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Formation of methylmercaptan and dimethylsulfide from methoxylated aromatic compounds in anoxic marine and fresh water sediments

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1. SUMMARY

Anaerobic formation of dimethylsulfide (DMS) and methylmercaptan (MSH) in anoxic sulfide-containing slurries from marine and fresh water sediments was stimulated by addition of syringate (4-hydroxy,3,5,-dimethoxybenzoate) and 3,4,5,-trimethoxybenzoate. The release of DMS and MSH occurred during the consumption of the aromatic monomers and ceased after their depletion. DMS was the dominant methylated sulfur compound in fresh waster sediments, in contrast to marine sediments where MSH was predominant. No production of volatile organic sulfur compounds was observed in slurries containing gallate (3,4,5,-trihydroxybenzoate) or in autoclaved controls. About 50–65% of the methoxy carbon could be accounted for by peak accumulation of DMS and MSH. In the saline sediments, large amounts of CH_4 were formed during the period when DMS and MSH disappeared. About 65–70% of the methylcarbon of the volatile methylated sulfur compounds (VMSC) could be accounted for in the produced CH_4. This study demonstrates a previously unknown microbial process by which DMS and MSH are formed during anaerobic decomposition of methoxylated aromatic compounds in marine and freshwater sediments.

2. INTRODUCTION

Volatile methylated sulfur compounds (VMSC) such as dimethylsulfide (DMS) and methylmercaptan (MSH) are widespread in nature and DMS, which is among the quantitatively important atmospheric sulfur gases, plays a key role in the global sulfur cycle [1–5]. To date, the anaerobic biological formation of DMS and MSH has only been reported from the metabolism of sulfur-containing precursors such as methionine or dimethylsulfoniopropionate (DMSP) and the pathways involving these compounds have been studied intensively during recent years [6–9]. Un-

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der oxic conditions, aerobic heterotrophic bacteria and protozoa, which possess a *S*-adenosylmethionine-dependent thiol methyltransferase, were reported to produce VMSC [10].

During enrichment experiments, designed to obtain aromatic compound-degrading sulfate reducers, a new obligately anaerobic acetogenic bacterium was discovered which was capable of fermenting methoxylated aromatic compounds (e.g. syringate or trimethoxybenzoate, see Fig. 1) with concomitant production of DMS and MSH (Bak et al., in preparation). As major constituents of lignin, methoxylated aromatic monomers are relatively abundant in natural environments [11,12]. Further studies with the new isolates revealed that the organic sulfur compounds were formed from free H_2S, added as reducing agent to the medium, and the methoxy groups of the aromatic substrates by a so far unknown pathway. The bacteria appear to be widespread in nature, since enrichment and isolation was possible from anoxic marine, brackish, and freshwater habitats (Bak et al., in preparation).

The present study was initiated to investigate if anoxic sediments have the capacity to produce volatile methylated sulfur compounds from methoxylated aromatic monomers via the newly discovered bacterial mechanism. The sediment samples used were from marine, brackish, and freshwater origin. Syringate was chosen as model compound because it is a potential product of lignin degradation [13].

3. MATERIALS AND METHODS

3.1. Sampling sites

Sediment samples were obtained from three different sites in Jutland (Denmark), which range from marine to fresh water: Skalling salt marsh (29‰ salinity) on the Danish west coast, Kysing Fjørd (7–18‰ salinity), and Vilhelmsborg Lake (0.5‰ salinity) south of Århus. Core sampling was accomplished with Plexiglas tubes of different diameters and lengths. The cores were sealed with rubber stoppers and stored in the dark at 4°C. Slurry experiments were carried out within 3 weeks after sampling.

3.2 Preparation and incubation of sediment slurries

Surface sediment (0–2 cm) of 2–3 cores (about 50 ml) was transferred to a 500 ml glass bottle that had been purged with oxygen-free N_2. A continuous stream of N_2 was maintained during the entire procedure to avoid oxygen contamination from air. The sediment was diluted with degassed and filtered water (0.45 μm cellulose acetate filters) from the sampling site to a final 1 : 5 ratio (volume sediment/volume water). The suspension was subsequently homogenized by vigorous stirring with a magnetic stir bar and 60 ml portions were carefully pipetted into 120 ml serum bottles. The headspace of the bottles was purged with oxygen-free N_2 (flow rate 1 l min^{-1}) for 2 min to remove air. The bottles were sealed with green Neoprene rubber stoppers and preincubated at 22°C in the dark for 24 h to remove residual oxygen. Free sulfide in the headspace was interpreted as an indicator of anoxic reduced conditions. Control experiments established that the Neoprene stoppers absorbed only small quantities of VMSC during the incubation periods (e.g. less than 10% MSH from about 20 μmol initially added).

Experiments were started by injection of substrates (e.g. aromatic compounds) from sterile concentrated stock solution. The bottles were incubated on a bottle roller at 22°C in the dark. VMSC were analysed in the headspace and the aromatic compounds in the slurry. Liquid concentrations of DMS and MSH were calculated from their respective distribution coefficients (liquid concentration/vapour concentration), 11.2 for DMS and 7.9 for MSH [14]. The detection limits for DMS and MSH in the slurry experiments were approximately 1 μM and those for the aromatic compounds in the range of 5–10 μM.

Periodically subsamples were taken through the stopper using syringes. Samples for syringate analysis were stored in screwcapped glass vials at −20°C and analysed at the end of the experiment. Concentrations of organic sulfur compounds and methane were determined immediately by direct injection of gas samples with

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gastight syringes into a gas chromatograph (GC) (see below).

3.3. Analytical techniques

3.3.1. Analysis of aromatic compounds. Aromatic acids were analysed by high pressure liquid chromatography using a Rainin HPLC system with Gilson model 302 pumps, a Rheodyne 725 injection valve with a 20 μl loop (Rheodyne Inc., Coati, CA) and a Kratos model 757 variable wavelength detector (Kratos Analytical Instruments, Ramsey, NJ). The acids were separated on a 10 cm $\times$ 4.6 mm Rainin Microsorb C-18 reverse phase column with 3 μm spherical packing using an isocratic mobile phase of 0.01 N H_2SO_4 in 40% methanol at a flow rate of 0.7 ml min^{-1}. Absorbance was measured at 228 nm. After thawing, suspended sediment was allowed to settle. Afterwards the supernatant was filtered (0.45 μm) prior to injection.

3.3.2. Sulfur gas analysis. Sulfur compounds (MSH, DMS, H_2S) were analysed on a Packard model 427 GC equipped with a flame photometric detector (Chrompack, Denmark) and a 1.5 m $\times$ 3.2 mm Carbopack BHT Column (Mikrolab, Århus, Denmark). Oven, injector, and detector temperatures were 100, 110, and 130°C, respectively. Helium was used as carrier at a flow rate of 25 ml min^{-1}. Permeation tubes containing H_2S, DMS and MSH were used as calibration standards as described by Jørgensen and Okholm-Hansen [15].

3.3.3. Methane analysis. A Shimadzu model 14A GC with a flame ionization detector was used for CH_4 analysis. The instrument was equipped with either DB1 or GSQ fused 30 m silica columns (0.53 mm i.d.) (JW Scientific, Folsom, CA). The operating conditions for the DB1 column were: column temperature 30°C; injector temperature 75°C; detector temperature 150°C and 60, 75 and 150°C, respectively, for the GSQ column. The injection volume was chosen according to the expected methane concentration, but never exceeded 0.3 ml.

3.4. Stock solutions and chemicals

200 mM stock solutions of aromatic compounds were prepared by carefully neutralizing the free acids with 4 M NaOH while continuously stirring to avoid precipitate formation and afterwards sterilized by filtration. The stock solutions were stored under a N_2 atmosphere at 4°C in the dark. Fresh stock solutions were prepared at monthly intervals.

All chemicals used were of analytical or reagent grade quality and were obtained from Merck, Darmstadt and Fluka, Neu Ulm, F.R.G. Methylmercaptan was purchased from Mathesen, Belgium. All other gases were from AGA, Århus, Denmark.

4. RESULTS

4.1. Anaerobic turnover of methoxylated aromatic compounds in sediment slurries

In order to determine if methoxylated aromatic compounds can serve as precursors of VMSC (e.g. MSH, DMS), sediment slurries from Kysing Fjørd were incubated with syringate (1 mM) or 3,4,5-trimethoxybenzoate (1 mM). Control slurries were incubated with gallate, which is structurally similar but contains no methoxy groups.

After 3 days of incubation, MSH production started in the slurries containing syringate (Fig. 1). During the following 2 days MSH continued to accumulate. In parallel small quantities of DMS were formed. DMS and MSH subsequently disappeared within the following 24 h.

In the TMB-containing slurry, DMS and MSH release began after 5 days and again pools of MSH and DMS built up within 2 further days. After 10 days, both MSH and DMS had disappeared. Sediment slurries that received gallate showed no DMS or MSH production.

Production of VMSC was observed down to depths of about 17 cm during analysis of the vertical distribution of DMS and MSH formation from methoxylated aromatic compounds in Kysing Fjørd samples (data not shown). Release of VMSC occurred after a lag period of 4 days in the uppermost part of the sediment (0–2 cm) and 5–6 days in deeper layers. On the basis of these results a more detailed study of syringate turnover using the 0–2 cm layers of different sediments was initiated.

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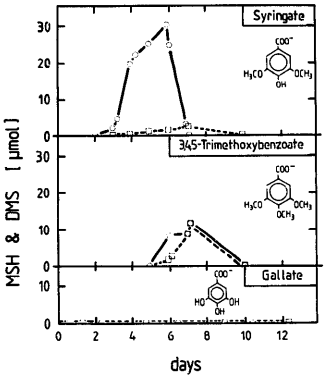

Fig. 1. Methylmercaptan (○——○) and dimethylsulfide concentrations (□–□) in slurries (60 ml) containing surface sediment (0–2 cm) from Kysing Fjørd (Denmark) after addition of 1.0 mM (final concentration): syringate (4-hydroxy-3,5-benzoate); TMB (3,4,5-trimethoxybenzoate); gallate (3,4,5-trihydroxybenzoate).

4.2. Sediment from Kysing Fjord

Sediment slurries were incubated with syringate (0.1 mM) at 23°C in the dark. The relatively low concentration was chosen because aromatic compounds can be toxic for anaerobic bacteria at higher concentrations [15].

After a lag period of approximately 2 days, syringate concentrations started to decrease (Fig. 2). The rate of syringate disappearance increased during incubation and was estimated as 10 µM syringate h^{-1} from the steepest part of the curve. After 12 h of syringate consumption, MSH could be detected in the gas phases of the slurries. The net production rate was calculated as 24 µM MSH h^{-1}. Production of MSH ceased when syringate was depleted. DMS was apparently produced at a minor rate (1.1 µM h^{-1}) and quantity (0.95 µmol versus 6.1 µmol of MSH). DMS appeared some hours after MSH was initially detected. CH_4 was released at a maximum rate of 3.8 µM h^{-1}, while MSH disappeared at a rate of 7 µM h^{-1}. CH_4 production ceased after MSH and DMS had been consumed. About 65% of the methoxy carbon was

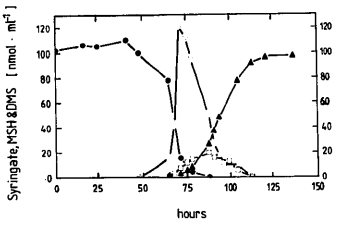

Fig. 2. Methylmercaptan (○——○), dimethylsulfide (□——□) and CH_4 (▲——▲) concentration in a slurry containing surface sediment (0–2 cm) from Kysing Fjørd (Denmark) after addition of 0.1 mM syringate (●——●).

recovered in the methyl groups of MSH and DMS prior to methane formation and almost 70% of the methyl carbon was found as CH_4 at the end of the experiment.

4.3. Sediment from Skalling salt marsh

The pattern of syringate turnover in slurries of sediment from Skalling salt marsh was comparable to that of Kysing Fjørd sediment, despite a prolonged lag period of about 3 days (Fig. 3). Syringate was consumed at a maximal rate of 7.1 µM h^{-1}. MSH and DMS were detected immediately after syringate degradation started. The apparent net MSH production rate was 7.2 µM h^{-1}. DMS was apparently produced at a much lower rate (0.7 µM h^{-1}) and reached a pool size of 0.86 µmol; less than 25% of the highest MSH

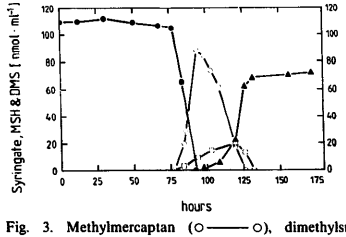

Fig. 3. Methylmercaptan (○——○), dimethylsulfide (□——□) and CH_4 (▲——▲) concentration in a slurry containing surface sediment (0–2 cm) from Skalling salt marsh (Denmark) after addition of 0.1 mM syringate (●——●).

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concentration. MSH production stopped when syringate was consumed and DMS was depleted 12 h after MSH. CH_4 was detected simultaneously with the start of MSH consumption. CH_4 was produced at a maximal rate of 6.8 μM h^{-1}; production ceased when both MSH and DMS were consumed. About 50% of the methoxy carbon was recovered in the pool of the organic sulfur compounds, and approximately 65% of the carbon from this pool was found as CH_4 at the end of the experiment.

4.4. Sediment from Vilhelmsborg lake

The pattern of syringate metabolism in slurries of fresh water sediment differed from the marine sediment slurries. Syringate concentrations declined without a significant lag period (Fig. 4). The syringate consumption rate increased throughout the experiment; the maximal rate was 7.8 μM h^{-1} In contrast to the marine slurries, DMS was apparently the dominant VMSC formed. DMS accumulated at a rate of 6.0 μM h^{-1} after a lag period of 36 h. 60% of the methoxy groups was converted to DMS. Only trace amounts of MSH were detected. The DMS concentration remained unchanged for about 36 h and decreased slowly afterwards. CH_4 release occurred independently of DMS consumption. Autoclaved controls of sediment from each of the three environments showed neither syringate consumption nor VMSC or CH_4 production. Background concentrations of VMSC in autoclaved controls were 1–5 μM.

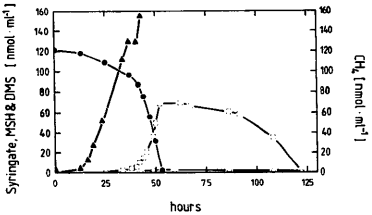

Fig. 4. Methylmercaptan (○——○), dimethylsulfide (□——□) and CH_4 (▲——▲) concentration in a slurry containing surface sediment (0–2 cm) from Vilhelmsborg Lake (Denmark) after addition of 0.1 mM syringate (●——●).

5. DISCUSSION

The present study documents for the first time that organic sulfur compounds (DMS and MSH) can be formed in anoxic sediment slurries during anaerobic microbial degradation of methoxylated aromatic acids. In addition, the production of MSH and DMS was not restricted to a specific environment but was detected in sediments of marine, brackish and fresh water origin. A similar bacterial process by which DMS and MSH are formed anaerobically from inorganic sulfide and sulfur free organic compounds has not been described previously.

The production of thiols from methoxylated aromatic monomers clearly depended on microbial activity, since autoclaved controls never showed VMSC formation. Interestingly, significant syringate consumption and VMSC production occurred only after a lag period, which may be explained by both initiation of population growth and enzyme induction. Slurrying of sediment samples may also have adversely affected the relevant bacterial populations and caused the observed lag periods.

Since neither gallate nor other aromatic compounds could be detected during syringate degradation, the decomposition of syringate seemed to proceed completely to acetate and VMSC without the release of detectable amounts of aromatic demethoxylated intermediates. The process is most likely catalysed by fermenting bacteria comparable to those that have recently been isolated from anaerobic enrichments with methoxylated aromatic compounds (Bak et al., in preparation). The principal biochemical reactions which lead to MSH and DMS formation during degradation of methoxylated aromatic compounds are not known at present. However, methylation reactions similar to those reported by Drotar et al. [10] for aerobic heterotrophic bacteria may be considered.

The incorporation of inorganic sulfur into organic matter by purely chemical reactions, e.g. into the humic fraction of the sediment and coal have recently been documented [17–19]. As a mechanism for incorporation, the addition of sulfur through either nucleophilic substitution of HS^- or a reaction with free sulfur radicals formed

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by homolytic cleavage of polysulfide was proposed. Moreover, addition of bisulfide and polysulfide to activated alkenes has been pointed out as an important mechanism for the generation of thiols in pore water of marine sediments [20]. For example, 3-mercaptopropionate, an abundant thiol in marine environments, can be formed by addition of sulfide to acrylate. Acrylate is probably formed primarily from another sulfur containing compound, DMSP [21–23].Interestingly, in this study DMS was apparently the dominant VMSC which accumulated in fresh water samples whereas in sulfide-rich marine samples methyl-mercaptan was prevalent. This may be due either to the type of organism that is involved in VMSC production or to the fact that hydrogen sulfide is usually limited in fresh water sediments. Differences in the specific adsorptive capacities for DMS and MSH between marine and freshwater sediments may have also influenced the observed VMSC-pools.

Ecologically, VMSC formation by sulfide-linked demethoxylation may be of considerable importance because of the abundance of both lignin monomers and hydrogen sulfide in nature. Previously, DMSP has been considered the primary precursor for DMS. However, in fresh water environments, where DMSP concentrations may be very low, DMS formation may be explained by a process similar to that described here. The potential importance of VMSC formation was illustrated by data of Nriagu et al. [24], who measured emissions of biogenic sulfur in remote areas of Canada and showed that biogenic sources account for up to 30% of the total acidifying sulfur burden. However, mechanisms explaining the relatively high contribution of DMS were not identified.

In marine habitats the formation of volatile methylated sulfur compounds from methoxylated aromatic compounds may occur in parallel to formation from DMSP and amino acid metabolism. In order to quantify the ecological importance of this process, detailed information about in situ concentrations of methoxylated compounds as well as their in situ turnover rates is necessary.

DMS and MSH may, at least at higher concentrations (> 2 μM), serve as 'non-competitive' substrates for methanogenic bacteria in sulfate-rich habitats [25–28]. Assuming that the volatile sulfur compounds are produced via incorporation of HS^- by the process described in the present work, H_2S can be considered as a catalyst of methyl group turnover during the anaerobic decomposition of methoxylated aromatic compounds (Fig. 5). Paradoxically, by generating sulfide, sulfate-reducing bacteria may be indirectly involved in the production of 'non-competitive' substrates which allow methanogenic bacteria to persist in marine surface sediments.

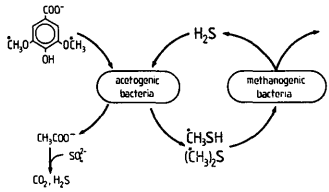

Fig. 5. Possible microbial interactions and the catalytic role of H_2S during anaerobic degradation of methoxylated aromatic compounds (here: syringate) in marine sediments.

ACKNOWLEDGEMENTS

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