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Dimethylsulfide and methane thiol in sediment porewater of a Danish estuary

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Abstract. Seasonal variation of dimethylsulfide (DMS) and methane thiol (MSH) concentrations in sediment porewater was determined in a Danish estuary. Dimethylsulfide (DMDS) was never found. Detectable DMS levels of up to 0.1 μM were found only in the summer and only within the upper 5 cm of the sediment. The DMS accumulation was probably associated with decomposing fragments of macro-algae in the surface layer. Significant MSH accumulation of up to 1 μM was found only in the deep, CH_4-rich sediment below the SO_4^{2-} zone. With depth, a detectable MSH level could thus be observed below the 1 mM SO_4^{2-}-isopleth which also marked the SO_4^{2-}-CH_4 transition. The transition zone was located deeper in the sediment in winter (20–25 cm depth) than in summer (5–10 cm depth). The absence of MSH in the SO_4^{2-} zone could be due to rapid utilization of the compound by SO_4^{2-}-reducing bacteria. A possible involvement of MSH in anaerobic CH_4 oxidation at the transition zone is discussed; CH_4 and sulfide (HS^- form, pH 7) are proposed to form MSH and H_2 which in turn may be metabolized by, e.g. SO_4^{2-}-reducing bacteria.

Introduction

Recent interest and research in natural sulfur gases has partly been due to the role of biogenic sulfur emissions into the atmosphere. Observations of sulfur in coastal air have thus indicated that biogenic emissions may contribute significantly to the local atmospheric sulfur budget (Hitchcock & Black 1984), and organic sulfur compounds have been found to be important (Lovelock 1972; Adams et al. 1981; Barnard et al. 1982; Andreae & Raemdonck 1983; Steudler & Peterson 1984).

Dimethylsulfide (DMS; $(CH_3)_2S$), dimethyldisulfide (DMDS; $(CH_3)_2S_2$) and methane thiol (MSH; CH_3SH) are methylated sulfur gases which appear in the gas emissions from coastal marine environments. The emission of DMS seems most important and may sometimes exceed that of H_2S; high DMS emissions have been found in salt marshes (*Spartina alterniflora* stands) (Aneja et al. 1979; Steudler & Peterson 1984) and in estuaries where decomposing macro-algae (*Ulva lactuca*) accumulated (Jørgensen & Ok-

holm-Hansen 1985). The pattern of DMS release indicates that the gas arises as a product from algae and higher plants, either by direct release or associated with decomposition of the osmolyte dimethylsulfoniopropionate, DMSP (Vairavamurthy et al. 1985). In seawater, the DMS concentrations are positively correlated with biomass and primary productivity of the phytoplankton (Andreae 1980; Andreae & Barnard 1984) and grazing was shown to enhance the DMS release (Dacey & Wakeham 1986).

When produced in the surface water, DMS may not be strongly affected by microbial metabolism before the gas is emitted to the atmosphere. Such transformations are obviously important in the sediments, where a complex pattern of microbial respiration and fermentation processes seems to be involved. In addition to decomposition of DMSP, the anaerobic degradation of methionine may be important for the production of organic sulfur gases (Segal & Starkey 1969; Kadota & Ishida 1972; Salsbury & Merricks 1975; Zinder & Brock 1978; Oremland & Polcin 1982). When emission of sulfur gases is detected, it may be due to the pumping activity of benthic animals or the draining and inundation of the mud flats which forces porewater out of the anaerobic sediment layers (Jørgensen & Okholm-Hansen 1985).

Recently, research in methylated sulfur gases has been further stimulated by their apparent role in methanogenesis, in particular where the CH_4 production occurs together with SO_4^{2-} reduction. It has been shown, for instance, that SO_4^{2-} reducers and methanogens compete for DMS at relatively low concentrations (μM level) (Kiene et al. 1986). There is a need to study this type of competition for all the methylated sulfur gases, ideally at their natural, nanomolar concentration level as was found for DMS in salt marshes (Howes et al. 1985) and in organic-rich shelf sediment (Andreae 1985).

To understand the emission patterns and transformations of the methylated sulfur gases, it is important to determine their depth distribution in the sediments. The present study was undertaken to describe the seasonal variations of DMS, DMDS and MSH concentrations in an organic-rich estuarine sediment. The results were related to the depth distributions of SO_4^{2-} and CH_4.

Materials and methods

The study was made at a site in the inner, freshwater-dominated part of a Danish estuary (Norsminde Fjord). Average water depth was about 0.5 m and salinity varied from 0.5‰ in winter to about 10‰ in summer. The

sampling site was a mud bank near the river outlet, characterized by a high content of silt and relatively few animals. The sediment was covered by a dense layer of benthic micro-algae in the spring and floating sea lettuce (*Ulva lactuca*) occasionally accumulated in late summer. Seasonal studies of total mineralization rate, nitrate and sulfate reduction, and emissions of nitrous oxide (N_2O) and sulfur gases (H_2S, DMS and others) were made at the station in 1984 (Jørgensen & Okholm-Hansen 1985; Jørgensen & Sørensen 1985). The seasonal variation of trimethylamine (TMA) concentrations and the regulation of TMA emission from the sediment were studied in 1985–86 (Sørensen & Glob 1987).

In the present study, undisturbed sediment cores were collected at 1–2 month intervals throughout 1986 to determine the distribution of methylated sulfur gases, SO_4^{2-} and CH_4 in the porewater. The cores were stored overnight at 3 °C and then cut into 1–2 cm segments. Because of the variability among cores, four segments from the same depth were quickly pooled before the porewater was extracted by pressure filtration (0.45 μ polycarbonate filters, 3 atm N_2). The first ml of filtrate was discarded and only the next 5 ml was collected in a 10 ml syringe.

One ml of the porewater sample was immediately transferred to a system for sulfur gas analysis (Jørgensen & Okholm-Hansen 1985; Sørensen et al. 1987). The sample was injected into a He-purged glass chamber which contained 0.1 ml 1 M phosphate buffer (pH 6.0). Efficient stripping of the sulfur gases was obtained within 5 min with a He flow of 25 ml min^{-1}. After cryogenic trapping in liquid N_2, the sulfur gases could then be injected into the gas chromatograph. A Packard model 427 GC with a 1.5-m long and 3.2-mm wide Carbopack BHT 100 column and Flame Photometric detection was used. Oven temperature was 110 °C and He carrier flow was 25 ml min^{-1}. The concentration of sulfur gases in the porewater was expressed in μM. Detection limit was about 0.01 μM.

A 1–2 ml subsample of porewater was used for a SO_4^{2-} analysis by ion chromatography. The porewater was first injected into a vial which contained 0.5 ml 1% $ZnCl_2$ solution to precipitate sulfide. After filtration (0.45 μm), the sample was then diluted 1–5 fold and a small volume (0.1–0.5 ml) injected into the ion chromatograph via a sample loop. The components were separated on a Vydac type 302 IC column using iso-phtalic acid (pH 4.6) as the eluent (1.25 ml min^{-1}). A Vydac conductivity detector was used and concentrations were expressed in mM. Detection limit was about 0.01 mM.

For CH_4 analysis, about 1 g of sediment was taken from a segment and transferred to a 35 ml serum bottle with 4 ml 2 M NaOH solution. The bottle was immediately capped and shaken vigorously to stop microbial activity

and to facilitate the transfer of CH_4 into the gas phase. After equilibration, a gas sample of 0.3 ml was injected into a Packard model 419 GC with Flame Ionization detection. A Porapak T column (2-m long and 3.2-mm wide) was used with He carrier at a flow rate of 25 ml min^{-1}. Oven and detector temperatures were 80 and 125 °C, respectively. After correction for the water content, the CH_4 concentration in the porewater could be calculated in mM units. Detection limit was about 0.0001 mM.

Results and discussion

DMS distribution

Both in the open ocean and in coastal waters, DMS concentrations are typically in the order of 1–5 nM; MSH is sometimes detected, but is generally much lower than DMS (Andreae & Barnard 1984; Jørgensen & Okholm-Hansen 1985). The author is not aware of DMDS determinations in marine waters. In estuaries, lower DMS concentrations have been found in the river-dominated region than in the marine part (Jørgensen & Okholm-Hansen 1985). In this study, a low DMS concentration (5–10 nM) was found in the water samples through most of the year (data not shown); MSH and DMDS were never detected. In the marine part of the estuary, however, DMS levels sometimes increased when the site was covered with macro-algae (*Ulva lactuca*). In such cases, typically from July to September, 10–50 nM DMS could be found along the shoreline of the estuary; extremely high concentrations (1–5 μM DMS) were observed sporadically in the sheltered parts. The results confirmed that DMS concentrations in the estuarine water and thus the gas emissions into the atmosphere was temporarily and locally dominated by gas released from decomposing macro-algae (Jørgensen & Okholm-Hansen 1985).

A comparison of concentrations in the water phase and in the sediment porewater may be useful to indicate the role of sediments in the emission of methylated sulfur gases. Howes & Wakeham (1985) have provided DMS distributions in salt marsh sediments. Concentrations were generally low (about 0.1 μM) in samples taken by in situ porewater samplers, but up to 100-fold higher when cores were sectioned by cutting. The authors suggested that the increase was due to a rapid transformation of the DMSP being released from damaged roots of *Spartina alterniflora*. Andreae (1985) measured DMS concentrations of less than 0.1 μM in sediments from the Peruvian upwelling region. The highest DMS levels were found at 1–5 cm depth. There was also higher DMS levels in the sediments of shallower water,

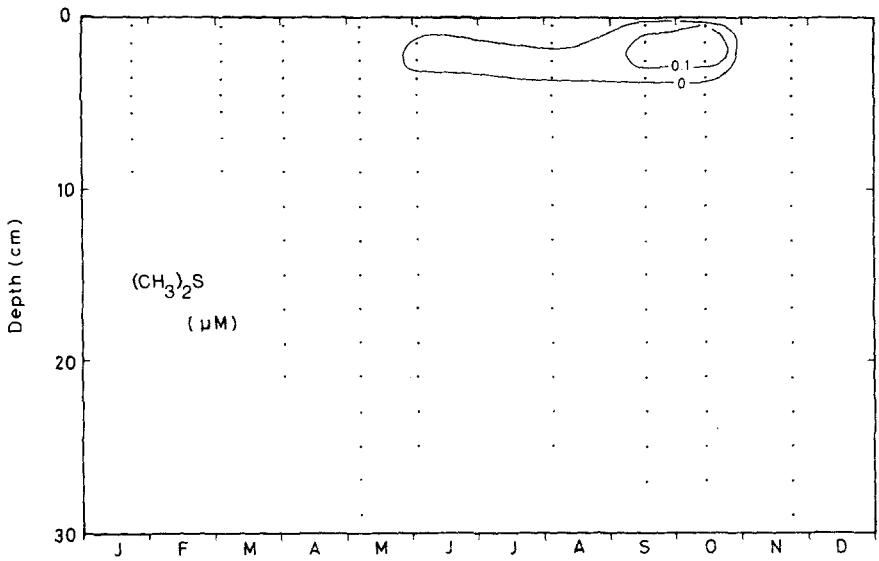

Fig. 1. Seasonal variation of $(CH_3)_2S$ (dimethylsulfide, DMS) concentrations (isopleths) in porewater from an estuarine sediment (Norsminde Fjord 1986).

probably because more decomposing phytoplankton was reaching the sediment. It may thus be expected that a maximum of DMS formation in the sediments is found in coastal waters with either a high sedimentation rate for phytoplankton or a high productivity associated with benthic micro-algae.

Figure 1 shows that detectable DMS levels were found only in the summer and only within the upper 5 cm of the sediment; the highest concentration of about 0.1 μM DMS was observed in late summer when a distinct subsurface maximum was formed. The accumulation of DMS was most likely associated with decomposing fragments of macro-algae, which were buried in the sediment during the summer. Even if DMS levels were overestimated by the coring and pressure-filtration technique (Howes & Wakeham 1985), the results clearly demonstrate that DMS concentrations must be relatively low in the sediment (0–0.1 μM) and that any accumulation is found only in the summer and only in the surface sediment. The estuarine sediment may be a source of DMS emission as judged from the subsurface maximum of DMS concentration (Fig. 1), but unfortunately, the actual flux cannot be estimated. In addition to tidal pumping (Jørgensen & Okholm-Hansen 1985), the DMS may be transported upwards from a subsurface layer by faunal activity (bioturbation) such as described for the emission of trimethylamine (Sørensen & Glob 1987). At the station near the river outlet, both the depth distribution and the seasonal accumulation of TMA were most similar to those of the DMS.

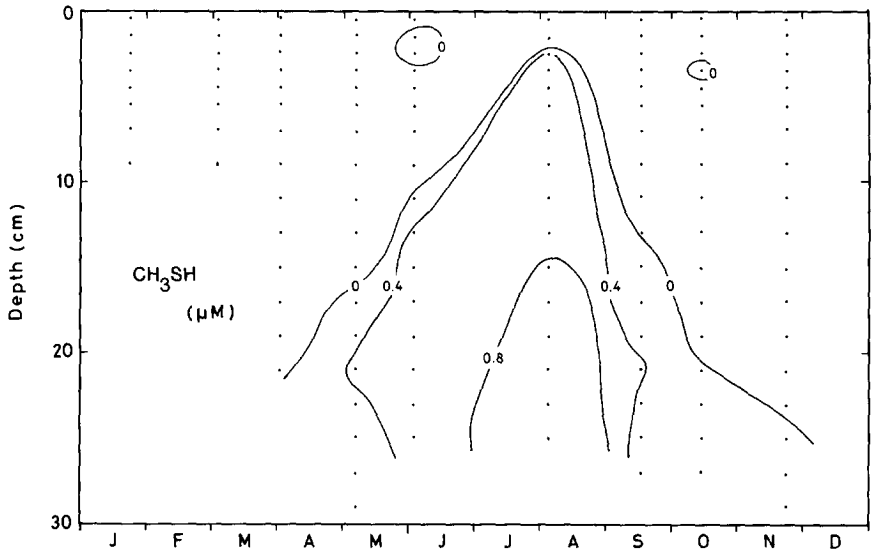

Fig. 2. Seasonal variation of CH_3SH (methane thiol, MSH) concentrations (isopleths) in porewater from an estuarine sediment (Norsminde Fjord 1986).

MSH distribution

To the author's knowledge, in situ concentrations of MSH have not previously been reported for marine sediments. As shown in Fig. 2, MSH occurred only in deep layers of the estuarine sediment, showing a distribution pattern completely different from that of DMS. MSH was absent from the surface to about 25 cm depth in the winter and to about 5 cm depth in summer. The maximum concentration was about 1 μM, measured below 20 cm depth in summer.

The sediment was previously shown to contain elevated SO_4^{2-} reduction rates within a narrow surface zone in the summer (Jørgensen & Sørensen 1985). Figure 3 (*top*) illustrates the rapid depletion of SO_4^{2-} with depth; the 0.1 and 1 mM isopleths for SO_4^{2-} moved upwards, from 20–25 cm depth in the winter to 5–10 cm depth in the summer. The annual patterns clearly demonstrated that detectable MSH levels were associated with the deeper layers below the SO_4^{2-} zone; the lowest, detectable MSH concentration was fairly well correlated with the 1 mM isopleth for SO_4^{2-}. As shown in Fig. 3 (*bottom*), the SO_4^{2-}-depleted sediment was characterized by a high accumulation of CH_4; A steep concentration gradient for CH_4 (0.1–0.5 mM isopleths) followed the SO_4^{2-} - CHS_4 transition throughout the year. Also the concentration of sulfide was high in the transition zone, about 1 mM (data not shown).

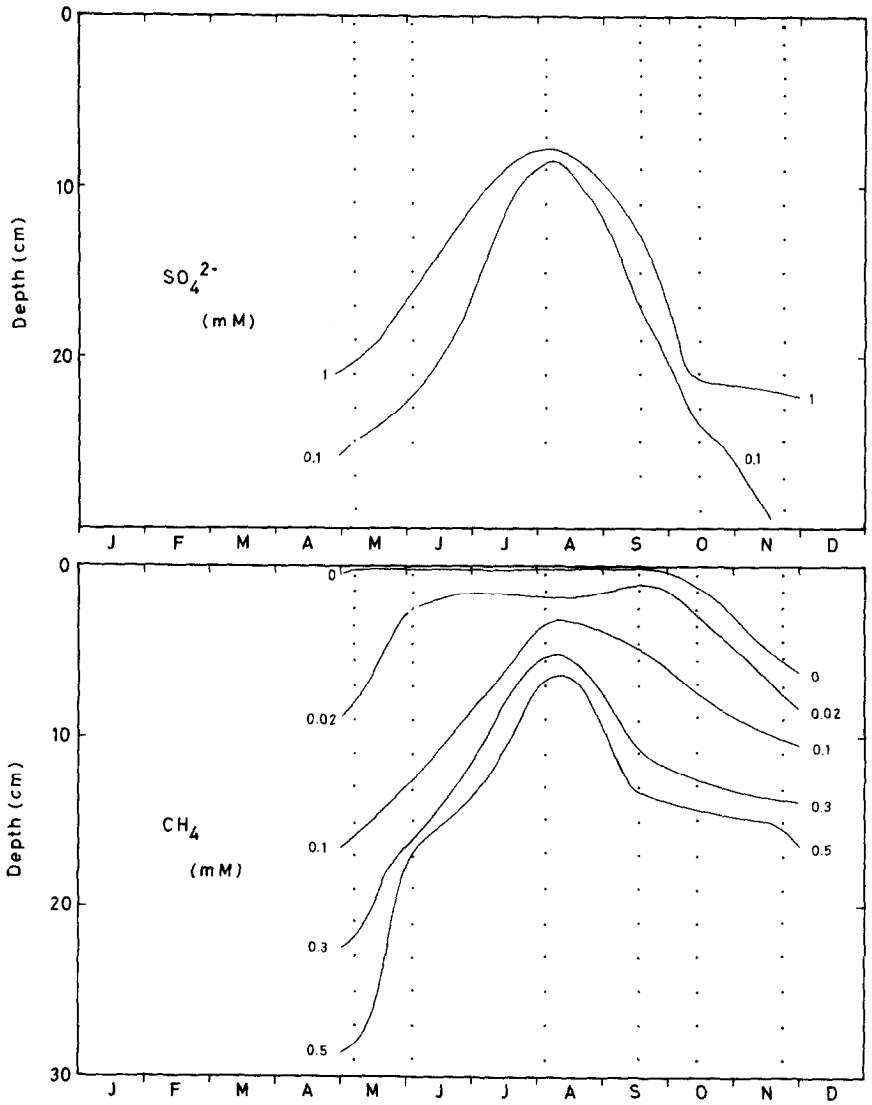

Fig. 3. Seasonal variation of SO_4^{2-} (*top*) and CH_4 (*bottom*) concentrations (isopleths) in porewater from an estuarine sediment (Norsminde Fjord 1986).

The absence of detectable MSH levels may indicate that the gas is not produced in the SO_4^{2-} zone. It is more likely, however, that the MSH is rapidly consumed (high turnover) by SO_4^{2-}-reducing bacteria. Methanogenic bacteria may also be involved in MSH consumption (Kiene et al. 1986), but it is uncertain, whether the methanogens compete efficiently at the very low MSH levels found in the SO_4^{2-} zone. In the CH_4-rich layers, the MSH is more likely to be a substrate for CH_4 production. Finally, since detectable

MSH levels are found in the transition zone with 0.1–1 mM SO_4^{2-}, the compound may also here be a "competitive" substrate for SO_4^{2-} reduction and methanogenesis. Verification could be obtained from an isotope study; However, any assay designed to resolve the substrate competition or measure MSH turnover must recognize the very low MSH concentrations in the sediment.

The transition zone is also finally a site of CH_4 oxidation, possibly by the SO_4^{2-}-reducing bacteria. Anaerobic CH_4 oxidation must explain the steep gradient of CH_4 concentration which occurs at the lower boundary of the SO_4^{2-} zone (Barnes & Goldberg 1976; Bernard 1979; Martens & Berner 1977; Reeburgh 1976; Reeburgh 1980; Reeburgh & Heggie 1977). It is still not clear, however, whether bacterial SO_4^{2-} reduction is directly involved:

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + H_2O + HS^-$$

Devol and Ahmed (1981) observed a maximum in SO_4^{2-} reduction rate at the SO_4^{2-} - CH_4 transition and the possible involvement of CH_4 oxidation was suggested. In two marine sediments, where SO_4^{2-} was depleted at depths of 1 and 1.5 m, substantial CH_4 oxidation and an elevated level of SO_4^{2-} reduction were found in the transition zone (Iversen & Jørgensen 1985). Both bacterial activities were at a maximum where SO_4^{2-} was depleted to a concentration level of 1 mM.

Based on the MSH distribution in the present sediment, it would be interesting to see if MSH can be involved in anaerobic CH_4 oxidation according to:

$$CH_4 + HS^- + H^+ \rightarrow CH_3SH + H_2$$

Standard free energy ($\Delta G^{\circ\prime}$) of the reaction is $+6.9\,kJ\,mol^{-1}$. MSH and H_2 are both substrates of SO_4^{2-} reduction (Kiene et al. 1986) and because of their rapid consumption, the MSH concentration and the H_2 partial pressure may be very low in the sediment (this study; Lovley et al. 1982). The actual free energy of the reaction ($\Delta G'$), calculated from in situ concentrations of the reactants and products, can therefore differ markedly from the $\Delta G^{\circ\prime}$. In fact, for a set of more realistic in situ concentrations (1 mM concentrations of CH_4 and HS^- and 0.01 μM concentrations of MSH and H_2, the calculated $\Delta G'$ is $-10.2\,kJ\,mol^{-1}$. It is here assumed, that pH is 7 and all sulfide present as HS^-. For MSH, the assumed concentration level corresponds to the detection limit (0.01 μM) and should be found close to the 0 μM MSH isopleth at the SO_4^{2-} - CH_4 transition. For H_2, the 0.01 μM level (10^{-5} atm) is realistic where efficient H_2 consumption by, e.g. SO_4^{2-} -

reducing bacteria is taking place (Lovley et al. 1982). A verification of this hypothetical reaction is probably best obtained by an isotope assay, but in addition to the requirement for low isotope concentration, such an assay must also attend the possible effect of H_2 pressure on the gas transformations.

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