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Compartment model for biological conversions of DMS in a microbial mat: Effect of pH on DMS fluxes

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Abstract

A model has been developed to describe the biological conversions of five functional groups of microorganisms in a microbial mat. Microbial metabolism and transport of nutrients are the two dominant processes that were considered. The microbial activity was described with Michaelis-Menten kinetics. Transport of nutrients through the mat was described by simple transport processes. The model was validated using documented measurements, and was used to simulate the fluxes of compounds and concentrations in a microbial mat during a light period of 12 hours. Experimental data from *Methylopila sulfovorans* cultures (isolated from a microbial mat) were incorporated in the model in order to describe DMS oxidation under varying conditions in a mat.

Keywords: Microbial mat; Mathematical model; Dimethylsulfide fluxes

1. Introduction

A microbial mat is a complex community of different groups of microorganisms in a laminated sediment [1], thriving on light as the primary energy source. Microbial mats can be found in a restricted range of habitats such as estuarine regions, alkaline and/or hypersaline lakes and hot springs [2]. The thickness of the microbial mat may vary with the composition of the sediment, but is in the order of few millimetres. The large group of different microorganisms in a microbial mat can be classified in four basic functional groups, based on their metabolic activity. These groups are: phototrophs, chemolithoautotrophs, chemoorganoheterotrophs, and sulfate-reducing bacteria. These groups each affect the environmental conditions (e.g. pH, sulfide and oxygen concentration) in a mat. The phototrophic organisms are located at or near the surface of the mat where light energy is available during the day. Oxygenic, eukaryotic or prokaryotic, phototrophs are responsible for primary production of organic compounds from carbon dioxide and water. In many mats phototrophic bacteria are responsible for secondary photosynthesis under anaerobic conditions. The organic compounds are mainly used by two functional groups: the aerobic heterotrophic bacteria and the sulfate-reducing bacteria. The heterotrophic bacteria are distributed throughout the mat, and oxidize organic carbon with oxygen, produced by the oxygenic phototrophic microorganisms. The size of this group is limited by the availability of oxygen or alternative

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electron acceptors, such as nitrate, in the mat. The heterotrophs are predominantly responsible for creating the anaerobic conditions required by the sulfate-reducing bacteria. The sulfate-reducing bacteria are situated in the lower, anaerobic, part of the mat. This group uses organic carbon as its energy source and produces hydrogen sulfide from sulfate reduction. The hydrogen sulfide is oxidized back to sulfate by the fourth functional group. This group is represented by either or both of two major types of bacteria, the chemolithoautotrophic colorless sulphur bacteria, and, if light is available, the phototrophic bacteria. Both groups are located at, or near, the oxic-anoxic interface of the mat.

These four functional groups constitute the basic microbial community in a mat. Note that the definition of 'functional group' is not strict. The different organisms within a functional group may vary, for example, H_2S may be oxidized by chemolithoautotrophic bacteria and/or anoxygenic phototrophic bacteria. In principle, it is possible that one organism belongs to different functional groups; depending on the conditions, aerobic metabolism may alternate with anaerobic metabolism for heterotrophic bacteria, and some of the phototrophic bacteria.

Our interest in microbial mats is in their role in the production and metabolism of dimethylsulfide (DMS). In these mats, DMS is produced during the degradation of dimethylsulfonio-propionate, an osmolyte present in phototrophs [3]. DMS is only a minor substrate, compared to the amounts of sulfide produced in such a system. However, understanding the fluxes of DMS in terrestrial and aquatic ecosystems is relevant because DMS is believed to affect the climate [4]. Due to the relatively high primary production rates in such mats, the contribution to the overall DMS production is significant. These mats can therefore serve as model systems to investigate and better understand the mechanisms and dynamics of DMS turnover and release. In order to accommodate the metabolism of DMS, a fifth functional group of bacteria, the methylotrophs which are capable of oxidizing DMS, have been included in this study of a microbial mat. This group of organisms was shown to be present in microbial mat sediments in significant numbers (10^{5-6} bacteria ml^{-1} sediment, [5]). The classification of this group is somewhat arbitrary. DMS may be classified as a heterotrophic substrate, which would group the DMS-oxidizing community among the heterotrophs. However, as their activity is the main subject of this study, these organisms are treated as a separate (functional) group, the methylotrophs.

Microbial mats, in most cases, only contain organic carbon from autochthonous origin [2]. Hence, photosynthesis in the upper layer is the driving force behind metabolism in a microbial mat. The community within a mat therefore depends on a range of interactions ranging from the provision of organic substrates by the phototrophs to the removal of potentially toxic, reduced sulfur compounds.

This paper describes the construction of a mathematical model to express the interdependence of the microorganisms within a mat in terms of substrate, oxygen, H_2S and DMS flows and concentrations in the different layers. The main purpose of the model is to understand the magnitude of the various fluxes in the mat. The results from simulations using the model are compared with documented measurements in order to test the model on its predictive value. The effect of changing pH in a mat during a period of light on the DMS fluxes was experimentally investigated with *Methylopila sulfovorans*, an isolate from a microbial mat (J.M.M. de Zwart and J.G. Kuenen, in preparation). The results of the experimental work were incorporated in the model.

2. Modelling the microbial mat

2.1. Basic structure

In the model, five functional groups of microorganisms are considered. These groups of organisms are listed in Table 1 in order of (vertical) appearance in the mat, with the most significant biological reactions carried out by these groups. It should be noted that several metabolic reactions, known to take place in the mat, such as anoxygenic photosynthesis, anaerobic DMS metabolism or anaerobic heterotrophic metabolism are not considered here for reasons of simplicity. However, the quantatively important reactions by phototrophs, colorless sulfur bacteria, sulfate-reducing bacteria and aerobic heterotrophs are taken into account in the model. As can be seen in these five reactions in Table 1, all com-

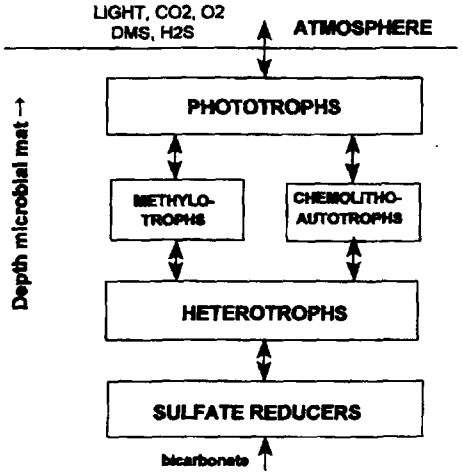

Fig. 1. Schematic representation of a microbial mat. Five functional groups are presented in distinct compartments.

pounds produced can also be consumed. Only light, sulfate and carbon dioxide from marine surface sediments enter the system. For the purpose of the model, it is assumed that the five groups of microorganisms are situated in separate compartments in the mat, each representing a functional group. These compartments are assumed to be homogeneous, with a depth of 5 mm [1,5]. A schematic representation is shown in Fig. 1. Exchange of compounds between the neighbouring compartments is possible through diffusion processes. There is no exchange of microorganisms between the different compartments. The variables considered in the model are: organic carbon (CH_2O), O_2, H_2S, DMS, CO_2, H^+, OH^-, HCO_3^- and CO_3^{2-}, for all five compartments, C_1 biomass for four groups (except the phototrophs) and the photosynthetic activity in the phototrophic compartment. This list includes the compounds that are crucial for the control of the pH in the mat, and the compounds that play a (quantitatively and physiologically) important role in this ecosystem. Both the biological reactions in the compartments, and the transport of compounds between the different compartments are considered. Biological consumption/production processes are described with Michaelis-Menten kinetics. Transport between the compartments is described with simple transport relations, based on diffusion.

2.2. Biological conversions

Metabolic activity is shown with Michaelis-Menten kinetics, expressed in Equation 1 where V stands for oxidation rate (mol substrate · unit of biomass^{-1} · time^{-1}), C_s for the concentration of the limiting substrate and K_s for the affinity constant.

$$V = V_{max} \cdot C_s/(K_s + C_s) \quad (1)$$

Throughout the model, units of biomass have been expressed as C-mol, which represents 12 g biomass. This expression (1) is used for the chemolithoautotrophs, the sulfate-reducing bacteria, the heterotrophs and the methylotrophs. The values for the maximum oxidation rates and affinity constants are derived from published values (Table 2). In case of oxygen depletion in the mat, the rate for substrate uptake is correlated with the affinity constant for oxygen, rather than with the affinity constant for substrate. It is assumed that the values for the affinity constants for oxygen are similar to the affinity constants for substrate for the heterotrophs, methylotrophs and colorless sulfur bacteria. The kinetic parameters for *M. sulfovorans* are used for the meth-

Table 1
List of the functional groups of microorganisms with their metabolic reactions, used in the mathematical model. The stoichiometric relations of the reactions are presented, except for the DMS production (*) by the phototrophic bacteria. The DMS formation rate is assumed to be coupled to the average DMSP content of photosynthetic bacteria and the photosynthetic rate, as explained in detail in the text. The functional groups are listed in vertical order of appearance in the model (see also Fig. 1)

Functional group	Metabolic reaction
Oxygenic phototrophs	$Light + H_2O + CO2 \rightarrow CH_2O + O_2 + (CH_3)_2S$ *
Chemolithoautotrophs	$H_2S + 2\ O_2 \rightarrow H_2SO_4$
Methylotrophs	$(CH_3)_2S + 5\ O_2 \rightarrow 2\ CO_2 + H_2SO_4 + 2\ H_2O$
Heterotrophs	$CH_2O + O_2 \rightarrow CO_2 + H_2O$
Sulfate reducers	$H_2SO_4 + 2\ CH_2O \rightarrow H_2S + 2\ CO_2 + 2\ H_2O$

Table 2
Kinetic and yield parameters of four functional groups in a microbial mat

Functional group	Substrate	μ_{max} (h^{-1})	K_s (μM)	Yield	Reference
Colorless sulfur bacteria	H_2S	0.35	1	4	[6]
Methylotrophs	DMS	0.025	1–3	5	de Zwart (in prep.)
Heterotrophs	CH_2O	0.5	1	8	[7]
Sulfate reducers	CH_2O	0.1	5	1.4	[8]

The maximum specific growth rate μ_{max} is expressed in h^{-1}, the affinity constant K_s in μM and the growth yield in g C-mol^{-1} substrate.

ylotrophic community as this organism was isolated from a marine microbial mat and appears to be representative of the DMS-oxidizing community in such a mat (J.M.M. de Zwart and J.G. Kuenen, in preparation). Growth of biomass was determined with the yield factor that indicates the amount of biomass formed per unit of substrate converted (Table 2). Substrate used for maintenance energy was not considered.

The phototrophic activity is dependent on the day/night cycle, amount of sunlight, temperature, specific maximum activity and the microorganisms involved. An average carbon dioxide fixation rate (mol m^{-2} h^{-1}) was derived from measurements with *O. limnetica*, as described elsewhere [2]. The oxygen production rate for this organism was 1 μM O_2 mg protein^{-1} h^{-1}. The amount of protein present in the top layer of the mat was derived from an average chlorophyll *a* content of 600 μg ml^{-1} [9] and a protein/chlorophyll *a* ratio of 30 μg chlorophyll *a* mg protein^{-1} in *Microcoleus chthonoplastes* [3]. This gave a protein content of 20 mg protein ml^{-1} sediment. The phototrophic activity was therefore estimated to be 20 μmol O_2 h^{-1} ml^{-1} (= 20 μmol C-fixation h^{-1} ml^{-1}) at a standard pH of 7.5. For a surface of 1 m^2 and depth of the top compartment of 5 mm, this gives a photosynthetic rate of 0.1 mol C m^{-2} h^{-1}.

The amount of DMSP, the precursor of DMS, in phototrophic microorganisms varies from 0 to > 1000 μmol g protein^{-1}, depending on the organism involved and the growth conditions [10]). Visscher and van Gemerden [3] found that *Microcoleus chthonoplastes* contained 37.3 μmol DMSP g protein^{-1}. Data on the kinetics and dynamics of the DMSP conversion to DMS by the phototrophic communities are not yet available, and therefore it is assumed in the model that the DMSP formed is coupled to the photosynthetic rate and the average DMSP content in phototrophs. The DMSP is assumed to be converted instantly to DMS. This introduces a large assumption in the model; however, when the DMSP pool in a mat is constant, the DMS production rate will mainly be dominated by the rate of photosynthesis. For the purpose of the model, it is therefore assumed that the phototrophic population contains 40 μmol DMSP g protein^{-1} $\approx$ 40 μmol DMSP g carbon^{-1}. DMSP formation is assumed to be coupled to carbon fixation and to be completely and instantly converted to DMS. If the carbon fixation rate is 0.1 C-mol m^{-2} h^{-1}, the DMS formation rate therefore is $40 \times 12 \times 0.1 = 48$ μmol DMS m^{-2} h^{-1}.

The pH in the top layer of a microbial mat can rise to pH 10, but not much higher [11]. This indicates that at pH 10 the photosynthetic activity (i.e. the OH^- production) is compensated by the diffusion of protons into the phototrophic layer. This diffusive transport is then the rate limiting step for photosynthesis. Since the diffusion of ions in sediment is relatively slow, the photosynthetic activity will be low, since the pH value in the upper layer of the mat stays constant. Actual activity measurements of *Coccochloris peniocystis* for different pH values also indicated that at pH 10 the photosynthetic activity was almost negligible [12].

The biomass concentrations used in the model at the start of a simulation run were determined as follows. A bloom period of fifty days was simulated with this basic model. In this period, the photosynthetic rate reached it maximum value relatively soon, as the limiting factor for photosynthesis wass the input of light energy. The biomass concentrations of the functional groups other than the phototrophs was low at the start and grew exponentially during the first days of the simulated bloom. After this period, the amount of biomass present was sufficient to metabolize the organic carbon produced by photosynthesis. This means that a linear growth of biomass was observed in the simulated bloom period. The concentration of biomass after this exponential phase

was used as start values for the simulations discussed in this paper. These concentrations are: for sulfate-reducers 20 mM C l^{-1}; chemolithoautotrophs, 10 mM C l^{-1}; heterotrophs, 15 mM C l^{-1}; and methylotrophs, 10 mM C l^{-1}.

2.3. Transport processes

Transport to and from the compartments was described using a simple transport equation based on diffusion. The compartments are considered to be homogeneous and well-mixed. The concept of compartmentalisation of a mat is a reduction of the continuous system where all concentrations progress smoothly in the mat. The concentration profiles in this model are gradual (i.e. step-by-step). For this reason a diffusive barrier (i.e. a diffusive boundary layer (δ)) must be introduced. This boundary layer is fictive, defined for a compartment model. In continuous systems, transport is described with diffusion coefficient D, in a compartment model transport is described with a mass transfer coefficient (symbol m) which is defined by D δ^{-1}. The bicarbonate concentration was assumed to be constant (2.5 mM) above the top compartment and below the lowest compartment. Therefore, the pH was also constant. The oxygen concentration above the top compartment was 235 μmol l^{-1}, assuming that diffusion in the sediment, rather than diffusion from the atmosphere to the sediment, is the rate-limiting step.

The difference in the concentration of a compound i in different compartments is the driving force behind transport. It can be expressed with the following equation, where J stands for the flux of component i (mol m^{-2} h^{-1}), C_{i1} and C_{i2} for the concentrations of component i in compartments 1 and 2, and m for the mass transfer coefficient (m h^{-1}) [13]:

$$J = m.(C_{i1} - C_{i2}) \quad (2)$$

This equation holds for defined systems with an interface between compartments 1 and 2. Soil and sediments are not defined systems, and the effect of their structure on the value of the mass transfer coefficient is significant. The water and air content of soil and sediment, their dry weight and porosity all decrease the value of the mass transfer coefficient for solutes. A 75% decrease of the value of the mass transfer coefficient in defined systems has been found in several biofilms [14] and sediment systems [15].

Table 3
List of values of diffusion coefficients in water [17–19] and calculated mass transfer coefficients: assuming a diffusive boundary layer of 40 μm (derived from [15]) and a decrease in activity of the optimal diffusion coefficient D in water of 75% to account for lower activity in soil [15] of solutes. It was assumed that DMS and H_2S were considered as solutes

Compound	D (10^{-9} m^2 s^{-1})	m (m h^{-1})
CO_2	1.94	0.044
O_2	2.3	0.052
DMS	1.04	0.023
H_2S	1.49	0.034
CH_2O	0.61	0.014
H^+	9.3	0.21
OH^-	5.3	0.12
HCO_3^-	1.18	0.027

Mass transfer coefficients were obtained by using the diffusion coefficient D (m^2 h^{-1}) and a value for the diffusive boundary layer (δ), inferred from concentration profiles in a biofilm [16]. The actual values used in the model are listed in Table 3.

2.4. Mass balances over a compartment

A general mass balance was set up in the model for each component in each compartment. These balances constitute the basis of the model. A general mass balance, for the exchange between compartments 1 and 2 can be expressed with the following equation:

$$dC_i/dt = m.A.(C_{i1} - C_{i2}) - r_{s,i}.V + r_{s,j}.V \quad (3)$$

$C_{i1,2}$ stands for concentration of compound i (mol m^{-3}) in compartment 1 or 2, suffix j stands for compound j from which compound i is produced, t for time (h), m for the mass transfer coefficient (m h^{-1}), A for the surface of the compartment (m^2), V for volume of the compartment (m^3) and r_s for the conversion rate of compound C (mol m^{-3} h^{-1}). Essentially, Equation 3 states that a change in concentration of a compound i in time equals the difference between the amount of compound i entering and leaving the compartment (i.e. diffusion) plus the difference of the amount that is produced and con-

sumed (i.e. Michaelis-Menten kinetics) in the compartment. For each of the five compartments mass balance equations are written for CH_2O, O_2, H_2S, DMS, H^+, OH^-, HCO_3^-, and biomass concentrations for four compartments (except the phototrophic compartment). This results in a large number of differential equations (i.e. 39; 5 compartments with 7 compounds and 4 biomass concentrations) which must be solved simultaneously, plus algebraic equations which must be solved for every integration step. The programming language PSI [20] was used to calculate the results of these equations over different time spans.

2.5. Calculations over 12-hour periods

The model describes the changes that take place in a microbial mat during a 12-h light period. During this period, photosynthesis starts and can build up to its maximum level of 0.1 mol m^{-2} h^{-1}. Activity will then decrease with the decrease in light intensity, stopping when the light is gone. The predicted photosynthetic activity, assuming a constant pH of 7.5 over a period of 12 h, is shown in Fig. 2. A linear decrease in photosynthetic activity from 0.1 to 0 C-mol m^{-2} h^{-1} was assumed for pH values ranging from 7.5 to 10.5.

Change in pH is obviously related to changes in the concentration of OH^- and H^+ ions. The concentrations of these ions are determined by the concentration of the buffering bicarbonate and the equilibrium equations of the acid/base bicarbonate, represented by the equilibrium equations $K_1 = 2.3 \times 10^{-8} = [OH^-].[CO_2]\ [HCO_3^-]^{-1}$, $K_2 = 5.6 \times 10^{-11} = [H^+].[CO_3^{2-}]\ [HCO_3^-]^{-1}$ and $K_w = 1 \times 10^{-14} = [H^+].[OH^-]$. The equilibrium constants are dependent on temperature and they are shown here for a standard temperature (25°C). During photosynthesis, carbon dioxide is withdrawn. In order to maintain the equilibrium, more OH^- ions will be formed. This leads to a rise in the pH. The effect of the 'production' of OH^- ions on the pH is dependent on the buffering capacity, i.e. the HCO_3^- concentration. In marine systems, the buffer concentration is about 2.5 mM bicarbonate [21]. The bicarbonate will decrease during photosynthesis as carbon dioxide is fixed into organic carbon. These aspects are dealt with in the model by means of elemental carbon balances.

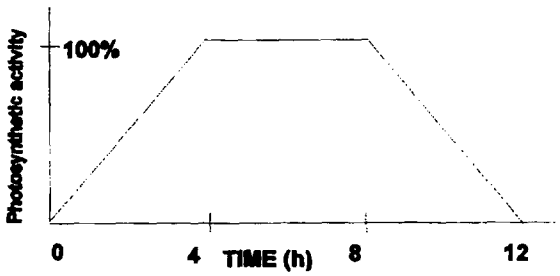

Fig. 2. Photosynthetic activity for a constant standard pH in a microbial mat during a 12 h light period.

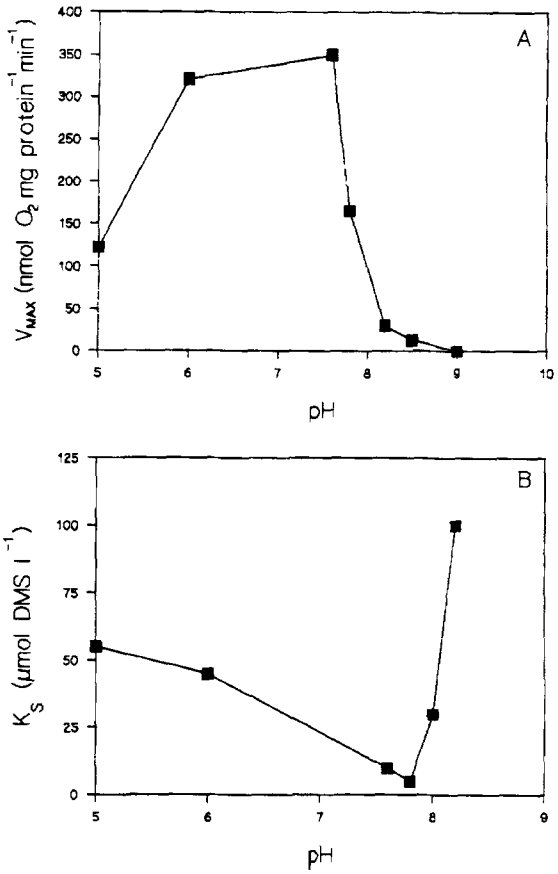

Fig. 3. Michaelis-Menten parameters for DMS oxidation for *M. sulfovorans* related to pH values. **A**: the maximum oxidation rate V_{max} versus pH; and **B**: the affinity constant K_{s2} versus pH.

2.6. Incorporation of the pH influence on the kinetic parameters of DMS oxidation

The effect of pH on the Michaelis-Menten parameters for DMS oxidation was determined using *Methylopila sulfovorans* as shown in Fig. 3. The results of the experiments were fitted as parabolic functions, and gave two relationships, of V_{max} as a function of pH and of K_s as a function of pH (J.M.M. de Zwart and J.G. Kuenen, in preparation). These functions indicated that V_{max} decreases by about 50% for 1 pH unit above the optimum pH of 7.6 and about 20% for 1 pH unit below the optimum pH value. The affinity constant K_s increased by about 50% for 1 pH unit above 7.6 and about 25% for 1 pH unit below 7.6. These parabolic functions of V_{max} and K_s were incorporated in the model.

3. Results and discussion of the model description of a microbial mat ecosystem

As already mentioned, the processes within a microbial mat can most easily be modelled by considering them to occur in compartments defined by the metabolic type of the organisms involved. The model was used to calculate the effects of microbial activity and transport processes on the concentration of compounds in such compartments. All constants used in the model (e.g. the affinity constants, yields and maximum oxidation rate constants for the different organisms, buffer concentration, mass transfer coefficients), the photosynthetic rate and the value of the initial biomass concentrations of the functional groups (with the exception of the phototrophs) were tested for parameter sensitivity. For this reason, all of the values of the constant were doubled and halved. With these new constants, simulations of a 12-h light cycle were carried out. The effect of the variability of constants was evaluated for two variables; DMS emission from the top layer of the mat to the atmosphere, and the pH rise in the phototrophic compartment, since these variables were of interest in the model. From this analysis, it appeared that biological and physical constants significantly affected both reference variables. The most influential biological parameters were the affinity constant for DMS oxidation and the size of the methylotrophic population. The most important physical constant was the mass transfer coefficient of the ions in sediment. Large variations can occur in carbon dioxide transfer from seawater to the atmosphere [22], largely because of the wind velocity. For the purpose of the model it was assumed that average mass transfer coefficients could be used.

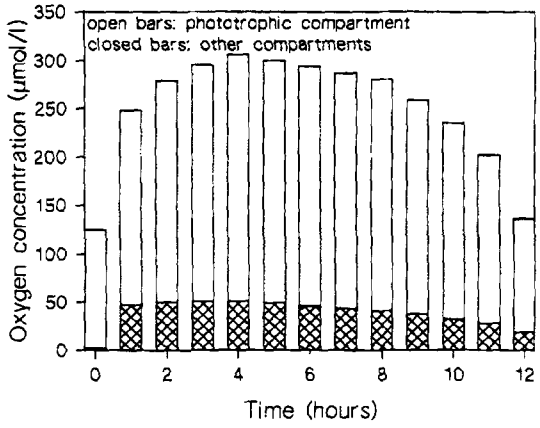

Fig. 4. Oxygen concentration in the phototrophic compartment (open bars) and in the deeper layers of the mat (closed bars).

Fig. 4 shows a simulation of the oxygen distribution through the mat for a period of 12 h. As can been seen, the oxygen concentration in the top layer of the mat rises above the oxygen saturation of water (≈ 235 µmol O_2 l^{-1} at 25°C). If the mass transfer of oxygen to the atmosphere was more effective (a higher mass transfer coefficient for oxygen), this would give a lower oxygen tension in the top layer of the mat. The results obtained (Fig. 4), agreed well with reported observations of supersaturation during a light period in a microbial mat [11].

The simulation of pH change in different layers of the mat (through photosynthesis and settling, or levelling out, of the pH) is shown in Fig. 5. It is assumed here that photosynthetic activity was at its maximum at neutral pH (Fig. 2), with a linear decrease in activity for higher pH values (adjusted from [12]). The rise in pH in the top layer of the mat was in accordance with experimental measurements of pH in the top layers of a mat. The effect of the time involved in the adjustment of the pH throughout the mat was considered in this model. The extent of the delay was mostly dependent on the value of the mass transfer coefficient, but also on the rate of

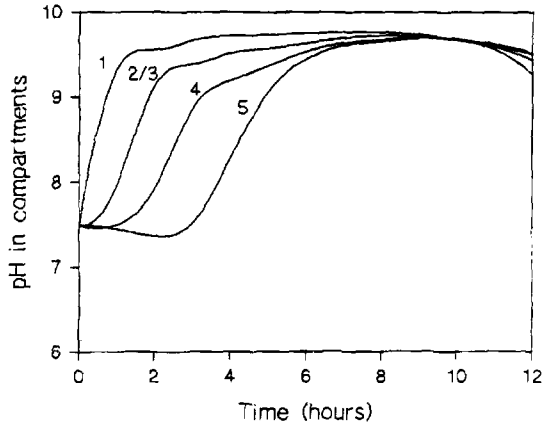

Fig. 5. pH Changes in compartments 1 to 5 during a light period of 12 h. Numbers 1 to 5 stand for the compartments of the phototrophs, methylotrophs, chemolithoautotrophs, heterotrophs and the sulfate-reducing bacteria.

photosynthesis, DMS oxidation (e.g. H_2SO_4 production), sulfate reduction, H_2S production, etc.). After 6 h, the pH in the whole system reached the predicted value of 9 or more. This prediction is solely based on the buffering capacity of bicarbonate. There is additional buffering capacity present in mats due to the large variety of compounds present in the mat. As a result, the pH rise will be less than predicted and the adjustment of the pH will take more time. However, high values of pH will be reached. The quantitative effect of high pH value on the microbial activity of the DMS-oxidizing community was not known. For this reason, the effect of pH on the oxidation of DMS by *Methylopila sulfovorans* was directly measured in the laboratory. From the results shown in Fig. 3 a quantitative relation of the Michaelis-Menten parameters with pH was obtained.

Fig. 6 shows the DMS emission from the mat by diffusion of DMS from the photosynthetic compartment into the atmosphere. This emission rate is a result of the rate of production and consumption of DMS, which determine the concentration of DMS in the compartment, which, in turn, results in a diffusion rate out of the compartment (Equation 2). Simulations with and without the effect of pH on DMS-oxidation were made. Ignoring the increase of the pH gave relatively low DMS emission rates. The amount emitted was strongly related to the affinity (V_{max}/K_s) of the DMS oxidizing-community for DMS. If the effect of increasing pH on DMS oxidation was taken into account, the affinity for the substrate became very low. The emission was then higher, since at higher pH values (after 2–3 h (Fig. 5)) the microbial oxidation of DMS is negligible. This means that DMS concentration in the compartments will build up. A higher concentration in the mat will give a higher emission rate. The emission from the mat of 4 μmol m^{-2} h^{-1}, when there is no microbial consumption of DMS (after 5 h, Fig. 5) fits well with the observed maximum DMS emission rates of 335 μmol m^{-2} day^{-1} which were detected above a sediment from a brackish estuary [23]. Assuming a constant emission of DMS during the day, this rate equals 14 μmol m^{-2} h^{-1}, which is in the predicted order of magnitude. Furthermore, Jørgenson and Okholm-Hansen [23] found that DMS was emitted in the late afternoon. The model predicts this effect (Fig. 6), since the pH rises in the mat during the day, which results in a decreased microbial activity for DMS removal.

It is clear that the model presented here gives a simplistic view of a complex ecosystem. Relatively important sinks for hydrogen sulfide and organic carbon, including anoxygenic photosynthesis and anaerobic heterotrophy [1], were not taken into account. Furthermore, anoxygenic photosynthetic bacteria can use DMS as an electron donor which provides an additional sink for DMS under anaerobic

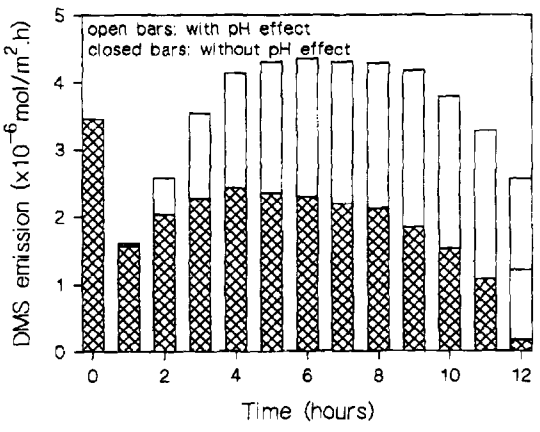

Fig. 6. DMS emission from the phototrophic compartment. The open bars show the results for the incorporation of the effect of pH on DMS oxidation. The closed bars represent DMS emission when there is no effect of changing pH on DMS oxidation.

conditions. As DMS is produced in the top layer of the mat, the anaerobic conversions of DMS that occur in such mats ([3,24]) was not taken into account. However, it should be emphasized that our model design is of a very general nature, and can be extended with such additional compartments without the requirement of new basic assumptions. This model may serve as a basic model that can be extended with new groups of organisms, of which the required kinetic and dynamic data can be determined. The mathematical model will be sent to interested readers on request.

In spite of its simplicity, the model gives satisfactory predictions of, for example, oxygen distribution, pH settling, and DMS emissions. The model will help in quantitative understanding of processes in microbial mats, and indicates the processes that must be examined in more detail in order to understand the carbon and sulfur fluxes.

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