gg S a⁻¹ globally. Volcanoes typically make a rather small contribution to the total flux (11 Gg S a⁻¹) of OCS to the atmosphere (Belviso et al., 1986). As a result, the total anthropogenic emission (595 Gg S a⁻¹) is just over half the size of the natural flux of 1056 Gg S a⁻¹ (Fig. 1 and Table 1).

Oxidation of CS₂ and DMS has been regarded as an important source of OCS. In the present work we take CS₂ oxidation to convert 0.415 of the sulfur to OCS (Stickel et al., 1993). This suggests that 58 Gg S a⁻¹ of OCS arises from the oxidation of marine CS₂ and some 36 Gg S a⁻¹ from oxidation of naturally produced CS₂ over land, which includes 18 Gg S a⁻¹ derived from marshes and 14.5 Gg S a⁻¹ from vegetation. The flux of OCS from DMS oxidation using the yield of 0.002 adopted in section 3.18 suggests some 56 Gg S a⁻¹ derived from marine DMS and almost 7 Gg S a⁻¹ from vegetation. In total we calculate that the oxidation of all

organosulfides in the atmosphere yields 317 Gg S a^{-1} (i.e. 249 Gg S a^{-1} from CS_2 and 68 Gg S a^{-1} from DMS).

4.2 CS_2

CS_2 emissions are important because the disulfide can be oxidized to OCS. The total anthropogenic CS_2 emission including rayon/cellulosics manufacture, pigment industry, pulp and paper industry, etc. is estimated to be 746 Gg S a^{-1} (Table 1). The major natural emission sources include saline and ocean water, vegetation and soils as well as volcanoes. Marine systems especially oceans have long been seen as a major source, with the total flux of 156 Gg S a^{-1} suggested by Kettle et al. (2001). Devai and Delaune (1995) imply a rough equivalence between OCS, 87 Gg S a^{-1} and CS_2 from marshes, so we have set them as equal. The global flux from vegetation is not at all secure (Wickenhäuser et al., 2005) as measurements of the flux are difficult because source strengths of vegetation are low. Furthermore it is hard to convert the limited data to global budgets, particularly as the sulfur loading in soil can influence fluxes. The vegetation and volcanic CS_2 emission fluxes are estimated as 70 (Watts, 2000) and 17 Gg S a^{-1} (Chin and Davis, 1993), respectively. This makes the size of natural emission less than half of anthropogenic estimate (Fig. 1 and Table 1).

4.3 MeSH

The global MeSH anthropogenic emission was estimated to be 2119 Gg S a^{-1} including pulp and paper industry, manure, rayon/cellulosics manufacture, wastewater, etc. (Table 1). The natural emissions are likely to be dominated by ocean emission of 4738 Gg S a^{-1} (Kettle et al. 2001). The other major contribution to natural emission is vegetation, which is estimated as 1735 Gg S a^{-1} by comparing it with DMS and taking it as half of the DMS in emission strength (Kesselmeier, 2005) in the absence of more specific measurements. This makes the natural emission about three times of larger in size than that from anthropogenic sources.

4.4 DMS

The global anthropogenic DMS emission including pulp and paper industry, manure, rayon/cellulosics manufacture, etc. is estimated to be 2197 Gg S a^{-1} . DMS makes a dominant contribution to the global sulfur budget, with much of the flux to the atmosphere arising from marine sources, whose emission was recently estimated as $28\,100$ by Lana et al. (2011). Adding that from vegetation of 3470 (Watts, 2000) and that from salt marshes which is estimated by setting it equal to that of OCS, according to the work of Devai and Delaune (1995), to be 87 Gg S a^{-1} , the natural emission flux is estimated to be $31\,657 \text{ Gg S a}^{-1}$. This

makes natural emission overwhelmingly dominate the anthropogenic (Fig. 1 and Table 1).

4.5 DMDS

The global anthropogenic dimethyl polysulfide emission (Gg S a^{-1}) is estimated to be 1103 Gg S a^{-1} including manure, pulp and paper industry, biomass burning etc. This magnitude can be compared to its natural emissions, which were estimated to be 1080 Gg S a^{-1} . This natural flux includes 213 Gg S a^{-1} from oceans and marshes and 868 Gg S a^{-1} from vegetation, obtained by relating emissions to DMS using Tanzer and Heumann (1992) for oceans and marshes and Kesselmeier (2005) for emissions from vegetation. The total dimethyl polysulfide emission (2184 Gg S a^{-1}) is substantial and represents a fifteenth the magnitude of large sulfur emissions that arise as DMS. This polysulfide flux includes some 393 Gg S a^{-1} originating as DMTS, which might make a surprisingly important contribution to the dimethyl polysulfides (Table 1 and Fig. 1).

4.6 Thiophenes

Thiophene and the aromatic forms such as the benzo and dibenzothiophene (BT and DBT) have few natural sources such as the miniscule releases of thiophene from volcanoes (e.g. Tassi et al., 2010, Schwandner et al., 2013). The global emission of all thiophenes was estimated to be 42.7 Gg S a^{-1} , which can be broken down to 31.5, 3.35 and 7.83 Gg S a^{-1} for thiophene, BT (including thia-arenes and benzisothiazole) and DBT (including BNTs, naphthothiophenes and various substituted DBTs) respectively (Table 1).

5. Sulfide removal fluxes

In this section, rather than attempt to balance the cycle the aim is to establish the likely proportion that might be attributable to various removal pathways as shown in Fig. 2

5.1 OCS

The six-year lifetime (Ulshöfer and Andreae, 1997) means that OCS has relatively high atmospheric concentrations so can be transferred to the stratosphere. OCS can have direct warming effect as a greenhouse gas, especially in the troposphere, but when transferred to the stratosphere is a source of the radiatively important sulfate aerosol (Brühl et al., 2012; Crutzen, 1976; Kremser et al., 2016; Turco et al., 1980). Atmospheric concentrations measured over oceans ranged from 395-655 ppt (Johnson and Bates, 1993; Ulshöfer and Andreae, 1997; von Hobe et al., 1999; Montzka et al., 2007). The long lifetimes also mean

that the trace gas is relatively well mixed in the atmosphere, but there are concentration differences especially in plumes from the industrialised continents (e.g. Blake et al., 2004). Net fluxes to the stratosphere have been estimated in the range of 34–66 Gg S a⁻¹ with a global stratospheric lifetime of 64 ± 21 a (Barkley et al., 2008; Sheng et al., 2015). Coffey and Hannigan (2010) examined conflicting claims about increases in the sulfate loading of the stratosphere from increasing OCS. However, their analysis of the temporal trend of stratospheric OCS between 1978 and 2005 did not suggest that an increase in background levels of sulfate aerosol could arise from an increased OCS source (Coffey and Hannigan, 2010). Sheng et al. (2015) have modelled the global atmospheric sulfur budget under volcanically quiescent conditions, including stratospheric processes and suggest that 30–40 Gg S a⁻¹ in net is transferred across the tropopause, which is in line with the estimate of 35 Gg S a⁻¹ (Fig. 2) made by Brühl et al. (2012). Recently there has been experimental work showing that the photo-oxidation in the atmosphere may be underestimated because oxidation can be promoted by the presence of SiO₂ and Al₂O₃ aerosols (Wu et al., 2005) and might lower the proportion transferred to the stratosphere.

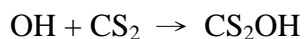
The difficulties in establishing the extent of removal via dry deposition is especially problematic for OCS, as the terrestrial surface can be both a source and a sink. Deposition of OCS to soils and especially vegetation (Campbell et al., 2008) is seen as increasingly important (Sandoval-Soto et al., 2005; Montzka et al., 2007; Launois et al., 2015b) such that currently more than 90% of the tropospheric OCS is regarded to deposit in terrestrial ecosystems (Berry et al., 2013). This is in reasonable agreement with Watts (2000), but larger than the 80% of Weisenstein et al. (1997). As sulfur is a key plant nutrient, the uptake of OCS by soils might be a path for sulfur supplement to vegetation, especially in remote areas (Liu et al., 2007; Yi et al., 2010). OCS can be oxidized in soils (e.g. Cox et al., 2013) and assimilated by plants.

5.2 CS₂

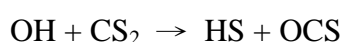
CS₂ has a much shorter residence time in the atmosphere than OCS with Bandy et al. (1981) setting it around 10 days, while Hynes et al. (1986) calculate oxidation via reaction with the OH radical yields a residence time of about 6 days. More recently a CS₂ lifetime 12 days has been suggested (Colman and Trogler 1997), which is in reasonable agreement given the variability of atmospheric OH concentrations. CS₂ can be oxidized in soils (e.g. Cox et al., 2013), which might be important where close to sources. The relatively short lifetime means that CS₂ shows a greater variability in concentration than OCS. Fifty two free tropospheric measurements of CS₂ over a latitude range 45°N to 45°S gave a mean of 5.7 ± 1.9 ppt, with the amount of CS₂ in the Northern and Southern Hemispheres statistically similar (Tucker et al., 1985). Johnson and Bates (1993) measured CS₂ concentrations from below detection limit

to 29 ppt over the North Atlantic. Almost all CS₂ measurements over the Tropical Atlantic were below the detection limit. CS₂ was measured in the northwestern Pacific Ocean, eastern Indian Ocean and Southern Ocean from not detected to 13 ppt (Inomata et al., 2006).

The reaction of CS₂ with OH is an important sink and also leads to the formation of OCS and SO₂ (Lovejoy et al., 1990; Seinfeld and Pandis, 2006)



The CS₂OH adduct reacts with O₂ to give a range of products, but an important pathway which gives OCS is:



Some 249 Gg S a⁻¹ is oxidized to OCS and 351 to SO₂, which would make the overall global loss to oxic soils 476 Gg S a⁻¹ (Fig. 2).

5.3 MeSH

Attack by OH and NO₃ are major routes for the oxidation of MeSH in the atmosphere. The measured rate constant for OH reaction with MeSH is $33 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (Butkovskaya and Setser, 1998), suggesting a lifetime for MeSH of just a few hours. Wilson and Hirst (1996) also note that MeSH oxidation is two to three times faster than that of DMS, explaining the comparatively low concentrations. Over the Amazon Basin, the concentration of MeSH (Andreae and Andreae, 1988) in the atmospheric boundary layer averages 0.9 ng S m^{-3} . However, close to industrial sources such as the large paper and pulp mills near Lake Baikal, Toda et al. (2010) found it to be as much as 10 ppb at times. At the edge of an industrial area in the city of Ansan, Korea the median MeSH concentration during long term monitoring through the year was 0.012 ppb (Susaya et al., 2011), much lower than the industrial site.

5.4 DMS

DMS has a lifetime of about a day (Chin et al., 1996), although Berresheim (1987) had estimated it to be somewhat longer in the Antarctic marine atmosphere; about 2–3 days during clear weather and 6–7 days during overcast conditions. Osthoff et al. (2009) examined the regional variation of DMS oxidation and showed that the average DMS lifetime with respect to oxidation by OH at noon was $13.5 \pm 3.4 \text{ h}$ (using a rate constant $4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$), while at night, DMS lifetimes with respect to NO₃ oxidation varied by sampling region from 11 min to 28 h. Their work suggests that oxidation during the day may occur via halogen

species, but the extent remains undetermined. These short residence times mean relatively low concentrations compared to a long lived gas, even with smaller source strengths, such as OCS. Over the Amazon Basin, the average concentration of DMS in the mixed layer was 11.8 ng S m^{-3} (Andreae and Andreae, 1988). Johnson and Bates (1993) measured DMS concentrations in the lower marine boundary layer, below 600 m altitude in the range from below detection limit to 150 ppt during flights over the North Atlantic, and from 9 to 104 ppt over the Tropical Atlantic. It was measured over the northwestern Pacific Ocean, eastern Indian Ocean, and Southern Ocean from below detection limit to 755 ppt (Inomata et al., 2006). In urban, agricultural and industrial environments concentrations in air can be much higher with concentrations in the range 0.02 – 6.4 ppb (Filipy et al., 2006; Susaya et al., 2011; Pal et al., 2009).

It has long been recognised that DMS is oxidized to SO_2 and additionally methanesulfonic acid, MSA (Berresheim, 1987). Oxidation of DMS at lower temperatures can lead to increasing amounts of organic products, although these are always smaller than SO_2 ; methylsulfinic acid being the largest along with smaller quantities of DMSO and MSA (Karl et al., 2007). The transformation of DMS leads to a wider range of organic and inorganic sulfur species, mainly SO_4^{2-} , SO_2 , OCS, methanesulfonic acid and MSA (Hatakeyama et al., 1982; Panter and Penzhorn, 1980; Pham et al., 1995; Faloon, 2009), with dimethylsulfone and dimethylsulfoxide as potential products (Harvey and Lang, 1986; Zhu et al., 2003). The small fraction of DMS converted to MSA is extremely soluble in the aerosol phase (Clegg and Brimblecombe, 1985). There are also examples of the transfer of partial oxidation products such as dimethylsulfone in rain water (Kiene and Gerard, 1994; Ridgeway Jr et al., 1992; Sciare et al., 1998).

5.5 DMDS

The removal of DMDS from the atmosphere is mainly through reaction with OH, likely the driver of oxidation, giving it lifetimes in the range 0.3-3.0 h, with loss by photodissociation less important (Hearn et al., 1990). This rapid transformation, a fission of the S-S bond leads to inorganic sulfur that would become associated with particles or rain. Short lifetimes mean that the DMDS will only be found at elevated concentration close to source. Monitoring DMDS concentrations in urban air for a year, gave the range 0.02-5.26 ppb (Susaya et al., 2011). In comparison, the maximum concentration for these compounds observed in an industrial region ambient air was 7.85 ppb (Pal et al., 2009). The observations of maximum ambient concentrations of DMDS observed at an open stall and a slurry wastewater lagoon in a dairy farm were relatively low by comparison at 2.3 ppb (Filipy et al., 2006). Meinardi et al. (2003) found very high DMDS and DMS mixing ratios in Australian bushfires with maxima at 113 and 35 ppb respectively.

5.6 Thiophenes

Thiophene has a lifetime of about 12 hours in the atmosphere (Cabañas et al., 2004), where the reaction rate with OH and NO₃ radicals has roughly the same impact on the atmospheric lifetime. Although the nitrate radical can abstract a hydrogen atom from the thiophene ring and produce a peroxy radical, a more likely route leads to the elimination of SO₂ and the oxidation to the C₁-C₃ aldehydes (Cabañas et al., 2005). The reactivity of thiophenes means that concentrations except close to source are likely to be low. Few ambient measurements are available, but simultaneous measurements of sulfur gases in the headspace of a large septic tank gave average thiophene values around 7 ppb, somewhat less than H₂S (Toda et al., 2004).

The relative level of thiophene in soils has been influenced by the deposition of sulfur from air pollutants (largely oxidized sulfur), which has led to a change from the more reduced sulfur to more oxidized organic S forms of the humic substances at an unfertilized grassland site in England, which has samples going back into the 19th century (Lehmann et al., 2008). The potential for cycling of thiophene in soils could allow dry deposition to be a pathway for its removal from the atmosphere. There are very few measurements of BTs and their removal, although estimates of the importance of these processes can be made from comparison with PAHs.

6. Discussion and conclusion

This study highlights the anthropogenic contributions to global fluxes, which make an important addition to the large sources from the oceans and vegetation. Perhaps most notable was the dominance of industrial sources of CS₂, but it also became apparent that polysulfides such as DMDS and DMTS look to be predominantly from land based sources, with the 393 Gg S a⁻¹ DMTS attributed entirely to landbased sources and almost 90% of the 1791 Gg S a⁻¹DMDS emissions being of terrestrial origin. Even MeSH appears to have substantial non-marine emission fluxes. As shown in Fig. 1 and Table 1, natural sources dominate in the release of OCS, MeSH and DMS to the atmosphere and also DMDS and the polysulfides, although it would be sensitive to whether biomass burning was classified as natural or anthropogenic. However, the budget suggests that more than a third of OCS arises from anthropogenic activities. Some 70% of the CS₂ comes from human activities and almost all of the thiophenes.

Although the emissions of sulfides from industries are often detailed and estimated with great care, these may be country specific and difficult to extrapolate to global emissions, as practices and control measures can vary widely. In addition the material related to industrial

emissions is often published outside the mainstream literature, so can be easily overlooked when assembling budgets. The paper industry seems to give rise to very large emissions, but control measures could also reduce the emission factors in future. The industries are also sensitive to the cycles of demand, and the cellulose, particularly rayon, can fluctuate considerably as manufacturers respond to the demands of the market. The paper industry releases a considerable range of sulfur gases, and for some such as EtSH (accounting for almost 10% of global alkylthiol emissions) and thiophene (about half of the global thiophene emissions) it is likely to be the dominant source. The industry also makes a large contribution to terrestrial MeSH (almost 30%) and DMS (about 25%). There is a need for more work on the ambient budgets of these compounds as there are comparatively few measurements, especially of the more complex organosulfides in the atmosphere, and this source is potentially an important one. Paper production could represent a major source of the little known polysulfides, especially DMTS, which is not often measured in the environment, but it has a low odour threshold. It is also possible that there are important sources of DMTS from agriculture, such as releases from manure. The polysulfides oxidize in a matter of hours, so any impacts are likely to be local. Additionally more observations would allow a better estimate of the emissions, particularly as DMDS, from biomass burning. The five predominant sulfides (OCS, CS₂, MeSH, DMS and DMDS) represent a source of some 46 000 Gg S a⁻¹; a flux dominated by DMS. The exotic compounds (here EtSH, propanethiol, DMTS and thiophene) are quite naturally have much smaller fluxes so make just a few percent of the total contribution at 1330 Gg S a⁻¹ and are dominated by industrial EtSH.

Marine sources are typically well studied and make significant contributions to the fluxes of OCS, MeSH, DMS and DMDS to the atmosphere. There has recently been much interest in the potential for anthropogenically induced climate change to lead to warmer temperatures and less cloud over the polar oceans. There are suggestions that such changes could significantly increase DMS flux from the margins of the Antarctic continent (Cameron-Smith et al., 2011), but it is likely that this effect is weak in many regions (Gunson et al., 2006; Vallina et al., 2007; Woodhouse et al., 2010; Quinn and Bates; 2011). A warmer world under a changing climate might also have an impact on other sulfide releases, in particular increasing the rate of putrefaction. The potential for very low or very high water flow rates in a changing world might limit the effectiveness of sewage treatment, or lead to overflow (e.g. Rosenzweig et al., 2007).

The flux of DMDS is less well known and although it is likely that the oceans are important, this source might not be dominant in terms of the emissions of the dimethyl polysulfides, because so many industrial waste streams and agriculture produce them. Although there is some merit in gaining a better idea of the DMDS flux from the ocean, other major sources, most particularly agriculture and the pulp and paper industry also need to be better understood. This is broadly of interest because the concentrations of DMDS in the air

at industrialized locations can exceed those of DMS. It is important to see these sources as more localised than the marine source, so may be relevant in regional contexts, e.g. as sulfur contributions to soils. Forest fires may be a further and potentially significant source of DMDS, but there are few field measurements.

The oxidation of CS₂ has long been seen as a key source of OCS in the atmosphere, but oxidation of DMS is likely a significant additional source of OCS, because the DMS flux is so great even this inefficient channel leads to substantial amounts of OCS. However, the production of OCS from DMS is very sensitive to the presence of NO (Patroescu et al., 1999; Albu, 2008), which may need to be better understood. Our estimates stress the importance of rayon, paper and pigment production. They contribute roughly 60% of the CS₂ emissions of some 1076 Gg S a⁻¹, a higher production than typical of earlier flux estimates. This leads us to larger estimates of the global flux of OCS than have been typical in recent publications. Tyre abrasion as a source of OCS and CS₂ looks to have been somewhat over estimated as a source in the past, so may need re-examination.

Coke production looks to be the major source of BTs and these emissions are localised, mostly around steel plants, and likely to cause noticeably higher concentrations in the surrounding atmosphere. However, emissions may alter with changing control measures. Bitumen production is probably the dominant source of DBT, but it is difficult to make a secure estimate of the global flux. High concentrations close to source may make these emissions relevant to health; BT and other sulfur compounds from the tyre industry can cause odours that are possibly at levels relevant to adverse health effects. Furthermore these compounds are also of concern because of release from wastewater treatment plants, leachate from tyre dumping sites and from waste generally. There are a range of toxicity values for DBTs in surface water as found in Irwin (1997), where it is regarded as toxic to wildlife.

Wastewater, while seemingly important never revealed high global fluxes in our estimates and importantly the tanning industry while known to release large quantities of H₂S (Masood and Malik, 2014) is rarely mentioned as a source. The source could be important, but it is difficult to estimate. However, more observations would be useful to make an estimate of the flux, and it could be relevant as along with the polysulfides there are some less often determined compounds e.g. the sulfides of propane and butane.

The detailed cycles that include removal pathways and oxidation products for the sulfides are not well understood in comparison with the comparative strengths of the major sources. The chemistry of the more complex polysulfides is rarely investigated, so their atmospheric lifetimes are similarly uncertain, though likely days or less. Oxidic soils are important sinks for OCS and CS₂, and Berry et al. (2013) have compared the drawdown of CO₂ with OCS that gives a new estimate of the uptake by the canopy of 738 Gg S a⁻¹. However, soils may also be a sink for the organosulfides, but the chemistry and assimilation

of these sulfides has not been extensively studied. The larger molecules might be important if they were to accumulate either through persistence or within the food chain. Their fluxes may also change in a warmer world with different precipitation regimes. It is also likely that changes in the biogeographical distribution of organisms as a result of climate change would alter regional and global sources and sinks of organosulfur compounds.

The organosulfides have a wide range of impacts, from local health effects to a long term contribution to the overall biogeochemical budgets of sulfur. The volatility, short lifetime and polymer forms make their chemistry a fascinating subject.

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Figure Captions

Figure 1. Major fluxes of carbonyl sulfide, carbon disulfide and the most important organosulfides into the atmosphere, carry labels listing sources with the fluxes enumerated as Gg S a^{-1} . The area of the arrows is proportional to the enumerated flux, with grey arrows denoting anthropogenic and black arrows the natural fluxes. The oxidative source of OCS is split between natural and anthropogenic sources 158 Gg S a^{-1} and 162 Gg S a^{-1} respectively. Part (f) of the diagram shows comparative fluxes of the major natural and anthropogenic fluxes of carbonyl sulfide, carbon disulfide and the most important organosulfides into the atmosphere. The numbers at the top denote the natural fluxes of MeSH and DMS, which are too large to fit on the scale. Notes: The individual fluxes marked as arrows may omit some minor pathways and therefore not add to the total global flux. The flux of DMDS from pulp and paper includes 63 Gg S a^{-1} DMTS; the flux of MeSH from pulp and paper includes 855 Gg S a^{-1} EtSH; the flux of MeSH from rayon manufacture was as 2-propanthiol.

Figure 2. Main removal pathways for the key sulfides discussed in the text. The proportion is marked as a percentage for OCS, CS_2 and DMS in bold italic font. The fluxes calculated from these are marked in regular font with the units Gg S a^{-1} , while the numbers for OCS in square brackets come from Berry et al. (2013). MeSH and DMDS may be somewhat similar to DMS, but not as well known. Removal of the thiophenes may be via oxidation in the atmosphere or deposition to the Earth's surface and oxidation there. Those more aromatic sulfides resistant to oxidation can be transferred to marine and estuarine sediments.

Figure 1

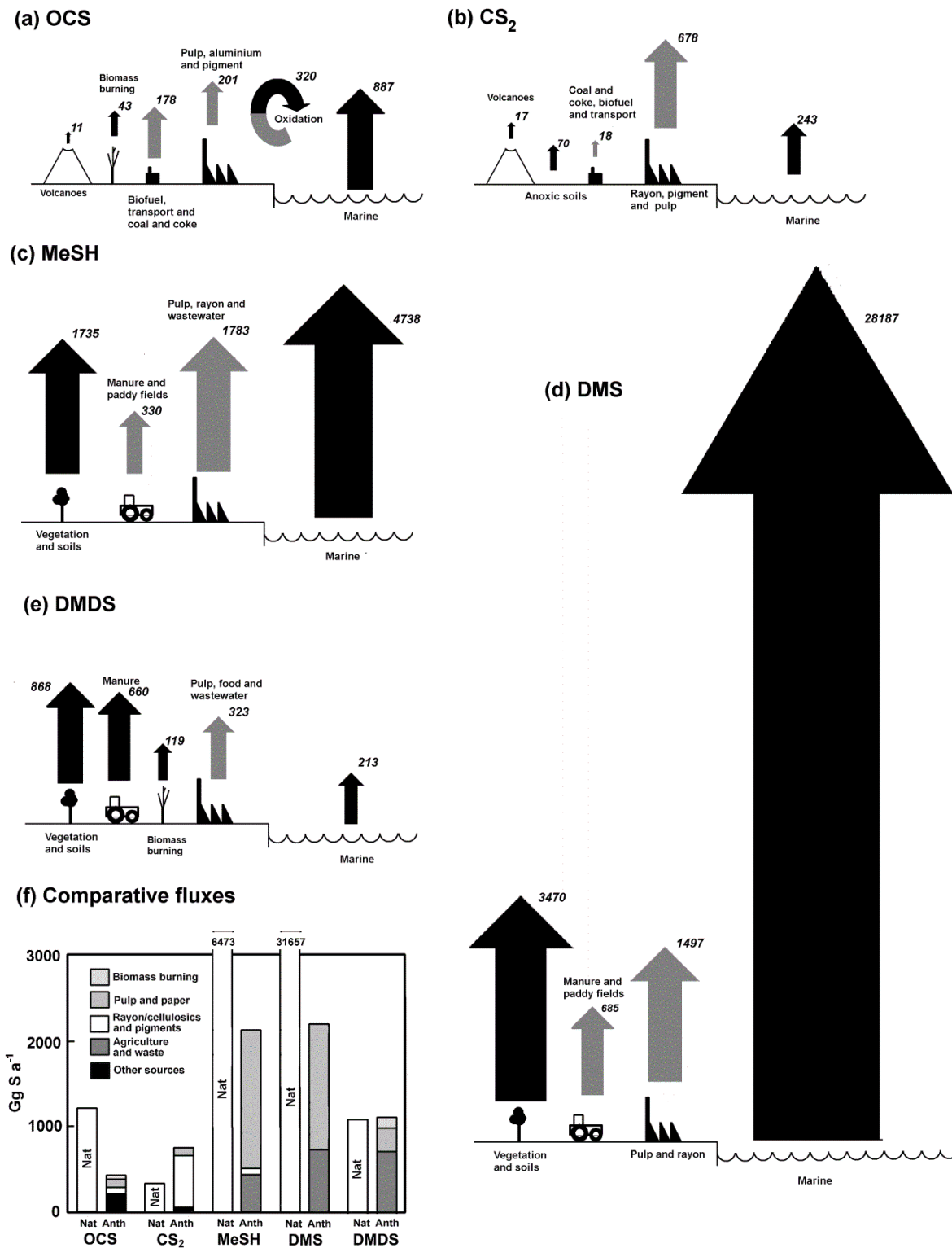


Figure 2

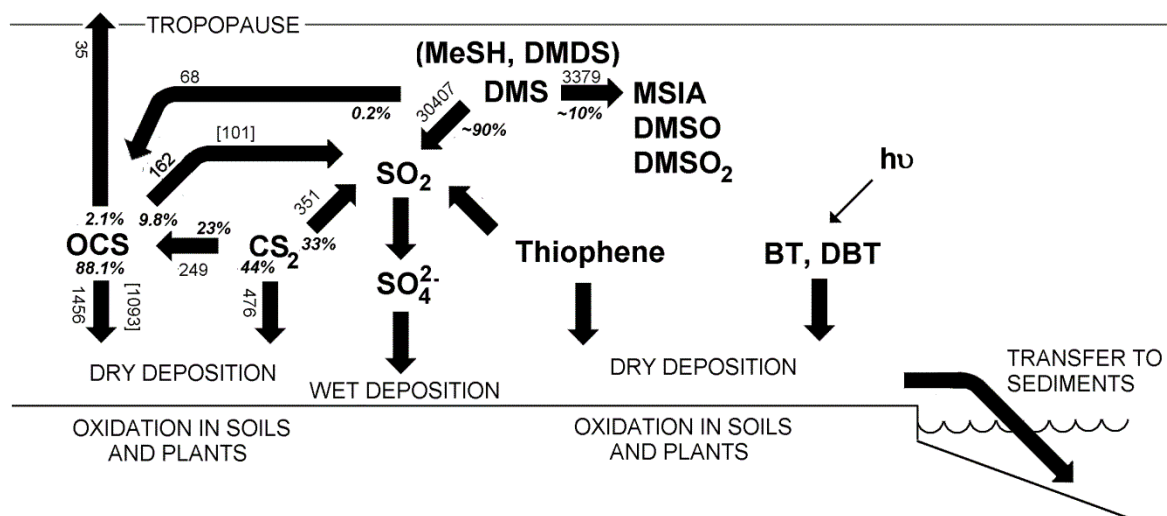


Table 1 Summary table of anthropogenic and for comparison natural emissions Gg S a^{-1} . Superscripts prefixed in Greek letters give range taken from literature. Superscripts in Roman letters give other additional information.

Sources	OCS	CS ₂	MeSH	DMS	DMDS	Thio ^a	BTs	DBT	Total
3.1 Biomass burning	^α 43	^α 1.8		^α 6	^α 119				170
3.2 Biofuel combustion	^β 73.1	2.9						0.035	75
3.3 Pulp and paper industry	97.2	78.5	1680 ^b	1462	273 ^c	17			3608
3.4 Rayon/cellulosics manufacture		^γ 395	51.4 ^d	35.6					482
3.5 Manure	*	*	330	^δ 660	^δ 660 ^e				1650
3.5 Paddy fields	0.38	26.9	0.76	25	0.57				53.6
3.6 Pigment industry	74	205							279
3.7 Food processing	0.63		*	3.97	28.9 ^f				33.5
3.8 Gas industry	0.7		4.8	0.84 ^g	0.1 ^h		^ε 0.005 ⁱ	^ζ 0.003 ^j	6.45
3.9 Wastewater	0.022	1.03	51	3.4	21.4				76.9
3.10 Aluminium industry	^η 30	4						*	34
3.11 Coal combustion	^θ 60	0.33				0.32	0.16 ^k	0.22 ^l	61
3.11 Coke production	9	14				14	3		40
3.12 Bitumen production and use								7 ^m	7
3.13 Vehicles	^ι 6	^κ 0.3				*	*	0.071 ⁿ	6.37
3.16 Shipping	30	1.5				*	*	1.5 ^o	33
3.14 Tyre wear	11.7	15.5							27.2
3.14 Tyre combustion	0.064		0.043			0.098 ^p	0.185 ^q		0.39
3.15 Landfill and waste	0.079	0.19	0.34 ^r	0.26	0.008	0.0004			0.88

3.17 Brickmaking		0.03							0.03
3.18 Oxidation [#]	162								162
Subtotal	598	747	2119	2197	1103	31.4	3.35	8.83	6807
Natural sources[‡]	(4.1)	(4.2)	(4.3)	(4.4)	(4.5)	(4.6)			
Saline and ocean water	^λ 887 ^s	^μ 243 ^s	^ν 4738	^ξ 28187 ^s	213 ^t				34268
Vegetation and soils		^ο 70	1735	3470	868				6142
Volcanoes	^π 11	^ρ 17	*			^σ 0.1			28.1
Oxidation [#]	158								158
Subtotal	1056	330	6473	31657	1080	0.1	0	0	40596
Total sources	1654	1077	8592	33854	2184	31.5	3.35	8.83	47403
Industry ^u	272	697	1741	1502	304	31.4	3.35	7.22	4557
Agriculture ^v	0.38	26.9	331	685	661				1704

(a) Thiophene - bitumen production and use and shipping are probably further sources (b) includes EtSH accounting for an additional 855 Gg S a⁻¹ (c) includes DMTS accounting for an additional 63 Gg S a⁻¹ (d) as 2-propanethiol (e) as both DMDS and DMTS (f) includes 0.25 Gg S a⁻¹ as methyl-1-propenylsulfide and 1.36 Gg S a⁻¹ methyl-2-propenyl disulfide (g) as dialkylsulfides (h) as dialkyldisulfides (i) as thia-arenes (j) as BNTs (k) all BTs (l) including naphthothiophenes 0.02 Gg S a⁻¹ (m) includes various substituted DBTs (n) includes BNTs at 0.024 Gg S a⁻¹ (o) includes BNTs

at 0.5 Gg S a⁻¹(p) includes methylthiophene (q) includes benzisothiazole (r) including EtSH 0.17 Gg S a⁻¹(s) includes 87 Gg S a⁻¹ from marshes (t) includes 9 Gg S a⁻¹ from marshes (u) including pulp and paper industry, rayon/cellulosics manufacture, pigment industry, food processing and waste, gas industry, wastewater/aluminium industry, coal combustion, coke production, bitumen production and use, tyre combustion and brickmaking (v) including manure and paddy fields

(α)Meinardi et al. (2003) suggests that they are all a factor of two or greater(β) \pm 23.4(Blake et al., 2004 and Watts, 2000) (γ) \pm 35% from Campbell et al. (2015) (δ) \pm 493(Filipy et al., 2006)(ϵ)0.003-0.011(Cass, 1993)(ζ) 0.002-0.006(Cass, 1993)(η)(\pm 7) (Campbell et al., 2015) (θ) \pm 30 (ι) \pm 4 (Watts, 2000) (κ) 0.2-0.5(Chin and Davis, 1993) (λ) range from seawater (40-520) (as the flux of Suntharalingam et al. (2008) comes from Kettle et al. (2002)(μ)range from seawater (3.3-2346)(Kettle et al., 2001)(ν)3.2-35330 (Kettle et al., 2001) (ξ)range from seawater (17600-34400) (Lana et al., 2011)(\omicron) \pm 40 (Watts, 2000)(π) 3-48 (Chin and Davis, 1993)(ρ) 5-76 (Chin and Davis, 1993)(σ)0.03-10 (Tassi et al., 2010)

* some hints of emissions, so unlikely to be zero

details of the split into anthropogenic and natural source described in section 3.18

‡ natural emissions are tabulated for comparison with section numbers referred to in parentheses. The total natural and anthropogenic sources of OCS from atmospheric oxidation account for natural and anthropogenic origins of the CS₂ and DMS precursors, while that for industry and agriculture includes only the primary sources.