



The mass budgets of carbonyl sulfide, dimethyl sulfide, carbon disulfide and hydrogen sulfide

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Abstract

This study investigates the distribution and magnitudes of the global sources and sinks of carbonyl sulfide (OCS), hydrogen sulfide (H₂S), carbon disulfide (CS₂), and dimethyl sulfide (DMS). For OCS, H₂S and CS₂, balanced mass budgets are proposed. An inventory of sources has been assembled for dimethyl sulfide (DMS). For OCS, total global sources and sinks are estimated as 1.31 ± 0.25 and 1.66 ± 0.79 Tg a⁻¹, respectively. Global sources and sinks of H₂S are estimated as 7.72 ± 1.25 and 8.50 ± 2.80 Tg a⁻¹, respectively. Estimates of sources and sinks of CS₂ are 0.66 ± 0.19 and 1.01 ± 0.45 Tg a⁻¹, respectively. For DMS only a sources estimate has been prepared, 24.45 ± 5.30 Tg a⁻¹. The budgets for OCS and DMS seem relatively secure, whilst those for H₂S and CS₂ contain much greater uncertainty. For DMS, more information on emissions from plants is required. For the other three species, data on soils and vegetation emissions are sparse, although the most urgent priorities might be to establish the role of freshwater wetlands and soils in non-tropical areas. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Carbon disulfide (CS₂), carbonyl sulfide (OCS) dimethyl sulfide (DMS) and hydrogen sulfide (H₂S) are trace sulfur gases found in most atmospheric and surface natural water samples (Turner and Liss, 1985; Kim and Andreae, 1987). They are all implicated in the formation of sulfur dioxide (SO₂) in the stratosphere and/or troposphere, and hence may have a role in global climate change. However, considering their possible importance, relatively little is known about these gases (Andreae, 1990). The global atmospheric OCS budget seems to have either an overestimation of sources, or underestimation of sinks, of approximately 30% (Chin and Davis, 1993). Data on CS₂ is sparse; our quantitative knowledge

about the budget of H₂S is rudimentary. The most recent reviews of these mass budgets are at least six years old (Chin and Davis, 1993; Bates et al., 1992) and since then significant progress has been made in some of these areas.

The aim of this review is twofold: to bring all four main components of the atmospheric reduced sulfur budget together in one place, and secondly to draw attention to the main problem areas in the mass budgets of these species. This should help to clarify the goals of future work in the area. Although the bases of all recommendations are given in the text, errors have been propagated using the root of the means of the squares throughout.

2. The budgets

2.1. Carbonyl sulfide

OCS is the most abundant, and probably the most long-lived sulfur gas in the atmosphere (Andreae and

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Table 1
Summary of recent OCS sea surface measurements

[OCS] _{mn} /10 ⁻¹² M	<i>n</i>	$\sigma_{(n-1)}$ /10 ⁻¹² M	Area	Comment /10 ⁻¹² M	Reference
51	13	27	N. Atlantic Ocean	<i>Open ocean</i> Top 100 m only. Seasonal variation (Apr. 40–Nov. 100).	Radford-Knoery and Cutter (1994)
6	17	2	N. Atlantic Ocean	Top 100 m only. All data Jan.	Flock and Andreae (1996)
20	107	4	C/S Pacific Ocean	Data not fully extractable, > 1000 determinations. Seasonal and diurnal variation	Wiess et al. (1995)
60	48	30	Indian Ocean	Feb., Apr. and July. Diurnal variation	Mihalopoulos et al. (1991,1992)
19	>	8.3	N. Atlantic Ocean	Data not fully extractable. Sept.	Ulshofer et al. (1995)
15	>	6.1	N. Atlantic Ocean	Data not fully extractable. April	
5	>	1.6	N. Atlantic Ocean	Data not fully extractable. January	
				<i>Coastal</i>	
18	10	8	Mediterranean Sea	Feb., Apr. and July. Diurnal variation	Mihalopoulos et al. (1991)
23	12	4	Ionian Sea	July 24 h data. Diurnal variation (12:00 UTC 30–04:00 UTC 18).	Ulshofer et al. (1996)
142	9	90	N. Sea, English Channel	Seasonal variation (Sept. 30–Jan. 30)	Watts (1991)
41	12	17	Aegean Sea	July 24 h data. Diurnal variation (12:00 UTC 65 – 04:00 UTC 17)	Ulshofer et al. (1996)
112	157	9	Caribbean Sea	November and May. Diurnal variation	Andreae and Ferek (1992)
156	266	10	African Coast and Amsterdam Is.	Data not fully extractable. Feb., Apr. and July. Diurnal variation	Mihalopoulos et al. (1991)
				<i>Estuarine</i>	
130	> 10	80	Yarmouth, UK.	Data not fully extractable	Turner and Liss (1987)
775	4	618	Yarmouth, UK.	Seasonal variation (Sept 1800 –Mar 400)	Watts (1991)

Ferek, 1992). It is relatively insoluble (K_H (25°C) $20.98\text{--}21.98 \times 10^{-3} \text{ mol dm}^{-3} \text{ atm}^{-1}$), and is seasonally out-gassed or taken up by the oceans (Wilhelm et al., 1977; DeBruyn et al., 1995; Wiess et al., 1995; Ulshofer et al., 1995,1996). Oceanic OCS concentrations display a diurnal cycle with a daylight maximum (Zepp and Andreae, 1994), and a seasonal variation with a winter minimum and summer/autumn maximum (Ulshofer et al., 1996). In general tropical and subpolar waters are richer in OCS than others (Radford-Knoery and Cutter, 1994; Flock and Andreae, 1996; Wiess et al., 1995), and coastal waters display higher concentrations than open oceans (Andreae, 1990; Watts, 1991). Table 1 contains a summary of recent marine OCS measurements. Oceanic OCS concentrations are the result of a number of processes:

- (i) photochemical production from dissolved organo-sulfur species (Zepp and Andreae, 1994),
- (ii) non-photochemical production from dissolved organo-sulfur species or sediments (Flock and Andreae, 1996)

- (iii) hydrolysis of dissolved OCS (Radford-Knoery and Cutter, 1994)
- (iv) air–sea exchange (Ulshofer et al., 1996)

The interaction of these factors at different times, places and seasons makes estimations of the mass fluxes of OCS between oceans and atmosphere a little fraught. Inspection of the available data (Radford-Knoery and Cutter, 1994; Mihalopoulos et al., 1991; Ulshofer et al., 1995; Wiess et al., 1995) show that on average the summer–autumn period for each hemisphere are the source periods, whereas winter–spring represent those times when the open oceans act as a sink. With regard to the open ocean, the balance between those times when they are a source rather than a sink is critical. Recent work (Wiess et al., 1995) has proposed that this balance is toward sink, i.e. the open oceans are a global sink of OCS. However, careful interpretation of their saturation factor data, with that from other workers (Radford-Knoery and Cutter, 1994; Mihalopoulos et al., 1991; Ulshofer et al., 1995) shows that the timing of their data collection effectively under-sampled the annual cycle

(i.e. their sampling was biased out of the summer/autumn maximal periods). Their seawater OCS concentrations and hence their saturation factors (used to calculate the flux) would thereby be lowered. Using their data, (with estimations of super-saturation data from other recent measurements), and weighting the June–November period, the results of the equinox and summer flux calculations change considerably. In the light of this a more reasonable value might be $0.10 \pm 0.15 \text{ Tg a}^{-1}$.

It is of interest to note that all of the above workers seem to have focussed their attention on light and wind speed as the main determinants of the flux of OCS from the oceans into the atmosphere (Radford-Knoery and Cutter, 1994; Mihalopoulos et al., 1991; Ulshofer et al., 1995; Wiess et al., 1995). Meanwhile, laboratory studies (Zepp and Andreae, 1994; Watts, 1991) have also highlighted dissolved organic matter (DOM) and dissolved amino acids as important in the production of OCS in seawater. It is noteworthy then, that the available observational data (both open and coastal ocean) all show maximal OCS production during the summer/autumn periods, when light levels and DOM and dissolved amino acids are maximal (Libes, 1992). Crucially, the same observational data (with one exception of (Ulshofer et al. (1996)), do not show high levels in spring and early summer when light levels are similar to autumnal periods, but when one would expect DOM to be low. These observations are consistent with DOM being one of the main factors in OCS production from ocean waters.

Flux estimates from coastal seas have been variously estimated as 0.47 Tg a^{-1} (Andreae and Ferek, 1992), 0.06 Tg a^{-1} (Ulshofer et al., 1996), $0.30\text{--}0.60 \text{ Tg a}^{-1}$ (Mihalopoulos et al., 1991). Conditions prevalent during the sampling led to the lowest estimate (Ulshofer et al., 1996), whilst the estimate of Andreae and Ferek (1992) may be high due to seasonal bias. The need for more data on coastal OCS concentrations has been highlighted before (Wiess et al., 1995). If the role of DOM in OCS production is important, it should be shown more in coastal than open ocean systems (Ulshofer et al., 1996). This would lead to maximum OCS concentrations asymmetrically in the year (approximately June–November in the northern hemisphere). Averaging the estimates with this asymmetry (Andreae and Ferek, 1992; Mihalopoulos et al., 1991), yields an annual coastal ocean to atmosphere flux of $0.20 \pm 0.10 \text{ Tg a}^{-1}$ to include estuaries and salt marshes. This gives a total ocean to atmosphere flux of $0.30 \pm 0.18 \text{ Tg a}^{-1}$. This compares with the previous estimate of $0.40 \pm 0.24 \text{ Tg a}^{-1}$ (Chin and Davis, 1993) (Table 1).

Measurements of OCS emissions from soils have been a little difficult to interpret as soils seem either to take up or emit OCS depending on soil type and other conditions (Chin and Davis, 1993; Lehmann and Conrad, 1996; Yang et al., 1996). In addition, there is a measurement problem: dynamic enclosures using either ambient or

sulfur free air are used to estimate fluxes of volatile sulfur fluxes from soils. Both of these main techniques are prone to inaccuracy. In the one case (S free air) to measure false soil–air fluxes (or overestimate them) (Castro and Galloway, 1991), and in the other, (ambient air) be subject to large uncertainties (Chin and Davis, 1993). However recent work (Kuhn et al., 1999) using a novel approach has overcome some of these measurement problems. Using two exposure chambers flushed with ambient air, (effectively using one of them as a blank), uptake and deposition to some soils and plant species have been measured. This work confirms that in terms of deposition or emission of OCS, soils may act differently according to their type. This is consistent with previous work (Devai and DeLaune, 1995) which indicated that the redox potential of the soil system determined whether it was a net source or sink of OCS. Accordingly, in this work soils have been split into two classes, “anoxic” and “oxic”. “Anoxic” soils comprise some alfisols, ultisols, spodosols, some mollisols (especially aquents of these) which seem to be net sources of OCS to the atmosphere (Castro and Galloway, 1991; Lamb et al., 1987; Kanda et al., 1995; Melillo and Steudler, 1989). Whereas “oxic” soils include some alfisols, aridisols and some drier mollisols which seem to be net sinks (Kuhn et al., 1999; Castro and Galloway, 1991).

2.1.1. “Oxic” soils

Measurements were made in a typical area of California coastal mountains which comprise of mixed evergreen forest, oak woodland, savanna and chaparral (Kuhn et al., 1999). The soil types were coarse sandy loams, mostly aridisols. Deposition rates varied diurnally with daytime maxima. Daytime deposition rates of OCS to these soils of $21.6 \pm 12.3 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$ are reported. These results agree well with previous measurements undertaken with ambient air (Castro and Galloway, 1991), which yielded values of $23.4 \pm 16.5 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$. For this reason, results of these two studies are used as the basis of this estimate. (There is also data from maize and wheat fields (Kanda et al., 1995) which implies a flux (air \Rightarrow soil) of $5.1 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$, but the data is adjusted for harvesting, and it is difficult to know how to compare them with other work). Using world soil maps (Briggs and Smithson, 1995; McHenry, 1992), and summing areas of similar soil types (see Table 5) an estimate of the global flux for this process is $0.92 \pm 0.85 \text{ Tg a}^{-1}$. The main source of error in this estimate is in the flux measurement itself (the error associated with the surface area measurement is $\pm 20\%$).

2.1.2. “Anoxic” soils

The work undertaken with ambient air (Castro and Galloway, 1991; DeMello and Hines, 1994; Lehmann and Conrad, 1996; Kuhn et al., 1999; Melillo and Steudler, 1989) in effect puts into doubt much previous work

done with sulfur free air (Goldan et al., 1987; Aneja et al., 1979; Lamb et al., 1987; Adams et al., 1981; Staubes et al., 1989). Using those data sets which were obtained with ambient air, and which seem most consistent with each other (Lehmann and Conrad, 1996), a mean flux of $1.2 \pm 0.6 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$ is calculated. (To be able to use one of the data-sets (Lehmann and Conrad, 1996), it was assumed that the soil density was 1.1 g cm^{-3} , and that most of the OCS is emitted from the top 5 cm of soil (Brown and MacQueen, 1985). Using a world soil map (Briggs and Smithson, 1995) and the data in Table 5, a global flux from anoxic soils of $0.02 \pm 0.01 \text{ Tg a}^{-1}$ can be calculated.

The combined results for both oxic and anoxic soils gives an overall flux of OCS from atmosphere to soils of $0.90 \pm 0.78 \text{ Tg a}^{-1}$. This is markedly different (and in the opposite sense) from the previous best estimate of $0.33 \pm 0.19 \text{ Tg a}^{-1}$ (Chin and Davis, 1993) which included both the data obtained with zero sulfur air and the marsh and salt marsh contribution. Although there is still only little data, and the estimate contains considerable uncertainty, it is now beginning to look like soils globally are a sink of atmospheric OCS. More work is urgently needed to re-assess different soil types using the enclosure method with ambient air.

For quite some time, deposition to vegetation has been thought of as the main sink of atmospheric OCS (Logan et al., 1979; Brown and Bell, 1986; Toon et al., 1987; Chin and Davis, 1993). Recently, however, there have been

a series of studies which allow better quantification of these processes (Kuhn et al., 1999; Gries et al., 1994; Kesselmeier and Merk, 1993). Mechanistically, it seems that a plant enzyme Higher Plant Carbonic Anhydrase (HPCA), as well as processing atmospheric carbon dioxide, can also process OCS (Protoschill-Krebs et al., 1996). Further, HPCA seems to take up OCS preferentially to CO_2 , and produce H_2S as a product (Kesselmeier and Merk, 1993).

Plants take up OCS (and most other trace gases) via their stomata. Studies to date seem to indicate that OCS uptake is closely correlated with photosynthetic CO_2 uptake (Kesselmeier and Merk, 1993). As the stomata are effectively closed at night, plants can only take up OCS during the daytime (Goldan et al., 1988). One method to estimate the impact of this process is to use the fact that OCS uptake is linked to CO_2 uptake (Kesselmeier and Merk, 1993). Global carbon fixation by plants is estimated at about $120 \pm 20 \times 10^3 \text{ Tg C a}^{-1}$ (Schlesinger, 1996; Brimblecombe, 1996). Experimental values for effective ratios of OCS/ CO_2 (taking into account that HPCA prefers OCS to CO_2) for various plant groups appear in Table 2.

The resultant estimate of $0.56 \pm 0.10 \text{ Tg a}^{-1}$ (atmosphere to plants) compares reasonably well to $0.53 \pm 0.40 \text{ Tg a}^{-1}$ (Chin and Davis, 1993), 0.63 Tg a^{-1} (Schlesinger, 1996), and $0.93 \pm 0.07 \text{ Tg a}^{-1}$ (Kesselmeier and Merk, 1993). This estimate will be refined, as data for the uptake ratios becomes clearer, because this approach

Table 2
Effective ratios of OCS/ CO_2 for terrestrial plant groups

Plant group	OCS/ CO_2 (μmol μmol^{-1})	Terrestrial phytomass ^a (%)	Reference	OCS flux (Tg a^{-1})
Coniferous forest	1.0 ± 0.2	16	Estimated from Kuhn et al. (1999) and Kindermann et al. (1995)	0.04 ± 0.008
Tropical forest	8.4 ± 2.0^b	43	Kesselmeier et al. (1993)	0.43 ± 0.10
Temperate forest	$\leq 2.17^c$	19	Kuhn et al. (1999)	0.05 ± 0.01
Crops	9 ± 3^d	0.5	Hofmann (1993); Velmeke (1993)	0.01 ± 0.003
Others	2 ± 1	4.5	Estimated	0.01 ± 0.005
Grassland	5.5 ± 1.2^e	15 ^f	Hofmann (1993)	0.01 ± 0.002
Desert/Tundra	3 ± 0.1^g	2	Calculated ^h from Gries et al. (1994)	$< 0.01 \pm 0.0003$
Totals		100		0.56 ± 0.10

^aAll data from Tolba et al. (1992).

^bAverage for a number of tropical tree and ground level species.

^cValue for *Quercus Agrifolia*.

^dAveraged value for rapeseed, corn, wheat and pea.

^eValue for wheat used.

^fIncludes chaparral, tropical savannah and shrubland.

^gValue calculated from lichen data.

^h6 months a^{-1} @ 10 h d^{-1} between 50–90 NS, provenance 740 kg ha^{-1} (Kuhn et al., 1999).

really requires detailed knowledge of the species composition of the different biomes.

The available measurements concerning bogs, fens, swamps and marshes, reveal very great variability (Adams et al., 1991; Lamb et al., 1987; Aneja et al., 1979). This may be because the term “wetland” encompasses very different types of environments: a peat bog behaves very differently to a swamp (Brown and MacQueen, 1985; Westhoff, 1990). Alternatively, it could be that the behaviour of these environments is inherently very variable (Aneja, 1986; Hines et al., 1993).

Finally, as with soils, there is also a measurement problem surrounding the use of sulfur free air in measurement enclosures. Here, data obtained using sulfur-free air have been excluded. Very little other data remaining is unequivocally freshwater wetland. Source strengths of $5.2 \pm 2.8 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$ (Fried et al., 1993) and $15.4 \pm 13.5 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$ (DeMello and Hines, 1994) for peat bog systems are comparable to each other. OCS fluxes from a freshwater Mangrove ($4.7 \pm 1.2 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$) and a grassy freshwater marsh ($2.6 \pm 0.6 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$) have also been reported (Hines et al., 1993). These latter figures are close to those derived above for anoxic soils: $1.2 \pm 0.6 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$ (Lehmann and Conrad, 1996). Data from tropical paddy fields (Kanda et al., 1992) yield a similar flux of $7.8 \pm 0.8 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$. This work uses an average of these six to obtain a global flux of $0.03 \pm 0.03 \text{ Tg a}^{-1}$ from wetlands to the atmosphere (see Table 5 for surface area data). Again, the main source of uncertainty is in the flux measurements. However, the existence of data (Thornton et al., 1996; Fried et al., 1993) which show depletion of atmospheric OCS where the air in question has passed over major bog or tundra systems may yet mean (despite the low redox potentials of these systems (Devai and DeLaune, 1995), that freshwater wetlands are sinks not sources of OCS. It could be that tropical and temperate/boreal wetlands are differentiated by some variable (e.g. the presence of lichens), which modifies the level of the OCS sink (Gries et al., 1994). There is an urgent need for data on temperate and boreal freshwater wetlands.

The methodology to estimate the source strength for biomass-burning has been to combine OCS : CO₂ ratios measured in laboratory or field experiments (Crutzen et al., 1979, 1985; Bingemer et al., 1990; Nguyen et al., 1990) with estimated carbon fluxes (Andreae, 1991; Crutzen and Andreae, 1991) and produce latitudinally differentiated zonal fluxes. Previous estimates have been made more uncertain by both the variation of the CO₂ : OCS ratio in different types of burning biomass, as well as the dearth of data on both boreal and savanna fires. The previous best estimates were $0.14 \pm 0.12 \text{ Tg a}^{-1}$ (Chin and Davis, 1993), 0.11 Tg a^{-1} (Kelly and Smith, 1990). More recent work however reports data from savanna and forest type environments, (Nguyen et al., 1995).

When this new data is added into the model, a lower flux, $0.07 \pm 0.05 \text{ Tg a}^{-1}$ is obtained (Nguyen et al., 1995). More work is needed on the OCS fluxes from boreal forest burning.

There have been two reports of precipitation being supersaturated with OCS (Belvisio et al., 1987; Watts, 1991). Both reports also indicate that OCS is present at greater concentrations in air masses with an anthropogenic history. Given the physico-chemical properties of OCS, it is very difficult to understand this supersaturation in terms of OCS scavenged from the atmosphere, indeed degassing would be the expected outcome. Previous work (Watts, 1991) determined a rate constant for OCS production from marine precipitation as $4 \pm 0.03 \times 10^{-6} \text{ s}^{-1}$ (August at 52°N, noon sunshine). In the absence of appreciable amounts of CS₂ (or any other volatile reduced sulfur compound), it was surmised that organic matter (including sulfur containing amino acids) in the precipitation was acting as the precursor (Mopper and Zika, 1987; Mukai and Ambe, 1986; Yokouchi and Ambe, 1986). Using average rain drop diameters of 0.20 to 1.0 mm (Warneck, 1988), and an annual estimate of global rainfall of $0.5 \times 10^{18} \text{ kg}$ (Brimblecombe, 1996), yields an atmospheric OCS source flux of $0.13 \pm 0.06 \text{ Tg a}^{-1}$.

Direct anthropogenic emissions of OCS to the atmosphere have been estimated at $0.04 \pm 0.02 \text{ Tg a}^{-1}$ (not including biomass burning) (Chin and Davis, 1993). There is an additional indirect source of CS₂ (from sulfur recovery operations of the oil industry) which is oxidized to OCS in the atmosphere (Chin and Davis, 1993). In this study, this latter process will be counted under the CS₂ budget, see later. Table 3 contains the estimates of the budgets of those processes recognized as direct anthropogenic OCS emitters. The emissions from aluminum production estimate is based on current data, although the comment assumes growth continuing in this industry at current rates (4%) and continued use of the Hall-Héroult Process with graphite anodes (Harnisch et al., 1992). The production of OCS by cars is an estimate based on sulfur contents and usage of modern petrols and diesels (Watts and Roberts, 1999) and the continued use of catalytic converters on cars. The total direct OCS production estimate presented here $0.124 \pm 0.061 \text{ Tg a}^{-1}$ is considerably higher than that previously proposed $0.04 \pm 0.02 \text{ Tg a}^{-1}$ (Chin and Davis, 1993) reflecting these changes.

There seems no reason to review the contributions to atmospheric OCS from volcanism, reaction of OCS with O and OH, or OCS photolysis following the previous best estimates for these sources (Chin and Davis, 1993). Because of changes to the CS₂ source fluxes proposed later in this work (see Table 7), the source of OCS caused by CS₂ oxidation has been revised from $0.39 \pm 0.22 \text{ Tg a}^{-1}$ (Chin and Davis, 1993) to $0.42 \pm 0.12 \text{ Tg a}^{-1}$. Equally, because of changes proposed

Table 3
Estimates of the budgets of those processes recognized as direct anthropogenic OCS emitters

Process	Flux (Tg a ⁻¹)	Comment (Tg a ⁻¹)	Reference
Coal combustion	0.036 ± 0.011		Chin and Davis (1993)
Industrial S recovery	0.002 ± 0.0015		Chin and Davis (1993)
Cars	0.006 ± 0.004	Dependant on sulfur levels in fuels	Fried et al. (1992); Watts and Roberts (1999)
Aluminum production	0.08 ± 0.06	Increasing to 0.32 by 2030	Harnisch et al. (1992)
Total	0.124 ± 0.061		

Table 4
Global sources and sinks of OCS to the atmosphere

Source/sink	Annual flux (Tg a ⁻¹)	Reference
<i>Sources</i>		
Open ocean	0.10 ± 0.15	See text
Coastal ocean (including salt-marshes and estuaries)	0.20 ± 0.10	See text
Anoxic soils	0.02 ± 0.01	See text
Wetlands	0.03 ± 0.03	See text
Volcanism	0.05 ± 0.04	Chin and Davis (1993)
Precipitation	0.13 ± 0.08 ^a	See text
DMS oxidation	0.17 ± 0.04 ^b	Barnes et al. (1994)
CS ₂ oxidation	0.42 ± 0.12 ^c	Chin and Davis (1993)
Biomass Burning	0.07 ± 0.05	Nguyen et al. (1995)
Anthropogenic (direct)	0.12 ± 0.06	See text
Total sources	1.31 ± 0.25	
<i>Sinks</i>		
Oxic soils	0.92 ± 0.78	See text
Vegetation	0.56 ± 0.10	See text
Reaction with OH	0.13 ± 0.10	Chin and Davis (1993)
Reaction with O	0.02 ± 0.01	Chin and Davis (1993)
Photolysis	0.03 ± 0.01	Chin and Davis (1993)
Total sink	1.66 ± 0.79	
Total imbalance	0.35 ± 0.83	Budget balanced to within uncertainties

^aAtlantic precipitation used as model, 50% of rainfall assumed to be nocturnal.

^bRe-calculated in light of modified DMS budget.

^cRe-calculated in light of modified CS₂ budget (Chin, 1992).

to the DMS source flux proposed later (see Table 10), the source of OCS due to DMS oxidation has been revised from 0.20 ± 0.10 Tg a⁻¹ (Barnes et al., 1994) to 0.17 ± 0.04 Tg a⁻¹.

Table 4 contains estimates of global sources and sinks for OCS. Most atmospheric OCS budgets, including recent work indicate a predominance of sources over sinks (Logan et al., 1979; Brown and Bell, 1986; Toon et al., 1987; Chin and Davis, 1993; Wiess et al., 1995), with deficits ranging between 0.7 and 1.0 Tg a⁻¹. Broadly, this budget is balanced to within the uncertainties of the estimates. The main sources of uncertainty are in the sinks. The oxic soils estimate is the most precarious.

2.2. Carbon disulfide

CS₂ is relatively insoluble (K_H (25°C) 54.95 × 10⁻³ mol dm³ atm⁻¹), (DeBruyn et al., 1995). There are very few oceanic measurements, but such as there are seem to follow the pattern of OCS with higher concentrations in coastal waters, and less high in open ocean situations (Kim and Andreae, 1987; Lovelock, 1974; Xie et al., 1997). Saline marshes and estuaries seem especially rich sources of CS₂ with very high concentrations (Stuedler and Peterson, 1984; Bandy et al., 1982; Watts, 1991; Turner and Liss, 1985). The main sources of CS₂ are thought to be rotting organic matter, whether in the

Table 5
Global surface areas of different types of environments

Type of area	Area (10^{12} m ²)	Precision (10^{12} m ²)	Reference and comment
Coastal and shelf ocean	49	5	Andreae (1990). 10% precision attached
Open ocean (total)	317	16	Andreae (1990). 5% precision attached
Open ocean (low productivity)	148	15	Andreae (1990). 10% precision attached
Open ocean (temperate)	83	9	Andreae (1990). 10% precision attached
Open ocean (upwelling)	86	9	Andreae (1990). 10% precision attached
Estuaries and salt marsh	0.03	0.005	Estimated using the data of Ketchum (1983) and Davidson (1991). 20% precision attached
Freshwater wetlands	4.8	0.5	Tolba et al. (1992). Not including lakes or floodplains. 10% precision attached
Freshwater dampland	6.2	1.3	Using USAEPA definition of wetlands (NRC, 1995) and world soil maps (Briggs and Smithson, 1994) 20% precision attached
Total soils	104	15	Estimated by assessing proportion of bare rock or ice (McHenry, 1992). 15% precision attached
Soils oxic	80	15	Estimated with world soil maps (Briggs and Smithson, 1994). 20% precision attached
Soils anoxic	19	4	Estimated with world soil maps (Briggs and Smithson, 1994). 20% precision attached
Tropical forest	22.3	2	Tolba et al. (1992). 10% precision attached
Boreal forest	16.4	1.5	Tolba et al. (1992). 10% precision attached
Temperate forest	13.4	1.5	Tolba et al. (1992). 10% precision attached
Total land area (without wetlands and Antarctica)	143	7	Estimated using data of Geddes and Grosset (1995). 5% precision attached
Total land area	148.3	0.8	0.5% precision attached
Total ocean area	361.3	1.8	0.5% precision attached

oceans, soils or marshes (Khalil and Rasmussen, 1984). There is some speculation that it could also have an oceanic photosynthetic source (Thornton and Bandy, 1991). Once in the atmosphere, it is quickly transformed to OCS and SO₂. Available sea surface measurements appear in Table 6. Extrapolating the available atmospheric concentration data (Thornton and Bandy, 1991; Thornton et al., 1996; Bandy et al., 1993; Cooper and Saltzman, 1993), with that in Table 6, the value of the Henry's Law constant indicates that it is likely that generally CS₂ is very supersaturated in all the surface oceans thus far analyzed. This in turn means that the oceans can be treated as a CS₂ source. However, CS₂, displays maxima in both the boundary layer and free troposphere. This with the variability of concentration with air mass history means it is likely that the ocean is neither the only, nor major source of global CS₂, in the way that DMS is, for example (Cooper and Saltzman, 1993).

Ocean ⇒ atmosphere flux estimates range 0.25 (0.13–5.0) Tg a⁻¹ (Kim and Andreae, 1987), 0.18 (0.13–0.24) Tg a⁻¹ (Xie et al., 1997), and 0.18 (0.09–0.36) Tg a⁻¹ (Chin and Davis, 1993). The two latter estimates are very close, and that of Xie et al. (1997) seems to be based on the larger data set. In terms of the

apportionment of separate coastal and open ocean fluxes, there is not yet sufficient data to be able to do this reliably. However, the relative surface areas of these reservoirs (see Table 5) allow tentative estimates such as those given in Table 7 as components of the Xie et al. (1997) budget. The coastal flux includes the estuarine and salt marsh contribution.

Much of the discussion above on fluxes of OCS from soils and wetlands also applies to CS₂. If anything, reported soil fluxes for CS₂ are more variable than those for OCS (Table 6). The main issue then is whether the data obtained with sulfur free air is at all indicative of the situation under natural conditions. The problem with OCS is exacerbated by the fact that it is present at relatively high concentrations (about 500 ppt). CS₂ on the other hand is present at much lower concentrations, and the problem should be less severe. However, the results of the comparison of the two techniques for CS₂ measurement (Castro and Galloway, 1991) are very convincing. In this study, work using sulfur free air (Goldan et al., 1987; Lamb et al., 1987; Staubes et al., 1989) has been excluded.

Source strength estimates remaining include $-18.5 \pm 14 \times 10^{-3}$ g m⁻² a⁻¹ (Castro and Galloway, 1991), $2.0 \pm 0.7 \times 10^{-3}$ g m⁻² a⁻¹ (Kanda et al., 1995),

Table 6
Summary of available CS₂ sea surface measurements

[CS ₂] _{mn} (10 ⁻¹² M)	<i>n</i>	σ _(<i>n</i>-1) (10 ⁻¹² M)	Area	Comment (10 ⁻¹² M)	Reference
				Open Ocean	
7	35	2	North Atlantic Ocean	July	Lovelock (1974)
8	97	4	North Atlantic Ocean	April–September	Kim and Andreae (1987)
6	?	?	North Atlantic and central Pacific Oceans	Data not fully extractable. Diurnal variation, range 9–20.	Xie et al. (1997)
				Coastal	
10	8	8	Irish Atlantic Coast	July	Lovelock (1974)
17	110	4	North Atlantic Shelf	April–September	Kim and Andreae (1987)
13	?	?	Coastal North Atlantic and coastal central Pacific Oceans	Diurnal variation, range 9–20.	Xie et al. (1997)
49	9	22	North Sea, English Channel	Seasonal variation (Sept. 90–Mar. 30)	Watts (1991)
				Estuarine	
120	1		Eastern seaboard, USA		Bandy et al. (1982)
263	4	195	Yarmouth, UK	Seasonal variation (Sept. 450–Feb. 80)	Watts (1991)

$10.2 \pm 8.7 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$ (Melillo and Steudler, 1989). These results seem very different until it is realized that the first two results are from oxic type soils, whereas the other is from anoxic soils.

In the absence of any other data, the approach adopted for OCS has been used for CS₂. Indeed, it is not unreasonable, and chemically it is not illogical (Devai and DeLaune, 1995).

The source flux (anoxic soils) has been calculated using the results from those soils (Melillo and Steudler, 1989), whilst the average of the results from the oxic soils (Castro and Galloway, 1991; Kanda et al., 1995) has been used to estimate the sink flux for the “oxic” soils. Using the data in Table 5, the source and sink fluxes are 0.07 ± 0.06 and $0.44 \pm 0.38 \text{ Tg a}^{-1}$, respectively. This means that from this analysis overall soils are a sink for atmospheric CS₂. It is entirely conceivable that this will change in the light of new data, which is urgently needed for this part of the CS₂ cycle.

For wetlands, it is a similar story of not much data. There is information from a freshwater mangrove swamp ($3.1 \pm 2.3 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$), and a freshwater grassy marsh ($1.3 \pm 0.7 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$) (Hines et al., 1993). There is also data from unfertilized paddy fields (Kanda et al., 1992), they report a flux of $5.6 \pm 0.7 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$. All of this data seem to be of a similar magnitude. With the surface area data in Table 5, a global wetland flux of $0.02 \pm 0.02 \text{ Tg a}^{-1}$ is proposed. There is very little data behind this estimate, and more data is urgently needed.

There seems no reason to modify the magnitudes of the contributions from volcanic or anthropogenic sources

from those previously proposed (Chin and Davis, 1993). Equally, the sink flux for reaction with OH is also unchanged (Chin and Davis, 1993).

Table 7 contains the global sources and sinks of CS₂ to the atmosphere. This budget is balanced within the uncertainty of the estimates. Most of the uncertainty is in the sinks. If CS₂ really is like OCS in its production and deposition to soils, then an increase on soils data will go some way to reducing this uncertainty – however, the problem will remain that this type of methodology (using ambient air) gives large errors (Kuhn et al., 1999). This budget differs substantially from that previously proposed (Chin and Davis, 1993), the reason for this is essentially the great uncertainty of the soils and wetlands fluxes. In recent years, experimental results have cast serious doubt on much of the enclosure chamber data, which until now has been used in these budgets. Having said that, the uncertainty range for the proposed budget is considerably reduced over previous one (Chin and Davis, 1993). More work is needed on CS₂ generally, and soil/wetland fluxes in particular.

2.3. Hydrogen sulfide

Of the four gases considered in this paper, the estimates for this one are the most tenuous. It may be that the budget presented here simply acts as an “Aunt Sally”, and others will refine the estimates. There are very little data, and very large uncertainties even in the size of the overall budget. Estimates vary between 16–60 Tg a⁻¹ (Kelly and Smith, 1990; Andreae and Jaeschke, 1992). H₂S is the main reduced sulfur gas emitted from the

Table 7
Global sources and sinks of CS₂ to the atmosphere

Source/sink	Annual flux (Tg a ⁻¹)	Reference
<i>Sources</i>		
Open ocean	0.11 ± 0.04	See text, Xie et al. (1997)
Coastal ocean (including salt-marsh and estuaries)	0.07 ± 0.04	See text, Xie et al. (1997)
Anoxic soils	0.07 ± 0.06	See text
Wetlands	0.02 ± 0.02	See text
Volcanism	0.05 ± 0.04	Chin and Davis (1993,1995)
Anthropogenic	0.34 ± 0.17	Chin and Davis (1993)
Total source	0.66 ± 0.19	
<i>Sinks</i>		
Reaction with OH	0.57 ± 0.25	Chin and Davis (1993)
Oxic soils	0.44 ± 0.38	See text
Total sink	1.01 ± 0.45	
Total imbalance	0.35 ± 0.49	Budget balanced to within uncertainties

continents and from plants, and is also a significant component of the marine budget (Möller, 1984a,b; Andreae, 1990; Butcher et al., 1992; Schlesinger, 1996).

It is a relatively insoluble gas (K_H (25°C) 87.14–103.23 × 10⁻³ mol dm⁻³ atm⁻¹), (DeBruyn et al., 1995; Wilhelm et al., 1977), and from the few available seawater measurements (Andreae, 1990) seems supersaturated in seawater. However, it is also clear that this compound has an extensive particulate/dissolved phase chemistry in seawater (Yao and Millero, 1996; Zhang and Millero, 1994). This not only acts to decrease the volatility of H₂S in seawater (hence reducing the sea–air flux), but also the complex speciation confuses as to exactly what is being measured by the conventional analytical procedure of sparge and trap (Radford-Knoery and Cutter, 1994; Walsh et al., 1994). The main source of H₂S in the oceans appears to be the hydrolysis of OCS (Elliot et al., 1989). It has also been suggested that marine algae emit H₂S directly (Andreae, 1990), whilst this is not yet generally accepted, there is now evidence that marine H₂S production may be linked to primary production, (Radford-Knoery and Cutter, 1994). Diurnal variation has been observed in both seawater and marine atmosphere concentrations (Andreae, 1990; Cooper and Saltzman, 1987).

With all this in mind the oceanic fluxes have been estimated by use of atmospheric concentrations, and a knowledge of the main sink reaction in the lower troposphere: reaction with OH (Cox and Sheppard, 1980). Marine boundary layer concentrations range from a few ppt to a few hundred ppt (Cooper and Saltzman, 1993; Gregory et al., 1993a,b; Herrman and Jaeschke, 1984), although the higher concentrations were influenced by polluted air masses, and H₂S concentrations were higher in the northern hemisphere. If a mean

tropospheric concentration of 7 pptv is used along with the reported standard deviations (Cooper and Saltzman, 1993; Andreae et al., 1993), this gives an open ocean sea-air flux of 1.5 ± 0.6 Tg a⁻¹. This is slightly lower than those calculated previously (Andreae, 1990; Toon et al., 1987), and this difference represents an increase in the number of observations available.

Given the small amount of data available, H₂S concentrations seem higher over (and in) coastal oceans (Andreae, 1993; Herrman and Jaeschke, 1984; Delmas and Servant, 1982). The coastal ocean source has been estimated by the same method as that used for the open ocean, assuming an average concentration of 14 ppt, this gives a sea–air flux of 0.3 ± 0.1 Tg a⁻¹.

Estuaries, mudflats, salt marshes and *Spartina Alterniflora* emissions have been grouped together as geographically they occupy the same areas. Many workers have determined H₂S concentrations in such environments, for example (Stuedler and Peterson, 1984; Goldan et al., 1987; Bates et al., 1992; Jaeschke, 1978; Jorgenson and Okholm-Hansen, 1985; Carroll et al., 1986; Castro and Dierberg, 1987; Jaeschke et al., 1994). Their observations have been characterized by great variability in measured concentrations both from the muds as well as the vegetation (a 10,000 fold difference has been observed at the same site (Harriss and Niki, 1984)). Many variables including the state of the tide, the temperature, light, pH have been found to be important in determining the measured H₂S concentration (Aneja, 1986).

Again, data collected by the sulfur free air methodology are not used in this review. Different workers have estimated various budget components of the salt-marsh/estuarine system. Emissions from *Spartina Alterniflora* have been estimated as 0.001–0.05 Tg a⁻¹ (Stuedler and

Peterson, 1984), whilst both estuaries and inter-tidal mudflats are each proposed as sources of up to 0.002 Tg a^{-1} (Bates et al., 1992; Jaeschke, 1978; Jorgenson and Okholm-Hansen, 1985). Tidal creeks have been estimated to have a source strength of 0.06 Tg a^{-1} (Stuedler and Peterson, 1984). Saline marshes an emission of up to 0.003 Tg a^{-1} (Bates et al., 1992), or $0.018 \pm 0.007 \text{ Tg a}^{-1}$ for a *Juncus* salt marsh and a Mangrove swamp (Castro and Dierberg, 1987) (surface areas used from Table 5).

A straight summation (averaging multiple determinations) of these using the data from Table 5 gives a range of $0.11\text{--}0.23 \text{ Tg a}^{-1}$ from the entire system. This is slightly less than the $0.8\text{--}0.9 \text{ Tg a}^{-1}$ from salt marshes proposed previously (Kelly and Smith, 1990). In the absence of any other reliable data, an average of these estimates seems a useful way forward, i.e. $0.5 \pm 0.35 \text{ Tg a}^{-1}$. The observation of non-emission by some particular *Spartina Alterniflora* (Carroll et al., 1986) has been noted.

It is known that many higher plants release H_2S into the atmosphere as a result of the HPCA enzyme reacting with OCS instead of (sometimes in preference to) CO_2 (Protoschill-Krebs et al., 1996; Kesselmeier and Merk, 1993). It is also entirely possible that the same mechanism is responsible for H_2S emission by lichens (Gries et al., 1994). It is known that plants emit H_2S when exposed to OCS (Bartell et al., 1993). As far as can be established, for every mole of OCS processed by HPCA, a mole of H_2S is emitted via the stomata (Protoschill-Krebs et al., 1996). If this is correct, then the sink of OCS to higher plants should be indicative of a minimum for the source of H_2S from them. This sink was estimated earlier (see Table 4) as $0.56 \pm 0.10 \text{ Tg OCS a}^{-1}$. This translates to $0.32 \pm 0.06 \text{ Tg H}_2\text{S a}^{-1}$.

There is one other specific mechanism known for emission of H_2S from plants. It is known that some plants emit H_2S when faced with excess sulfur compounds (Materna, 1966), it is thought that this is a detoxification mechanism (Rennenberg, 1991). This behavior has now also been observed with conifers (Kindermann et al., 1995a,b), and importantly at ambient atmospheric SO_2 levels. As this process is separate from the OCS mechanism, and most of the remaining Boreal Forest is in areas not remote from pollution; it may be that this could be a new release path for H_2S into the atmosphere. Although by using the SO_2 uptake rate of these trees, in conjunction with the photosynthetic respiration rates, the flux from this process cannot be much more than $0.05 \pm 0.03 \text{ Tg a}^{-1}$. The sample numbers involved in the original studies mean that these estimates are tenuous in lieu of further work in this area.

Tropical forests (or more possibly, wet tropical forest soils) seem to be prodigious sources of H_2S . Direct estimates based on measurements include $2.0 \pm 1.0 \text{ Tg a}^{-1}$, (Delmas et al., 1980; Delmas and Servant, 1983), (vegetation) 0.23 Tg a^{-1} (soils) 0.01 Tg a^{-1} (Andreae and Andreae, 1988; Andreae et al., 1990). Others not based on

direct measurements include $22 \pm 19 \text{ Tg a}^{-1}$ (Schlesinger, 1996; Kelly and Smith, 1990), $3.2 \pm 2.4 \text{ Tg a}^{-1}$ (Shooter et al., 1995).

There have also been some newer measurements of H_2S above and in tropical forests, which allow independent estimation of these sources. An average concentration of $7.3 \pm 1.9 \times 10^{-8} \text{ g m}^{-3}$ over the lowest 700 m can be calculated from the pooled results of two studies (Andreae and Andreae, 1988; Andreae et al., 1990). Using the data contained in Table 5 and a residence time of 1 d, (for H_2S in the lower troposphere) (Cox and Sheppard, 1980), a global source flux of $0.42 \pm 0.12 \text{ Tg a}^{-1}$ can be calculated. Careful interpolation of data from polluted sites in Brazil (Jaeschke et al., 1994) indicate what appear to be background concentrations of H_2S at $2.5 \times 10^{-6} \text{ g m}^{-3}$ over the lowest 700 m. However, these concentrations seem so high compared to any other available data, they have not been used in this estimation.

This soils estimate will exclude emissions from tropical forest soils as this has already been dealt with above. Much of the discussion on soils for the other sulfur compounds is not irrelevant when applied to H_2S . Again, the range of available measurements is very small, and characterized the use of sulfur free air in sampling enclosures. If those measurements are ruled out, there appears to be very little other direct data on non-tropical forest soils. Measurements from German bogs and swamps (Jaeschke and Herrmann, 1981) have been used in lieu of data from anoxic soils, and yield concentrations (1 m above the surface) of $0.68 \pm 0.54 \times 10^{-9} \text{ g m}^{-3}$. The author's comment that possibly the flux from these soils has been over-estimated in the past is noted. These three single measurements, combined with data in Table 5 and a boundary height of 500 m yield an annual flux from soils of $0.002 \pm 0.0016 \text{ Tg a}^{-1}$. Clearly, this can only be a provisional "stab in the dark".

As for soils, the estimates for freshwater wetlands are again rather tenuous. Previous estimates of the source strength range in $0.004\text{--}12 \text{ Tg a}^{-1}$ (Cooper et al., 1987; Harriss and Niki, 1984; Kelly and Smith, 1990). Other data (Pearce, 1998) from peat bogs indicates that the very high end of this range is not probable. Those measurements which are based on ambient air include that mentioned above (Jaeschke and Herrmann, 1981); which with the data in Table 5 for wetlands and the same boundary height yields a source strength of $< 0.001 \pm 0.001 \text{ Tg a}^{-1}$. There is also work (Castro and Dierberg, 1987) on a Cypress marsh in which a flux of $0.12 \pm 0.03 \text{ g m}^{-2} \text{ a}^{-1}$ was measured. Using the data from Table 5, this translates into a global flux estimate of $0.6 \pm 0.16 \text{ Tg a}^{-1}$. In the same work, the authors failed to detect an H_2S flux from a riverine marsh.

The category "freshwater wetlands" is very much a mixed bag of profoundly different systems, e.g. a peat bog and a riverine marsh. This said, and bearing in mind the notorious variability of these systems (Aneja, 1986),

a series of numerically similar flux estimates might not be expected. The proposal for H₂S emissions from freshwater wetlands will be taken as the mean of the three (including the zero) measurements above (Jaeschke and Herrmann, 1981; Castro and Dierberg, 1987), i.e. $0.20 \pm 0.21 \text{ Tg a}^{-1}$. This estimate has closed down considerably both the magnitude and uncertainties in this system and makes this a very different estimate from those previously proposed (Cooper et al., 1987; Harriss and Niki, 1984; Kelly and Smith, 1990).

Available estimates for the Volcanic/Geothermal flux range between $1.0 \pm 0.1 \text{ Tg a}^{-1}$ (Andreae, 1990), less than 2 Tg a^{-1} (Möller, 1984b), “greatly under-estimated” (Jaeschke and Herrmann, 1981), $1.05 \pm 0.94 \text{ Tg a}^{-1}$ (Shooter et al., 1995). This final estimate (which was independent of the prior two, assumed that there are on the planet somewhere in the region of 140 active volcanoes (McHenry, 1992), along with associated geothermal areas. It also assumed an average area of 1 km^2 per system, and a boundary height of 500 m. The most recent data on H₂S composition of volcanic atmospheres (Jaeschke and Herrmann, 1981) was then averaged within that 1 km^2 area to yield the flux. This estimate has been selected as it is not only based on a transparent methodology, it also conforms to what we know from ice-cores of the historical restraints on volcanic emissions (Möller, 1984b).

There seems no reason to review the anthropogenic H₂S flux of 3 Tg a^{-1} (Möller, 1984b), except that the source from car exhausts has been included (Fried et al., 1992; Watts and Roberts, 1999) and a 10% uncertainty has been added, see Table 8.

The only other known source in the atmosphere is the oxidation of OCS by the OH radical. This is a multi-step process, and has been studied in detail (Chin, 1992). The results of that work indicate a net source to the atmosphere of $0.08 \pm 0.07 \text{ Tg H}_2\text{S a}^{-1}$ (Chin and Davis, 1993).

There seems to be only one sink in the atmosphere for H₂S. It is a multi-step process of which the first step is the abstraction reaction with the OH radical (Brimblecombe, 1996). Assuming a 2 km scale height and 10 ppt as an average atmospheric concentration, this yields a sink of circa $8.5 \pm 2.8 \text{ Tg a}^{-1}$.

Table 8 contains a provisional budget for H₂S. This budget is approximately balanced, although the uncertainty is very large. This proposed budget is smaller than previously ($16\text{--}60 \text{ Tg a}^{-1}$ (Kelly and Smith, 1990; Andreae and Jaeschke, 1992)). However, many of the estimates put forward here are based on very little data, and crucially, soils and wetlands data obtained with sulfur-free air has been excluded. More work on H₂S is required to allow a narrowing of the uncertainty associated with the vegetation and open ocean sources, as well as the soils/wetlands problem.

Table 8
Global sources and sinks of H₂S to the atmosphere

Source/sink	Annual flux (Tg a ⁻¹)	Comment/Reference (Tg a ⁻¹)
<i>Sources</i>		
Open ocean	1.50 ± 0.60	See text
Coastal ocean	0.30 ± 0.10	See text
Salt-marshes and estuaries	0.50 ± 0.35	See text
Vegetation	0.37 ± 0.07	See text
Tropical forests	0.42 ± 0.12	See text
<i>Soils</i>		
(not tropical forest soils)	0.002 ± 0.002	See text
Wetlands	0.20 ± 0.21	See text
Volcanism/Geothermal	1.05 ± 0.94	Shooter et al. (1995)
OCS + OH	0.08 ± 0.07	Chin and Davis (1993)
Anthropogenic	3.30 ± 0.33^a	Möller (1984b); Fried et al. (1992); Watts and Roberts (1999)
Total source	7.72 ± 1.25	
<i>Sinks</i>		
Reaction with OH	8.50 ± 2.80^b	See text
Total sink	8.50 ± 2.80	
Total imbalance	0.78 ± 3.1	Budget balanced to within uncertainties

^aAutomobile emissions assume 2.5% of SO₂ emission assumed to be emitted as H₂S in UK, Europe and Eurasia, anthropogenic SO₂ emissions from this area estimated at 13.7 Tg a^{-1} for year 2000.

^bIn the absence of other data, the efficiency of this reaction has been assumed to be unity.

2.3.1. Dimethyl sulfide

In terms of sea \Rightarrow air flux, DMS is thought to be the major sulfur gas released from the oceans (Andreae, 1990), and as such has been the subject of much work. To protect their cells from dehydration (via osmotic pressure effects) it is thought (Vairavamurthy et al., 1985) that marine algae produce a Zwitter ion molecule (dimethyl sulfonium propionate or dimethyl- β -propiothetin (DMSP)) to act as an internal osmotic pressure regulator. DMSP is released in the normal life operations of the algae (the “leaky cell” model (Vairavamurthy et al., 1985)), as well when the cell walls are ruptured by either copepod grazing (Dacey and Wakeham, 1986), or senescence following a bloom condition (Nguyen et al., 1998). DMSP is then converted to DMS by cleavage of the secondary S–C bond, also giving acrylic acid. This process is not well understood, but is thought to be mediated by biological or biochemical, rather than chemical means (Kelly and Smith, 1990). This gas is very insoluble ($K_H = 0.474\text{--}0.478 \text{ mol dm}^{-3} \text{ atm}^{-1}$ ($T = 298 \text{ K}$ and 32.5 salinity units, (Dacey et al., 1984; DeBruyn et al., 1995)), and is therefore degassed to the atmosphere quite rapidly. Whilst in solution it also undergoes photosensitized oxidation to form dimethyl sulfoxide (DMSO) (Brimblecombe and Shooter, 1986).

Estimates of the size of the total global budget range from 15–109 Tg a⁻¹ (Erickson et al., 1990; Kelly and Smith, 1990; Andreae, 1990; Bates et al., 1992; Schlesinger, 1996). The main reasons for this large range are differences in the way that the marine portion (by far the largest) of the budget is calculated. There are two approaches to the problem, but both require data of large seasonal and geographic coverage (Holligan et al., 1987). The first approach involves the use of the measured seawater concentrations and a mass transfer coefficient (or piston velocity) (Liss and Slater, 1974). The other is to base the flux estimate on atmospheric concentrations and residence times. Much of the uncertainty with these DMS flux calculations hinges around the use of the first approach, and uncertainties in this mass transfer coefficient. It can be based on CO₂, ³He or Rn emission rates and it varies with wind-speed (Liss and Merlivat, 1986; Nguyen et al., 1984; Wanninkhof, 1992; Upstill-Goddard et al., 1991). It is also affected by the composition and nature of the surface micro-layer, which itself is not well understood. In this work, the latter approach (atmospheric concentrations and residence times) has been adopted to estimate the marine DMS fluxes. The results of these calculations will then be compared to those based on seawater concentrations.

It is thought that the main sinks of DMS are reaction with OH during the daytime, and with NO₃ during the nighttime (Wilson and Hirst, 1996). The rate constants for these processes are such that an average residence time between 24 and 28 h (shorter times in polluted systems) is appropriate (Barnes et al., 1988).

Some of the earlier gas phase measurements (Barnard et al., 1982; Andreae et al., 1985) suffered from an analytical problem (oxidants co-trapped with DMS). This resulted in lowered DMS concentrations (Andreae et al., 1985; Johnson and Bates, 1993), and hence those measurements are either excluded from this work, or used as minimum values. Seasonal and diurnal variation in marine atmospheric DMS concentrations have been observed (Andreae and Raemdonck, 1983). Table 9 contains a summary of atmospheric DMS measurements along with flux estimates. Methodologies of estimation are given in Table 9. Surface area data from Table 5 has been used throughout.

The recommendation for the annual DMS flux from the oceans is $20.7 \pm 5.2 \text{ Tg a}^{-1}$ (Table 10). Although this is very different from earlier estimations (Andreae, 1990), it is at the lower end of the range of DMS flux estimates adopted by most recent workers (Erickson et al., 1990). The estimate $31 \pm 21 \text{ Tg a}^{-1}$ (Bates et al., 1992) which is based on air–sea exchange models is higher but not inconsistent with the recommendation from this work.

Salt marshes and estuaries have been the subject of a number of studies. As previously, work carried out using sulfur-free air is excluded from this review. The flux of DMS from salt marshes (including those containing *Spartina spp.*) has been variously measured as $5560 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$ (Stuedler and Peterson, 1984,1985), $455 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$ (Cooper et al., 1987a), $60.2 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$ (Hines et al., 1993). Like the other reduced sulfur compounds, great variability in DMS fluxes (often on the scale of metres) has been reported (Cooper et al., 1987a,b; Aneja, 1986). Interestingly, well-drained tidally flooded sites seem to produce much more DMS than similar sites with less good drainage (Hines et al., 1993). Emissions estimates from tidal creeks have been measured as $310 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$ (Stuedler and Peterson, 1984,1985), $110 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$ (Cooper et al., 1987a). Confirming previous work, Jaeschke et al. (1994) failed to measure any significant flux of DMS from mudflats. Addition of these component fluxes (averaging within each class) along with the data in Table 5 yields an annual flux from estuaries, salt marshes of $0.07 \pm 0.06 \text{ Tg a}^{-1}$.

The emissions of DMS from vegetation are also a little uncertain, as there seems an almost total dearth of data from temperate and boreal regions, but more from tropical forests. There is laboratory data which show that DMS emissions from plants are temperature dependant (Fall et al., 1988). This might be expected to give seasonal cycles at high latitudes.

For the tropical forest in the rainy season, estimates vary between $27.7 \pm 1.6 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$ (Brazil) (Jaeschke et al., 1994) to $15.0 \pm 6.5 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$ (Brazil) (Andreae et al., 1990). For the dry season the flux estimates are $67.9 \pm 34.0 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$ (Guyana) (Gregory et al., 1986) to $179.2 \pm 80 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$

Table 9
Boundary layer maritime DMS measurements

Location and area	Concentration (10^{-9} g m $^{-3}$)	Derived flux (Tg a $^{-1}$)	Reference and comment
<i>High productivity</i>	<i>Minimum</i>	5.0 ± 1.1 ^a	
Equatorial Pacific	156 ± 36	2.9 ± 0.7 ^b	Andreae and Raemdonck (1983). Diurnal variation
Equatorial Pacific	301 ± 78	6.5 ± 1.8 ^c	Andreae et al. (1985). Reported as low
Antarctica	806 ± 300 ^d	5.8 ± 2.2 ^{c,e}	Wylie et al. (1992). Austral summer
Arctic Ocean	830 ± 800	5.9 ± 5.8 ^{c,e}	Hobbs et al. (1992). June
Equatorial Pacific	108 ± 10	1.7 ± 0.2 ^f	Bandy et al. (1993a,b)
Equatorial Atlantic	213 ± 43	6.9 ± 1.6 ^b	Gregory et al. (1986). August/September
<i>Transition or temperate</i>	<i>Minimum</i>	1.9 ± 0.7 ^g	
South Pacific	335 ± 99	7.2 ± 2.3 ^c	Andreae et al. (1985). Reported as low, summer
South Pacific	41 ± 9 ^h	0.1 ± 0.02 ^c	Harvey et al. (1992). Seasonal, winter
North Atlantic	122 ± 122	1.9 ± 1.9 ^f	Johnson and Bates (1993). Diurnal variation, August
North Atlantic	152 ± 81	3.2 ± 1.7 ^c	Andreae et al. (1985). Reported as low, summer
North Atlantic	112 ± 20	2.3 ± 0.5 ^c	Herwitt and Davison (1992). Annual average of 2 yr data
<i>Low productivity</i>	<i>Minimum</i>	7.5 ± 2.1 ⁱ	
Tropical Atlantic	125 ± 56	3.5 ± 1.6 ^f	Johnson and Bates (1993). Diurnal variation, August
Tropical Atlantic	177 ± 50	6.6 ± 2.0 ^c	Andreae et al. (1985). Reported as low, summer
Tropical Atlantic	213 ± 43	6.9 ± 1.6 ^b	Gregory et al. (1986). August/September
Tropical Atlantic	248 ± 120	9.2 ± 4.5 ^c	Putard et al. (1992). October
Tropical Pacific	248 ± 136	9.2 ± 5.1 ^c	Nguyen et al. (1984). Austral spring
Atlantic	422 ± 329	15.6 ± 12.3 ^c	Andreae et al. (1985). Reported as low, summer
North Pacific	47 ± 25	1.7 ± 0.9 ^c	Andreae et al. (1988). May (marine)
<i>Coastal/shelf</i>	<i>Minimum</i>	6.3 ± 4.6 ^j	
Brittany, France	41 ± 40	0.5 ± 0.5 ^c	Nguyen et al. (1983). air mass terrestrial
Brittany, France	868 ± 372	10.6 ± 4.6 ^c	Luce et al. (1992). Summer (coastal and marine)
Brittany, France	1581 ± 1556	31.5 ± 31.2 ^k	Putard et al. (1999). May-June, 1993 (coastal)
Brittany, France	1085 ± 620	21.6 ± 12.5 ^k	Putard et al. (1999). May-June, 1989, (marine)
North-West USA	207 ± 194	1.6 ± 1.5 ^l	Berresheim et al. (1993). April (marine)
North-West USA	69 ± 19	1.4 ± 0.4 ^m	Berresheim et al. (1993). April (coastal)
North-West USA	136 ± 37	1.7 ± 0.5 ^c	Andreae et al. (1988). May, terrestrial
Total	Minimum	20.7 ± 5.2	

^aAverage of data.

^bBoundary layer 700m, τ set at 28 h.

^cAssumed marine boundary layer of 800m, $\tau = 28$ h.

^dAlso consistent with Staubes and Georgii (1992); Kirst et al. (1992) and Leck (1992).

^ePolar oceans assumed productive for only 4 months a $^{-1}$.

^fBoundary layer 600m, τ set at 28 h.

^gAverage balanced seasonally: Harvey et al. (1992) data weighted.

^hData not entirely extractable, mean of 9 ppt assumed.

ⁱAverage of data, oligotrophic data not seasonal for DMS (Staubes and Georgii, 1992).

^jOnly data with marine air mass back trajectories used, average balanced seasonally using dismantled data (Hewitt and Davison, 1992).

^kBoundary layer 1300m, τ set to 28 h.

^lBoundary layer 500m, τ set to 28 h.

^mBoundary layer 1300m, τ set to 28 h.

(Amazon Basin) (Andreae and Andreae, 1988). Averaging within the wet and dry seasons, this yields an annual flux from tropical forests of $72.5 \pm 21.8 \times 10^{-3}$ g m $^{-2}$ a $^{-1}$. Using the data in Table 5, this gives an annual emission of 1.6 ± 0.50 Tg a $^{-1}$.

There are annual mean measurements of DMS emissions from maize and wheat which suggest a source of $4.94 \pm 0.50 \times 10^{-3}$ g m $^{-2}$ a $^{-1}$ (Kanda et al., 1995). Finally, work on lichens yields an annual DMS emission flux of $0.93 \pm 0.62 \times 10^{-12}$ g dw $^{-1}$ s $^{-1}$ (Gries et al.,

Table 10
Global sources and sinks of DMS to the atmosphere

Source/sink	Annual flux (Tg a ⁻¹)	Comment/reference (Tg a ⁻¹)
<i>Sources</i>		
Oceans	20.70 ± 5.20	See Table 9 and text
Salt-marshes and estuaries	0.07 ± 0.06	See text
Vegetation	1.58 ± 0.86	See text (not including tropical forests)
Tropical forests	1.60 ± 0.50	See text, Andreae et al. (1990)
Soils	0.29 ± 0.17	See text
Wetlands	0.12 ± 0.07	See text
Anthropogenic	0.13 ± 0.04	See text
Total source	24.49 ± 5.30	

Note: In the absence of other data, the efficiency of this reaction has been assumed to be unity. Automobile emissions assume 2.5% of SO₂ emission emitted as H₂S in UK, Europe and Eurasia, anthropogenic SO₂ emissions from this area estimated at 13.7 Tg a⁻¹ for year 2000.

1994). If a typical provenance of lichens is 740 kg dw ha⁻¹ (Kuhn et al., 1999), this yields a DMS flux from this source of $2.17 \pm 1.45 \times 10^{-3}$ g m⁻² a⁻¹. This is about half the rate for maize and wheat (Kanda et al., 1995).

The lichen source can be estimated if it is assumed that the growth area is the temperate and boreal forests with damp-lands (see Table 5). If production is assumed as 6 months of the year with an average 10 h light day (Gries et al., 1994) a global source of 0.08 ± 0.05 Tg a⁻¹ can be calculated.

For the other members of the terrestrial plant kingdom, there is very little data. However, quite apart from the fact that some plants do emit DMS (see above), there is a lot of other circumstantial evidence that most vegetation generally is a source of DMS (Lovelock et al., 1972). A hypothetical DMS production rate for all other plants could be a mean of those used above for lichens, tropical forests and wheat and maize, i.e. $26.5 \pm 13.3 \times 10^{-3}$ g m⁻² a⁻¹ (50% uncertainty attached). Using the data in Table 5 (total soil area - damp-lands, anoxic soils and tropical forests) yields an annual source of DMS to the atmosphere of about 1.50 ± 0.86 Tg a⁻¹. With the rest of the terrestrial plants, this gives a global flux of 1.58 ± 0.86 Tg a⁻¹. Clearly, this is very much an educated guess until firm data is forthcoming.

DMS fluxes from soils have been measured in tropical forests and from more temperate crop soils. The annual average production of DMS over a number of different upland Chinese and Japanese soils was $2.3 \pm 0.5 \times 10^{-3}$ g m⁻² a⁻¹ (Kanda et al., 1995; Yang et al., 1996). Other work on tropical forest soils yielded emission fluxes of (dry season) $7.1 \pm 5.9 \times 10^{-3}$ g m⁻² a⁻¹ (Jaeschke et al., 1994; Andreae and Andreae, 1988) and (wet season) $1.3 \pm 0.26 \times 10^{-3}$ g m⁻² a⁻¹ (Andreae et al., 1990). These soils were in the Amazon Basin and Braz-

ilian tropical forests. Averaging these flux rates gives a source strength of $3.6 \pm 2.0 \times 10^{-3}$ g m⁻² a⁻¹. Using the data in Table 5 (without tropical forests) yields an annual soil flux of 0.29 ± 0.17 Tg a⁻¹.

Sulfur emissions from freshwater wetlands are not dominated by DMS (Bates et al., 1992), however, these areas do seem to produce DMS (Hines et al., 1993). In wetlands where there is standing water, it is likely that it is produced from DMSP (ex algae) as in marine systems but at much lower levels. However, it can lead to significant transient concentrations $40\text{--}100 \times 10^{-9}$ g dm⁻³ (temperate lake-water, bog water and ponds) (Caron and Kramer, 1994; Bechard and Rayburn, 1979). A series of summertime measurements on Canadian bogs yielded considerably higher concentrations of $466 \pm 357 \times 10^{-9}$ g dm⁻³ (Nriagu et al., 1987). Using a transfer coefficient these authors estimated a flux into the atmosphere from these systems of $81 \pm 20 \times 10^{-3}$ g m⁻² a⁻¹. In many bog systems, the bacteria responsible for methanogenesis are in direct competition with those which are sulfur reducers (Urquhart and Gore, 1973). In these cases, sulfur production is limited by aerial sulfur input because this the main source of sulfur to the bog system. In this Canadian study, it was shown by using isotope data that the bog system was effectively re-emitting about 30% of this incoming (anthropogenic) sulfur flux. Hence in this study, the flux determined will be split between biogenic and anthropogenic, i.e. 33% anthropogenic and 66% biogenic. This study (Nriagu et al., 1987) then yields an anthropogenic flux of $27 \pm 7 \times 10^{-3}$ g m⁻² a⁻¹ and a biogenic flux $54 \pm 12 \times 10^{-3}$ g m⁻² a⁻¹.

Emissions from paddy fields have also been measured as $15.1 \pm 4.1 \times 10^{-3}$ g m⁻² a⁻¹ (Kanda et al., 1992; Yang et al., 1996). In a major study, emission fluxes of DMS were measured in a freshwater mangrove ($22.1 \pm 5.1 \times 10^{-3}$ g m⁻² a⁻¹) and marsh-grass site

($8.5 \pm 2.1 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$) (Hines et al., 1993). The “biogenic” portion of the Canadian DMS emission flux (Nriagu et al., 1987) is considerably higher ($54 \pm 12 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$) than the others cited above. However, this is thought to reflect the heterogeneity of the “freshwater wetlands” classification. To estimate the freshwater wetlands emission, all of these measurements have been averaged ($24.9 \pm 13.8 \times 10^{-3} \text{ g m}^{-2} \text{ a}^{-1}$). Along with the data in Table 5 a DMS flux from freshwater wetlands is proposed as of $0.12 \pm 0.07 \text{ Tg a}^{-1}$.

The main sink of DMS in the atmosphere is reaction with OH by day, and NO_3 by night (Turnipseed and Ravishankara, 1993; Jensen et al., 1991; Wilson and Hirst, 1996). The detailed mechanisms are understood at a basic level (Yin et al., 1990a,b; Barnes et al., 1996). The OH reaction can be either an abstraction or an addition reaction: effectively the two paths compete. However, only at low temperatures ($< 300 \text{ K}$, temperate winter) is the addition reaction the major pathway (Wilson and Hirst, 1996). The NO_3 reaction is an abstraction, with a reaction rate that is of the same order as the OH abstraction. Kinetic studies (Barnes et al., 1988, 1994) indicate residence times of DMS in the atmosphere between 24–28 h dependent on atmospheric composition and temperature. The major source term in the mass balance is marine. It, as well as some of the other source terms have been calculated by using atmospheric residence times. Hence, it seems not useful to then estimate the sinks in the same way – the balance or not of the budget would be meaningless.

3. Conclusions

This study investigates the distribution and magnitudes of the global sources and sinks of the four main reduced sulfur compounds in the atmosphere, OCS, DMS, H_2S and CS_2 . Full budgets are presented for all except DMS, for which an inventory of sources has been assembled.

For OCS, total global sources and sinks are estimated as 1.31 ± 0.25 and $1.66 \pm 0.79 \text{ Tg a}^{-1}$ respectively. This budget is balanced within the uncertainties of the estimates. The most urgent need here is meaningful soil emission fluxes. Global sources and sinks of H_2S are estimated as 7.72 ± 1.25 and $8.50 \pm 2.80 \text{ Tg a}^{-1}$ respectively. Again, broadly this budget is balanced within the uncertainties. It should be stressed that of all the budgets presented here; this is based on the least data, and should be regarded as provisional. Estimates of sources and sinks of CS_2 are 0.66 ± 0.19 and $1.01 \pm 0.45 \text{ Tg a}^{-1}$, respectively. This budget is relatively unbalanced (although a balance is within the uncertainties of the estimates). More data is urgently needed on soils emissions to enable a judgement to be drawn on whether this gas acts like OCS with soils. For DMS only a sources esti-

mate has been prepared, $24.45 \pm 5.30 \text{ Tg a}^{-1}$. The proposed emissions inventory is consistent with more recent budgets.

The budgets for OCS and DMS seem relatively secure, whilst those for H_2S and CS_2 contain much greater uncertainty. For DMS, more information on emissions from plants is required. For all of these gases, data on soils and vegetation emissions are sparse, although the most urgent priority might be the role of freshwater wetlands in non-tropical areas.

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