APPLIED AND ENVIRONMENTAL MICROBIOLOGY, Dec. 1977, p. 859-860
Vol. 34, No. 6

Printed in U.S.A.

Production of Volatile Sulfur Compounds During the Decomposition of Algal Mats

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Received for publication 11 July 1977

Blue-green algal mats incubated anaerobically rapidly produce large amounts of volatile sulfur compounds, including hydrogen sulfide, methyl mercaptan, and dimethyl sulfide. The major organic sulfur compound is methyl mercaptan, in contrast to previous results with marine eucaryotic algae. Light inhibited production of volatile sulfur compounds, apparently because the algae then produced O_2, rendering the system aerobic.

The importance of volatile inorganic sulfur compounds (hydrogen sulfide and sulfur dioxide) in the sulfur cycle has been known for many years (5, 7). In 1972, Lovelock et al. (8) reported on the presence of dimethyl sulfide in seawater and suggested that volatile organic sulfur compounds could play a major role in the global sulfur cycle. The sources of volatile organic sulfur compounds were not clear, although it is known that dimethylpropiothetin, a sulfonium compound present in marine algae, decomposes to dimethyl sulfide (2). Methyl mercaptan and dimethyl sulfide are produced by a variety of bacteria and fungi, especially during the decomposition of methionine (6, 9), but little work has been done on natural production of these compounds.

As part of a larger study on decomposition processes in blue-green algal mats in thermal environments (3, 4), we carried out a study on the production of volatile sulfur compounds. Our original studies had shown that decomposition occurred fairly rapidly under anaerobic conditions and that the upper layers of these stratified mats showed the most rapid decomposition rates. Because of the intense self-shading that the algae experienced in these compact mats, net photosynthesis occurs only in the top 3 mm of mat, and, beneath this zone, decomposition is the primary process occurring. As the mat grows upward, the algae beneath go into darkness and decompose.

In the present work, cores of algal mat collected from a hot spring effluent in Yellowstone National Park (Octopus Spring) (4) were placed under anaerobic conditions in spring water in serum vials capped with Mininert valves (Precision Sampling Co., Baton Rouge, La.). The vials were incubated at in situ temperature in the dark, and samples of the head space were analyzed periodically for volatile sulfur compounds by using a Packard model 419 gas chromatograph equipped with a flame photometric detector (Tracor Instruments, Austin, Tex.), following the procedures outlined by Banwart and Bremner (1).

In several preliminary experiments, it was found that decomposition was most rapid in the top 3 mm of the mat. This is illustrated by the results from one experiment (Table 1) in which the production of hydrogen sulfide was measured. Presumably, the lower layers were less active because breakdown of easily decomposable proteinaceous materials had already occurred. As shown by Doemel and Brock (3), if sulfate is added in the form of ferrous ammonium sulfate, copious amounts of black ferrous sulfide are formed in the lower layers, but not in the top layer. Thus, it appears that sulfate reduction occurs primarily in the lower layers, and protein decomposition occurs primarily in the top layer. In the further study of production of volatile organic sulfur compounds, only the top layer was studied.

TABLE 1. *Production of hydrogen sulfide during anaerobic decomposition on an algal mat*[a]

Core depth (mm)	H_2S production (nmol/vial)
0-3	370
3-5	3
5-8	2
8-10	4
10-13	2
13-18	6

[a] Values represent total accumulation of H_2S in the head space after 4 days of incubation in the dark at 55°C. Core diameters were 16 mm. Core segments were placed in 5-ml serum vials, flushed with N_2, and sealed with Mininert valves. Protein content per vial was between 1 and 2 mg.

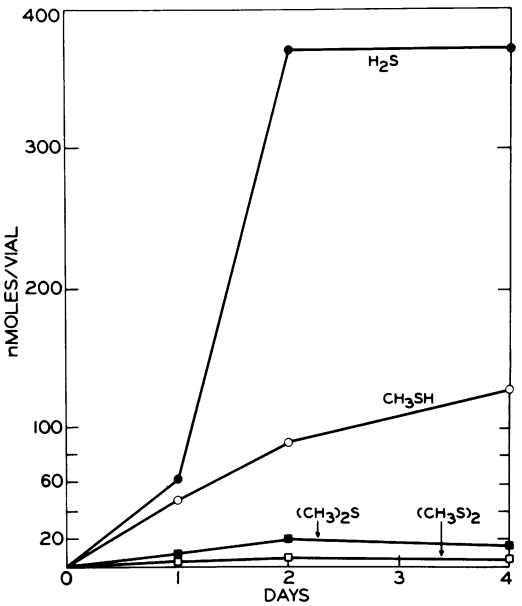

FIG. 1. *Rate of appearance of volatile sulfur compounds during dark decomposition of top algal layer. Conditions were as in Table 1.*

The rate of production of various volatile sulfur compounds from one of several experiments is shown in Fig. 1. The values in this figure are given in terms of sulfur so that the rates for the various compounds can be compared directly. Clearly, the major product formed is hydrogen sulfide, but considerable methyl mercaptan is also formed, as well as a small amount of dimethyl sulfide. Traces of dimethyl disulfide were also found, but this compound can arise as an oxidation product of methyl mercaptan.

In one set, 5 mg of methionine was added to a vial containing a top layer of algal mat. Interestingly, production of H_2S was strongly inhibited, but a large amount of dimethyl disulfide was formed. When cores were incubated in the light instead of the dark, the production of all volatile organic compounds was much lower, presumably due to the conversion of the system to aerobic as a result of algal O_2 production.

Hydrogen sulfide, methyl mercaptan, and dimethyl sulfide probably arise directly during the decomposition of algal protein constituents. The proportion of volatile sulfur compounds that are organic probably depends at least in part on the presence or absence of iron and other metals that will form insoluble complexes with the hydrogen sulfide. In the waters under study, iron concentrations are low (3), and little ferrous sulfide accumulates in the mats unless a source of iron is added experimentally. It is conceivable that in other environments, the bulk of the hydrogen sulfide formed during decomposition would be retained in the system, so that the proportion of volatile sulfur compounds released that are organic would be higher. Even in this low-iron system, a surprisingly large amount of volatile organic sulfur is released. However, the major product is not dimethyl sulfide, as is apparently the case during the decomposition of marine algae (2), but methyl mercaptan. There are several possible biochemical mechanisms for the formation of methyl mercaptan from the decomposition of methionine (6). Further work on the anaerobic fermentation of methionine in algal mats and sediments would be of importance.

This work was supported by a research contract from the U.S. Energy Research and Development Agency (COO-2161-34) and the College of Agricultural and Life Sciences, University of Wisconsin, Madison.

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