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Contributions of H_2S to the Atmospheric Sulfur Cycle

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Abstract – H_2S is a most important biogenic sulfur compound with regard to the atmospheric sulfur cycle. Our present knowledge of the spatial and temporal distribution of this trace gas is rather incomplete owing to unreliable analytical methods. Therefore, a new method for the analysis of H_2S in the μg-range was applied. This paper deals with the results of ground- and aircraft measurements of H_2S in unpolluted air over swamps and tidal flats. Based on the measured vertical distributions a removal coefficient of 2.3×10^{-5} sec^{-1} and an average lifetime of 12 hours were calculated. Some conclusions of the contribution of H_2S to the atmospheric sulfur budget are added.

Key words: Hydrogen sulfide; Lifetime; Measurements; Sulfur budgets.

Introduction

In the atmospheric sulfur cycle, the biosphere is of great importance as a source of several gaseous sulfur compounds. To balance the global sulfur cycle several authors estimated that 50 percent or more of the total atmospheric sulfur budget originates from biogenic H_2S. Kellogg *et al.* (1972) assume 268×10^6 ton yr^{-1} as production-rate from soils and coastal waters. More recently Robinson and Robbins (1975) have figured the amount of 116×10^6 ton yr^{-1} as the contribution of biogenic sulfur to the atmospheric sulfur cycle. All authors agree that there is a great uncertainty in the estimation of the amounts of naturally generated sulfur since only few data on the atmospheric distribution of H_2S or other gaseous organic sulfur compounds are available (Georgii, 1975). Some years ago Junge described the situation as follows (1972): 'It looks as if a substantial progress in our understanding of the sulfur cycle cannot be expected unless better analytical methods for H_2S become available.'

We were therefore motivated to develop a sensitive method for the analysis of atmospheric H_2S in unpolluted air using a filter technique similar to the procedure described by Natusch *et al.* (1972). Using a new way of handling which is described by Jaeschke *et al.* (1977) a detection limit of 0.001 μg Nm^{-3} was obtained. Before the method was applied for atmospheric measurements the microbiological sulfur cycle had to be considered in order to have an idea about where and in which amounts

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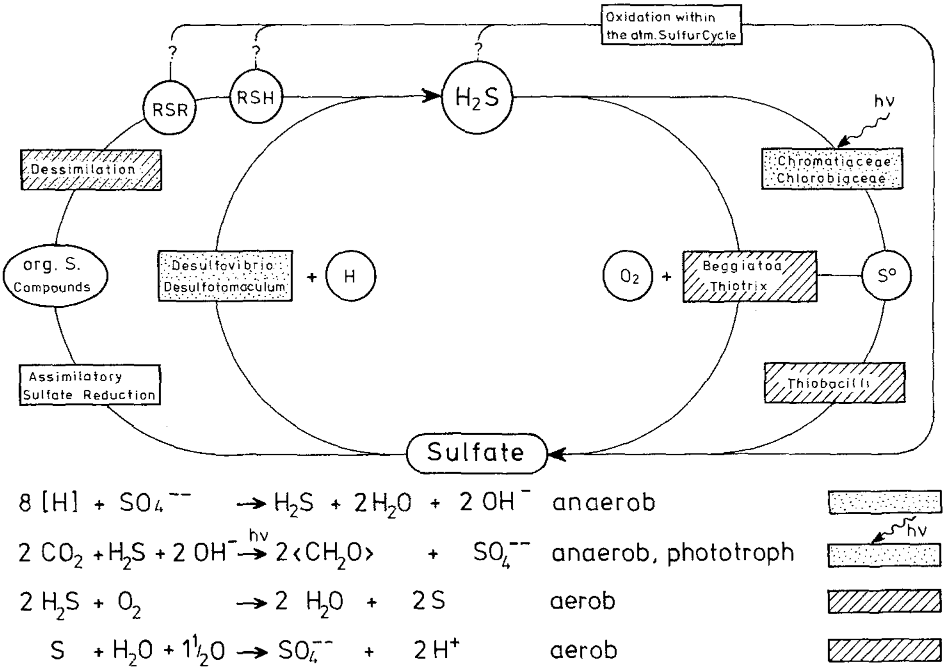
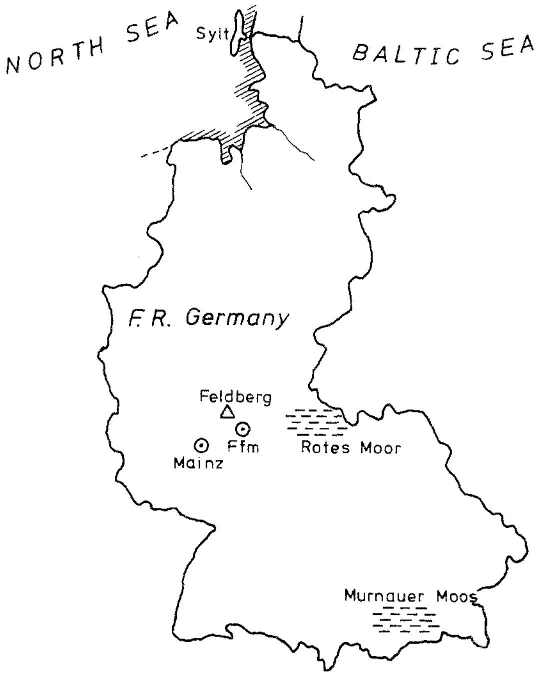


Figure 1
Schematic diagram of the microbiological sulfur cycle and its possible influence on the atmosphere.

H_2S is released from the surface of the earth by natural sources. This cycle is shown schematically in Fig. 1.

Beside the assimilatory sulfate reduction the sulfate respiration of the strict anaerobes. Desulfofibrio and Desulfotomaculum is the most important biogenic source of H_2S. These bacteria reduce sulfate to hydrogen-sulfide using incorporated organic acids as H-donors. This activity is located in anaerobic swamps, muds and in eutrophic water layers in the absence of oxygen. The H_2S generated by this process is normally unable to escape from the anaerobic regions into the atmosphere, because it is recycled by microbiological oxidation. The colored sulfur bacteria Chromatiaceae and Chlorobiaceae perform an anaerob photosynthesis in the boundary layer between the anaerobic and aerobic zone. Using the energy of light carbonhydrates and sulfate are formed by CO_2 and H_2S. Furthermore, under aerobic conditions the bacteria Beggiatoa and Thiotrix are able to oxidize the H_2S directly with oxygen to form sulfur or sulfate (SCHLEGEL, 1974). This leads to a recycling of the H_2S generated in anaerobic soils or in eutrophic waters before it reaches the atmosphere and there is only little chance to detect measurable amounts in the atmosphere, even with the most sensitive method.

Biogenic H_2S may only escape to the atmosphere in measurable amounts when the anaerobic zone of the ground is close to the atmospheric boundary layer. These



H_2S CONCENTRATIONS 1m ABOVE GROUND

DATE	PLACE	CONC (µg/Nm³)	GROUND	REMARKS
8.10.1975	RANTUM/SYLT	0,11	TIDAL FLAT	STRONG WIND
8.-11.3.1976	KL. FELDBERG	0,35	ROCKS	MEAN-DAYTIME
8.-11.3.1976	KL. FELDBERG	0,08	ROCKS	MEAN-NIGHTTIME
14.5.1976	MURNAU MOOS	0,25	MOOR	-
14.5.1976	UPPER BAVARIA	0,06	HEATH	-
14.5.1976	UPPER BAVARIA	0,05	MEADOW	-
1.7.1976	ROTES MOOR	1,09	MOOR	EAST WIND
8.7.1976	BALTIC SEA	0,08	STRAND	EAST WIND
13.7.1976	RANTUM/SYLT	0,95	TIDAL FLAT	LIGHT AIR
10.11.1976	MAINZ	1,65	SAND	CHEM.FACTORIES

Figure 2
Map of W. Germany showing the approximate locations of the sampling sites and a table containing typical H_2S concentrations.

conditions are given in tidal flats, where the layer which contains H_2S oxidizing bacteria is very thin (1–10 mm) and liable to be damaged by different influences of the bio- and atmospheric environment. Similar conditions are found in swamps on the banks of eutrophic waters. These regions were the objects of our investigations.

Results

Measurements performed in swamps and tidal flats situated in Germany (Fig. 2) verified the assumption that because of the microbiological recycling of H_2S in the ground only small amounts of H_2S are released into the atmosphere, even from anaerobic soils.

The table in Fig. 2 contains the values of H_2S-concentrations at a height of one meter above several different soils. It can be seen that the atmospheric H_2S concentration above swamps and tidal flats varies between 0.11 $\mu g\ Nm^{-3}$ and 1.09 $\mu g\ Nm^{-3}$. In upper Bavaria in the environment of some swamps the soils containing anaerobic bacteria were covered with heath and meadow as an H_2S oxidizing layer and only very weak H_2S concentrations could be measured.

The concentrations measured on the Kl. Feldberg hill (800 m) or in the Mainz–Wiesbaden area are probably caused by transport from anthropogeneous sources.

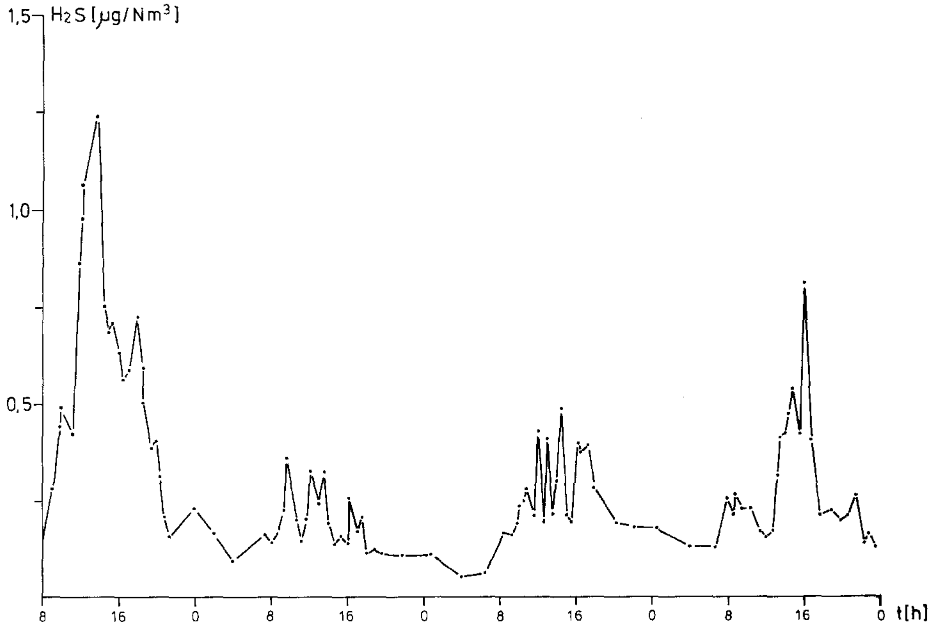


Figure 3
Diurnal variation of the H_2S concentration measured on Kleiner Feldberg hill during a period of four days in March 1976.

The high values between 0.35 and 1.65 μg Nm^{-3} indicate that the contribution of these sources to the sulfur cycle cannot be neglected. For the location K1. Feldberg mean values are given in the table. These values are calculated from measurements of the diurnal variation of the H_2S concentration within a period of four days in March 1976 (Fig. 3).

The lifting of an inversion layer up to the altitude of the hill at noon time probably accounts for the increasing H_2S concentration at that time. This may be considered as an indication, that the H_2S distribution in this area is influenced by the transport of anthropogeneously generated H_2S from the Rhein–Main area and not by local sources in the rocky ground.

In order to distinguish whether the ground is a source or sink the following qualitative method was used: After measuring the H_2S concentration in the ambient air in an altitude of 50 cm, the soil was covered with a PVC-chamber containing 1000 litres of air. After one hour, the H_2S concentration of the air trapped inside the chamber was measured as reference.

In Fig. 4, the results of such measurements conducted on several typical European soils are compared with the results obtained over anaerobic soils. It can be seen that typical soils normally act as sinks.

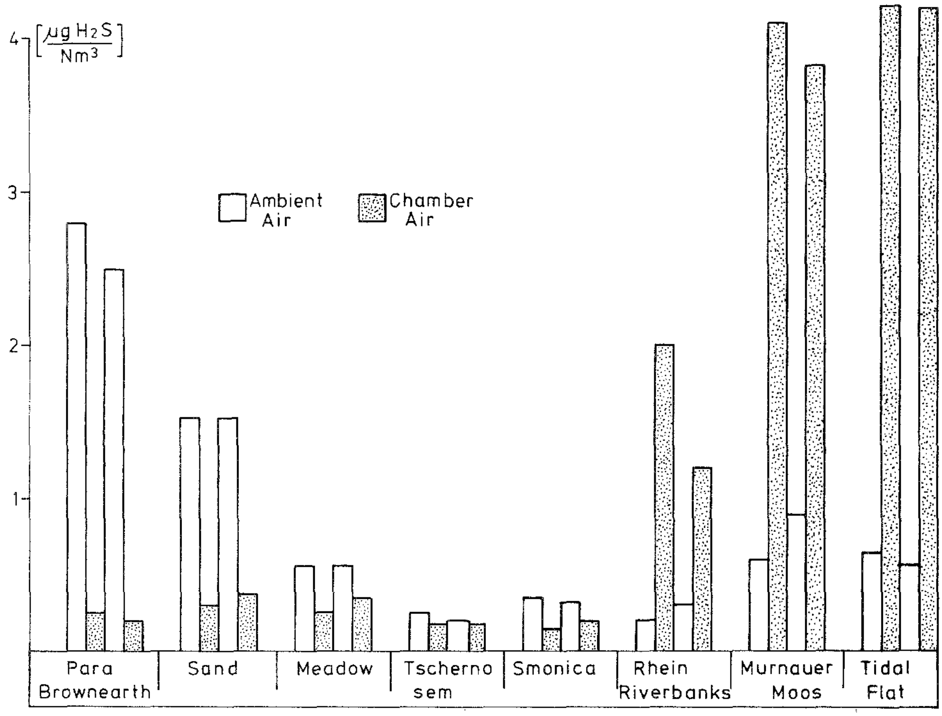


Figure 4
Comparison of some European soils acting as sources or sinks of H_2S.

After these preliminary results further investigations were concentrated on the measurement of the vertical distribution of H_2S above the swamp Murnauer Moos and the tidal flats near the island of Sylt.

In Fig. 5 the vertical distributions of the H_2S concentrations during different seasons are shown. Up to an altitude of 2 m four concentrations were measured simultaneously. The figure shows that the H_2S concentration increases with the seasonal rise of the temperature. On the other hand, with the rising temperature, the concentration decreases more strongly with the altitude. The reason for these observations is not yet apparent.

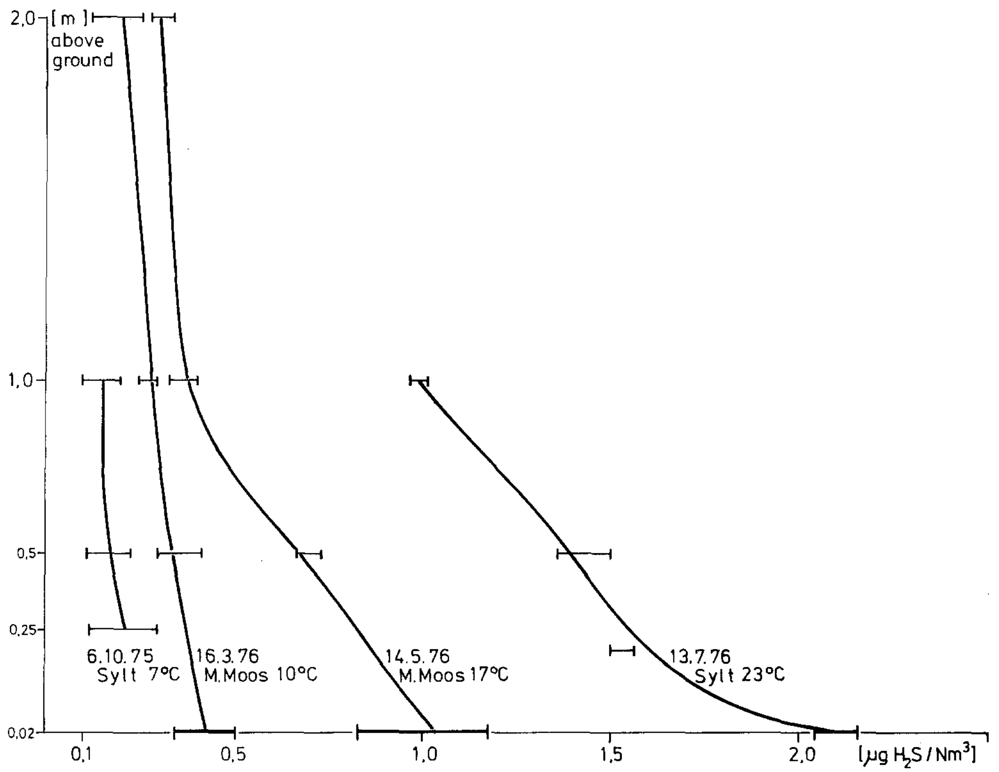


Figure 5
Vertical distribution of H_2S near the ground measured at different seasons.

In the altitude of 2 m mean H_2S concentrations between 1.2 and 1.5 μg Nm^{-3} seem to be rather independent from seasonal influence. In higher altitudes reproducible H_2S concentrations have been measured during 5 aircraft ascents in the autumn of 1975 and during one ascent in the summer of 1976 above the tidal flat. The obtained concentration profile is plotted in Fig. 6 as profile (a).

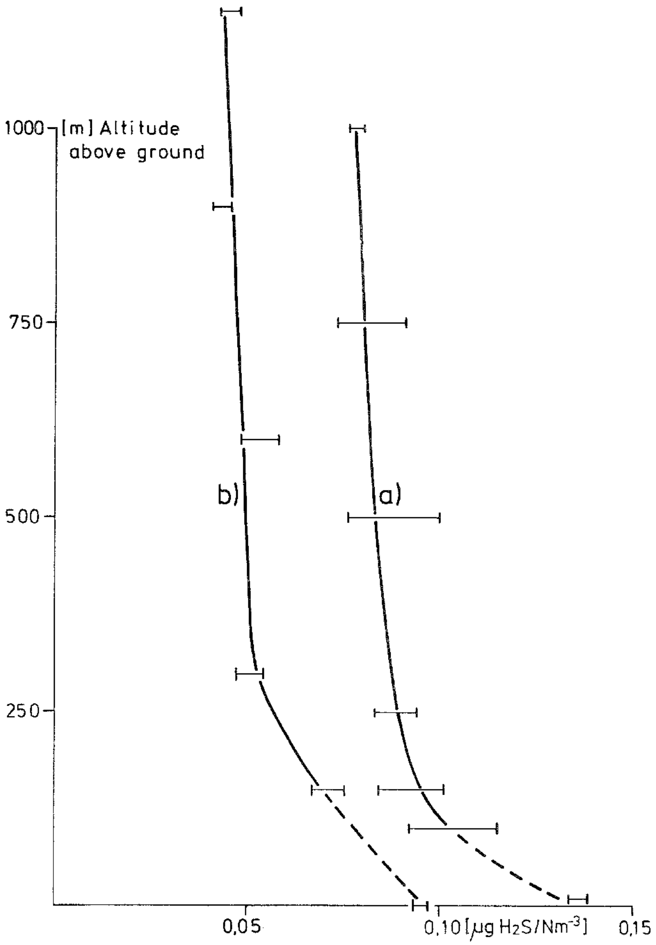


Figure 6
Vertical distribution of H_2S above Northern Germany.
(a) Tidal flats at the North Sea (6 ascents)
(b) Rural regions leeward, close to the Baltic Sea (1 ascent).

Profile (b) in Fig. 6 was measured about 80 km (leeward) to the east of the tidal flat close to the Baltic Sea. The high H_2S-values at higher altitudes are probably caused by horizontal transport of H_2S. At lower altitudes, the influence of some weak sources in the coastal swamps of the Baltic Sea may be noticeable, because about 0.1 µg Nm^{-3} were found at ground level in this region. Similar concentration profiles were obtained during three aircraft ascents in the lower troposphere above the Murnauer Moos. The results are plotted in Fig. 7 as profile (a). These values are compared with the H_2S concentration profile which was measured above the Island of Sylt, and one may, with caution, assume that the vertical distribution of H_2S above the Moos is comparable to the distribution above the tidal flat.

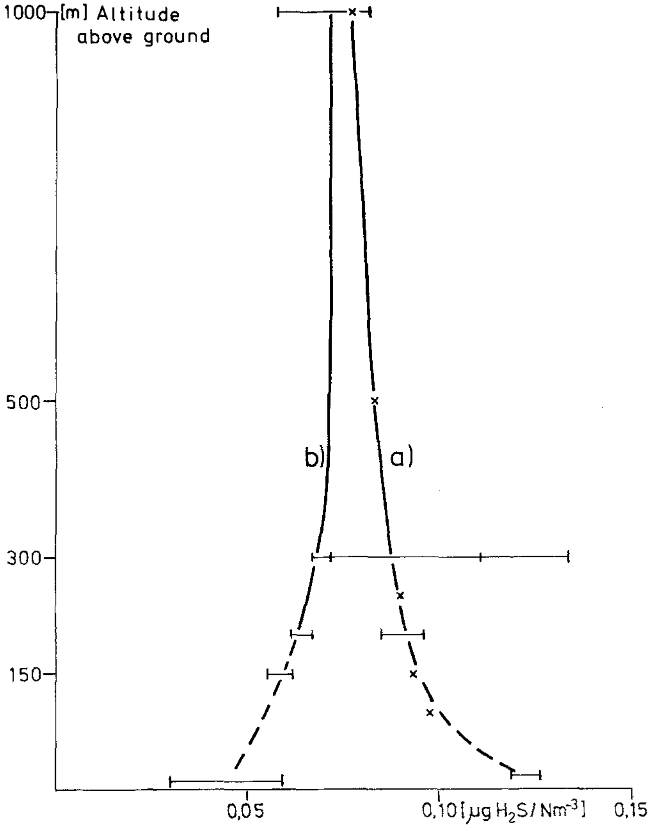


Figure 7
Vertical distribution of H_2S above Upper Bavaria.
(a) Murnauer Moos (3 ascents compared with the values (×) obtained above the island of Sylt).
(b) Rural regions in the environment of the Moos (1 ascent).

Profile (b) in Fig. 7 which was measured in the environment of the Moos indicates that the soils in this region of Upper Bavaria covered with meadow and heath act as sink for H_2S since the concentration of about 0.05 µg Nm^{-3} measured 1 m above the ground are lower than the concentration of about 0.08 µg Nm^{-3} measured in altitudes of 300 and 1000 m.

In the air above the swamp Rotes Moor, in the middle part of Germany, no further measurements have been performed owing to the influence of chemical factories in the Rhein–Main area. Two vertical H_2S distributions in the luff and lee of these anthropogeneous sources are shown in Fig. 8 to give an impression of the H_2S concentration in this area. Even in the luff, the air has already been polluted. At 1000 m altitude leeward of the sources concentrations up to 0.3 µg Nm^{-3} are found. In contrast to this, in remote areas above the natural sources, only concentrations below 0.1 µg Nm^{-3} are found in this altitude.

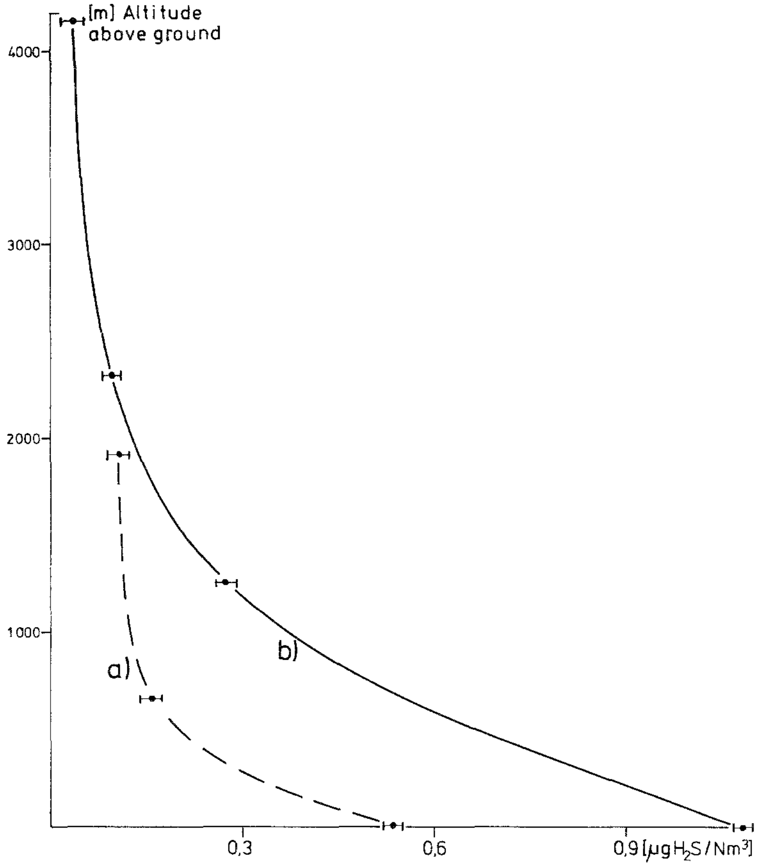


Figure 8
Vertical distribution of H_2S above Rhein–Main area.
(a) Mainz–Nierstein (luff 1 ascent)
(b) Aschaffenburg–Gelnhausen (lee 1 ascent).

Conclusions

Performing the aircraft measurements near the island of Sylt attention was paid to the fact that the tidal flats as a source of H_2S were homogenously distributed and that their horizontal extension was large compared with the measuring altitude. Therefore steady-state conditions could be assumed for the measured concentration profiles. The reproducibility of the data which were received from six aircraft ascents in the autumn of 1975 and the summer of 1976 verified this assumption.

Therefore the data of the mean profile (a) shown in Fig. 6 were used to calculate the flux of H_2S into the atmosphere by the gradient method (CLAUDE, 1977). The eddy diffusion coefficients $D(Z)$ used in this calculation are computed following a method developed by O'BRIEN (1970). The results of these calculations are presented in Table 1.

The obtained data for the fluxes with increasing altitude show a decrease. At an altitude of 1000 m the flux is reduced to a value of 0.18 μg m^{-2} h^{-1} compared to a value of 4.97 μg m^{-2} h^{-1} at an altitude of 150 m.

Table 1

Calculated data, based on the measured vertical H_2S *distribution.*

Altitude [m]	D_Z [m^2 s^{-1}]	$\Delta C/\Delta Z$ [μg m^{-4}]	Flux [μg m^{-2} h^{-1}]	A [s^{-1}]	$[\cdot OH] = A/3.1 \times 10^{-12}$ [molec cm^{-3}]
150	2.30×10^1	6×10^{-2}	4.97	4.86×10^{-5}	1.5×10^7
250	2.68×10^1	3.5×10^{-2}	3.38	2.65×10^{-5}	8.5×10^6
500	1.84×10^1	1.0×10^{-2}	1.32	1.44×10^{-5}	4.6×10^6
750	5.70×10^0	1.3×10^{-2}	0.267	1.22×10^{-6}	3.9×10^6
1000	5.00×10^0	1.0×10^{-2}	0.180		

This indicates a high atmospheric removal rate for H_2S. To calculate the removal coefficient it was assumed that the overall H_2S removal reaction is in equilibrium with the vertical transport of H_2S by eddy diffusion to establish a steady-state concentration of H_2S in a definite altitude. As the most simple case for the overall H_2S removal reaction, a first-order process was assumed. The calculated removal coefficients also presented in Table 1 are decreasing with increasing altitude. This may depend on the decreasing concentration of the oxidizing species, indicating that the removal reaction is really a second-order process.

COX and SANDALLS (1974) suggested the oxidation of H_2S with OH radicals to be the main sink in the lower troposphere. STUHL (1974) has measured the rate constant of this reaction to be $K = 3.1 \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1}. Assuming that our calculated removal coefficients are the product of this rate constant and the concentration of the oxidizing species, one can calculate the OH radical concentration which had to be available for the oxidation of H_2S in different altitudes. These calculations have been performed in order to show the plausibility of the previously effected measurements.

The obtained results are shown in Table 1 in the last column. The OH concentration ranges between 1.7×10^{-7} and 3.9×10^6 cm^{-3} and is comparable to OH concentrations measured directly by PERNER *et al.* (1976) or by WANG *et al.* (1974). Based on a mean removal coefficient of 2.27×10^{-5} sec^{-1} a mean *lifetime of 12.2 h for* H_2S was calculated. Therefore, no long-range transport of H_2S is to be expected.

It can be taken from the measured and calculated data that the *contribution* of natural H_2S sources described in this report is probably not as high as was previously expected. We want to emphasize the local character of this study. The global distribution of natural H_2S sources is yet unknown. In tropical regions a higher source strength is to be expected because of the temperature dependence of the microbiological production rate. From the results gained up to now we do not feel in a position to extrapolate on the global H_2S production rate.

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