Kinetic models of diagenesis in disturbed sediments. Part 2. Nitrogen diagenesis

Jean-Pierre Vanderborght, Roland Wollast, and Gilles Billen[1]

Laboratoire d'Environnement, Institut de Chimie Industrielle, Université Libre de Bruxelles, Brussels, Belgium

Abstract

A two-layer mass transfer model developed to describe the vertical silica profile in the sediments of a muddy zone of the North Sea along the Belgian coast is applied to the description of the microbiological processes involved in nitrogen diagenesis in the same sediments. Intense aerobic heterotrophic activity and nitrification are postulated in the upper layer. Denitrification and sulfate reduction are assumed to be preponderant in the lower layer. Vertical profiles of oxygen, sulfate, nitrate, and ammonium are then calculated according to the model and adjusted to experimental profiles. The fluxes of nitrate and ammonium across the water–sediment interface and the rates of ammonification, nitrification, and denitrification in the two layers are calculated from the results of the models.

It has been shown (Vanderborght et al. 1977) that the mass transfer mechanisms in the muddy sediments of the coastal region of the North Sea can be described by considering two distinct layers, with two different mass transfer coefficients. In the purely physicochemical model built up for silica, the same expression for the reaction rate was used in the two layers. The application of a similar model to other nutrients like nitrogen, for which microbiological action is of importance, requires that we consider not only different mass transfer mechanisms for the dissolved species, but also the fundamental changes in the biological processes occurring in the two layers. In an organic-rich sediment, the most important factor controlling microbiological activity is probably the availability of oxidants. Therefore the behavior of these oxidants has to be taken into account in any model where microbiological activity occurs. On the other hand, as the overlying water is the major source of these oxidants, their availability is strongly influenced by the mass transfer properties of the two layers.

Kinetic models for O_2, SO_4^{2-}, NO_3^-, NH_4^+

The most important oxidants for biological activity are oxygen and sulfate. Manganese oxide, nitrate, and iron hydroxide utilization, which can account for part of the oxidation of the organic matter in the sediments, will not be taken explicitly into consideration in our simplified models.

The results of Eh measurements and the experimental sulfate profile (Vanderborght et al. 1977: fig. 3) suggest that oxygen is available in the upper layer and prevents sulfate utilization, while sulfate is extensively used as an oxidant in the lower layer. The microbiological decomposition of organic matter can thus be represented by coupling Eq. 1 with Eq. 2 in the disturbed layer and with Eq. 3 in the lower compacted layer:

$$CH_2O + 2H_2O \rightarrow HCO_3^- + 5H^+ + 4e^-; \quad (1)$$

$$4e^- + O_2 + 4H^+ \rightarrow 2H_2O; \quad (2)$$

$$4e^- + \tfrac{1}{2}SO_4^{2-} + \tfrac{9}{2}H^+ \rightarrow \tfrac{1}{2}HS^- + 2H_2O. \quad (3)$$

Ammonification, a result of the heterotrophic utilization of organic matter, will thus be under the control of oxygen concentration in the upper layer and of sulfate concentration in the lower layer. Because it is an obligate aerobic process, nitrification is supposed to occur in the upper oxygenated layer while denitrification is only possible in the lower anaerobic layer. The behavior of O_2, SO_4^{2-}, NH_4^+, and NO_3^- in the pore water of the sediment can be described by the general equation

[1] Research Fellow at the Fonds National de la Recherche Scientifique.

$$\partial C/\partial t = D(\partial^2 C/\partial z^2) - \omega(\partial C/\partial z) + r,$$

where C is the concentration of the dissolved substance (mol liter^{-1}), r is the rate of production ($r > 0$) or consumption ($r < 0$) (mol liter^{-1} s^{-1}), and z, D, and ω stand for depth, mass transfer coefficient, and sedimentation rate. Under the assumption of steady state, $\partial C/\partial t = 0$. The expression of the rates of reaction will now be discussed briefly for each constituent.

Oxygen—A Michaelis-Menten function would be the best way of expressing the oxygen consumption rate. However, for mathematical simplification, this Michaelis-Menten kinetics has been approximated by zero-order kinetics at an oxygen concentration higher than some critical value (around 1% saturation) and by first-order kinetics at lower concentrations. It is also assumed that this critical oxygen concentration is reached at the boundary between the upper and the lower layer, so that

$$r_{O_2} = -k_{O_2} \quad \text{for } z < z_n$$
$$= -k'_{O_2} \times (O_2) \quad \text{for } z > z_n,$$

where z_n is the thickness of the upper layer.

Sulfate—As stated above, sulfate reduction does not occur in the well aerated part of the sediment, but only in the lower layer. The kinetics of bacterial sulfate reduction have been studied by several workers, and the effects of sulfate concentration and of organic matter availability on the reaction rate have been investigated. Laboratory experiments performed on synthetic substrates or natural organic-rich muds have shown that the sulfate reduction rate is independent of sulfate concentration above some limit, between 1 and 10 mM, and proportional to the sulfate concentration below this limit (Postgate 1951; Harrison and Thode 1958; Ramm and Bella 1974; Martens and Berner 1974; Rees 1973). Accordingly, a two-layer model may be considered, with no reaction in the upper layer and with sulfate reduction following Michaelis-Menten kinetics in the lower layer:

$$r_{SO_4} = k'_{SO_4} \times \frac{(SO_4^{2-})}{K_m + (SO_4^{2-})} \quad \text{for } z < z_n.$$

As no general agreement has been reached so far concerning the precise value of the limiting concentration, both first-order and Michaelis-Menten kinetics have been applied over the entire reducing layer. Both calculations fit the experimental profile quite satisfactorily, and no selection of the most probable mechanism can be made through comparison with the experimental results. For mathematical simplification, only first-order kinetics have been used here under:

$$r_{SO_4} = 0 \quad \text{for } z < z_n$$
$$= -k_{SO_4} \times (SO_4^{2-}) \quad \text{for } z > z_n.$$

Nitrate—The modeling of nitrification and denitrification in sediments has been extensively discussed by Vanderborght and Billen (1975). The same model is used here; a constant nitrification term is assumed in the upper layer and a first-order denitrification rate is postulated in the lower one. Thus

$$r_{NO_3} = k_{NO_3} \quad \text{for } z < z_n$$
$$= -k'_{NO_3} \times (NO_3^-) \quad \text{for } z > z_n,$$

with

$$NH_4^+ + 2O_2 + 2H^+ \rightarrow NO_3^- + H_2O \quad (4)$$

in the upper layer.

Ammonium—As ammonium production is an effect of heterotrophic activity, its rate is related to the rate of oxygen consumption in the upper layer and to the rate of sulfate reduction in the lower layer. A consumption term due to nitrification must also be taken into account in the upper layer. On the other hand, denitrification in natural water and sediments produces essentially nitrogen, and no ammonium (Chen et al. 1972; Wheatland et al. 1959; Chan and Campbell 1973). There is thus no additional production term in the lower layer:

$$r_{NH_4} = -k_{NO_3} + k_{NH_4} \quad \text{for } z < z_n$$
$$= \alpha k_{SO_4} \times (SO_4^{2-}) \quad \text{for } z > z_n,$$

where α is the stoichiometric ratio between ammonium production and sulfate utilization in the anaerobic degradation of the organic matter.

Table 1. Diagenetic equation of oxygen, sulfate, nitrate, and ammonium in the two layers of muddy sediment of the North Sea.

	Upper layer ($z < z_n$)	Lower layer ($z > z_n$)
Oxygen	$D_1\frac{d^2(O_2)}{dz^2} - \omega\frac{d(O_2)}{dz} - k_{O_2} = 0$	$D_2\frac{d^2(O_2)}{dz^2} - \omega\frac{d(O_2)}{dz} - k'_{O_2}(O_2) = 0$
Sulfate	$D_1\frac{d^2(SO_4)}{dz^2} - \omega\frac{d(SO_4)}{dz} = 0$	$D_2\frac{d^2(SO_4)}{dz^2} - \omega\frac{d(SO_4)}{dz} - k_{SO_4}(SO_4) = 0$
Nitrate	$D_1\frac{d^2(NO_3)}{dz^2} - \omega\frac{d(NO_3)}{dz} + k_{NO_3} = 0$	$D_2\frac{d^2(NO_3)}{dz^2} - \omega\frac{d(NO_3)}{dz} - k'_{NO_3}(NO_3) = 0$
Ammonium	$D_1\frac{d^2(NH_4)}{dz^2} - \omega\frac{d(NH_4)}{dz} - k_{NO_3} + k_{NH_4} = 0$	$D_2\frac{d^2(NH_4)}{dz^2} - \omega\frac{d(NH_4)}{dz} + \alpha\, k_{SO_4}(SO_4) = 0$

Table 2. Solution of diagenetic equations for two-layer model.

General diagenetic equation *

Upper layer :

$$C = C_o\frac{\eta\sinh(\theta\xi) + \omega\cosh(\theta\xi)}{\eta\sinh(\theta z_n)+\omega\cosh(\theta z_n)}e^{\theta z} + \frac{\{\beta_1(\eta-\omega)z_n+2D_1\beta_1\}\sinh(\rho z)}{\omega\{\eta\sinh(\theta z_n)+\omega\cosh(\theta z_n)\}}e^{-\theta\xi} - \frac{\beta_1}{\omega}z$$

Lower layer :

$$C = C_o\frac{\omega\, e^{\sigma\xi} + \theta z_n}{\eta\sinh(\rho z_n) + \mu\cosh(\rho z_n)} + \frac{\{\beta_1(\eta-\omega)z_n+2D_1\beta_1\}\sinh(\rho z_n)}{\omega\{\eta\sinh(\theta z_n)+\omega\cosh(\theta z_n)\}}e^{\sigma\xi} - \frac{\beta_1}{\omega}z_n\, e^{\sigma\xi}$$

Diagenetic equation for ammonia†

Upper layer :

$$C = C_o + \frac{h}{\omega^2}e^{-2\theta z_n}(1-e^{2\theta z}) + \frac{h}{\omega}z - \alpha(SO_4^{2-})_o\left\{\frac{\omega\cosh(\theta\xi)+\beta\sinh(\theta\xi)}{\omega\cosh(\theta z_n)+\beta\sinh(\theta z_n)}e^{\theta z} - 1\right\}$$

Lower layer :

$$C = C_o + \frac{h}{\omega^2}(e^{-2\theta z_n} - 1) + \frac{h}{\omega}z_n - \alpha(SO_4^{2-})_o\left\{\frac{\omega\, e^{\gamma\xi} + \theta z_n}{\omega\cosh(\theta z_n)+\beta\sinh(\theta z_n)} - 1\right\}$$

*$\xi = z - z_n$; $\mu = (\omega^2+4\alpha_1 D_1)^{\frac{1}{2}}$; $\eta = (\omega^2+4\alpha_2 D_2)^{\frac{1}{2}}$; $\theta = \frac{\omega}{2D_1}$; $\rho = \frac{\mu}{2D_1}$; $\sigma = \frac{\omega-\eta}{2D_2}$

†$h = k_{NH_4} - k_{NO_3}$; $\beta = (\omega^2+4k_{SO_4}D_2)^{\frac{1}{2}}$; $\gamma = \frac{\omega-\beta}{2D_2}$

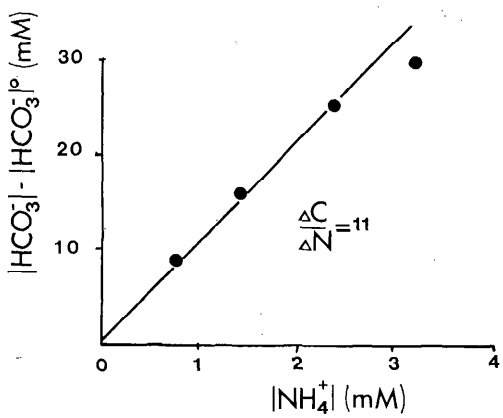


Fig. 1. Correlation between ammonium concentration and excess bicarbonate concentration with respect to seawater concentration as function of depth in interstitial water of lower layer of muddy sediments of the North Sea.

It must be emphasized that the expressions of the rate of microbiological processes represent only an operational schematization of a much more complex reality. Most of the processes considered above are in fact the result of the complementary action of several bacterial groups, each utilizing the metabolic product of the other. A very simple and well understood example is the process of nitrification, performed by two separate groups of bacteria, the first one oxidizing ammonia to nitrite and the second oxidizing nitrite to nitrate. The anaerobic oxidation of organic matter with sulfate as oxidant is also not the result of the activity of a single bacterial group. Sulfate-reducing bacteria are generally considered to be specially adapted to the degradation of C-3 or C-4 organic compounds (Goldhaber and Kaplan 1974). Recent studies have shown that lactate is the main source of energy for sulfate reduction in mud of freshwater lakes (Cappenberg 1974) as well as in marine or brackish water environments (Vosjan 1975). This implies that sulfate-reducing bacteria are closely associated with fermenting organisms producing lactate from more complex organic matter. Similar phenomena of substrate interactions between several groups of bacteria must also occur for aerobic organic matter oxidation, ammonification, etc. The expressions of the microbiological reaction rates discussed above are not intended to be an accurate description of the complex metabolic mechanisms along the bacterial chain, but rather to account in the simplest way for the effect of the whole sequence of limiting steps.

The equations for each species are summarized in Table 1. They can be put under the more general form

$$D_2(d^2C/dz^2) - \omega(dC/dz) - \alpha_1 C - \beta_1 = 0$$

for the upper layer, with $\alpha_1 = \beta_1 = 0$ (no reaction), $\alpha_1 = 0$ and $\beta_1 \neq 0$ (zero-order reaction) or $\alpha_1 \neq 0$ and $\beta_1 = 0$ (first-order reaction). For the lower layer, where only first-order reactions have been considered, the general equation is

$$D_2(d^2C/dz^2) - \omega(dC/dz) - \alpha_2 C = 0.$$

This system can be solved analytically with the conditions

$$C = C_0 \text{ for } z = 0; \quad C_{z_n^-} = C_{z_n^+};$$

$$-D_1(dC/dz)\,|_{z_n^-} = -D_2(dC/dz)\,|_{z_n^+}.$$

The general solution of the system is reported in Table 2. As the ammonium profile is dependent on sulfate concentration in the lower layer, the diagenetic equations for ammonium have been solved separately. Eleven parameters (z_n, ω, D_1, D_2, k_{O_2}, k'_{O_2}, k_{SO_4}, k_{NO_3}, k'_{NO_3}, k_{NH_4}, α) have to be fixed for calculation of the concentration profiles from these theoretical solutions. Of these, four (z_n, ω, D_1, D_2) have been determined in the silica model (Vanderborght et al. 1977). A further parameter, α, can be easily estimated. The results of determining alkalinity and ammonium in the pore water of the lower layer (Fig. 1) show that 1 mole of ammonium is produced for each 11 moles of organic carbon oxidized. This value is in close agreement with the organic carbon : nitrogen ratios cited by Emery (1960) (11.2 for sediments between 0- and 35-cm depth). It is also known that this ratio shows a large range of variation in the first centimeters of the sediments

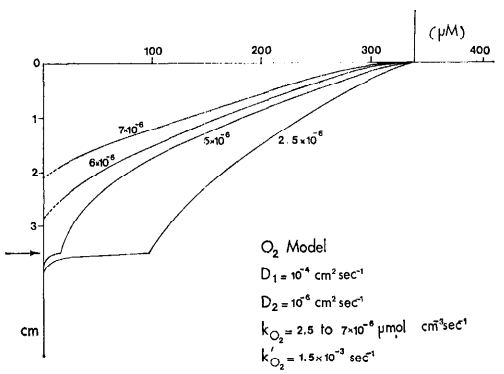


Fig. 2. Solution of diagenetic equation of oxygen for a set of k_{O_2} values.

Table 3. Rates of microbiological activities deduced from model.

Reaction	Depth (cm)	Rate (10^{-6} μmol cm^{-3} s^{-1})
Sulfate reduction	0 - 3.5	0
	3.5 - ∞	0.7 - 0
Ammonification	0 - 3.5	2
	3.5 - ∞	0.12 - 0
Nitrification	0 - 3.5	1.5
	3.5 - ∞	0
Denitrification	0 - 3.5	0
	3.5 - ∞	1 - 0

because of the rapid degradation of amino acids soon after burial (Berner 1971). C:N ratios of 8 and 11 have thus been chosen for the upper and lower layer of the sediment. Considering the stoichiometry of reactions 1 and 3, the value of α is then $2/11 \simeq 0.18$. Furthermore, a relation must exist between three other parameters, k_{O_2}, k_{NO_3}, and k_{NH_4} since the oxygen consumption is indeed the result of both aero-

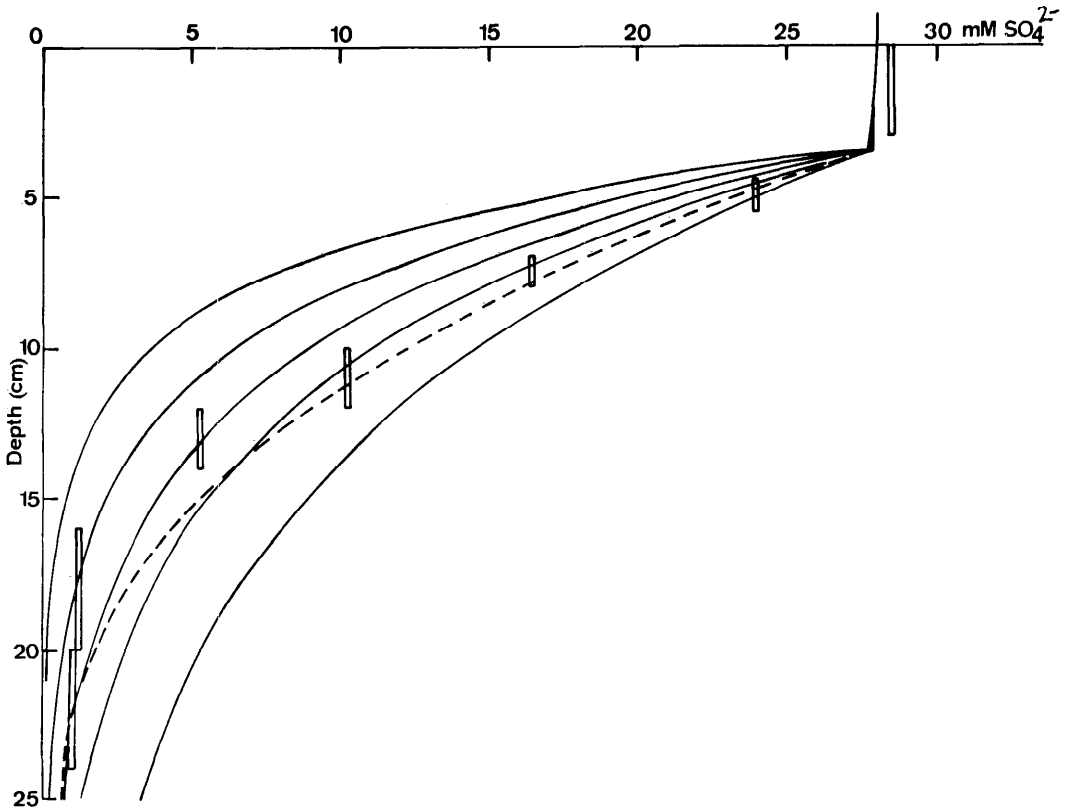


Fig. 3. Solution of diagenetic equation of sulfate for a set of k_{SO_4} values (first-order kinetics). Broken curve is solution of model for Michaelis-Menten kinetics with $k'_{SO_4} = 2.0 \times 10^{-7}$ μmol cm^{-3} s^{-1} and $K_m = 2.0$ μmol cm^{-3}. Vertical bars are experimental concentrations.

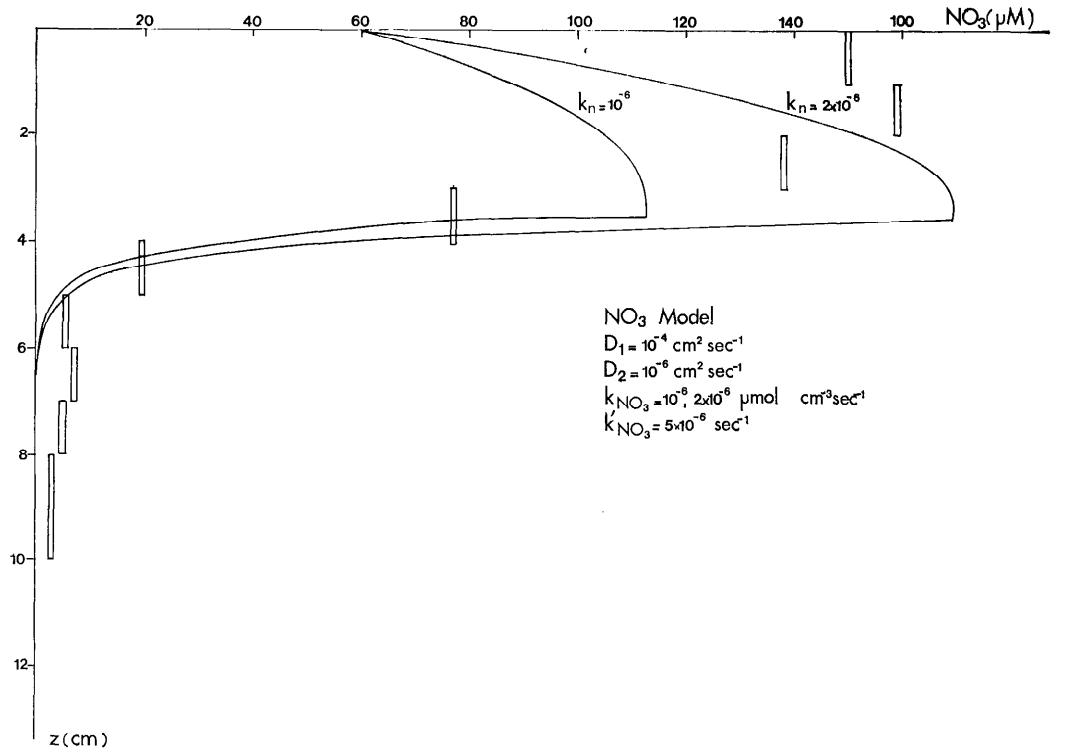
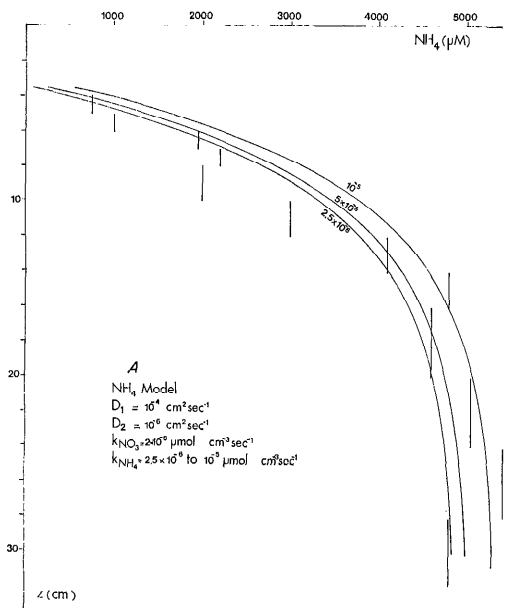


Fig. 4. Solution of diagenetic equation of nitrate for a set of k_{NO_3} values. Vertical bars are experimental concentrations.



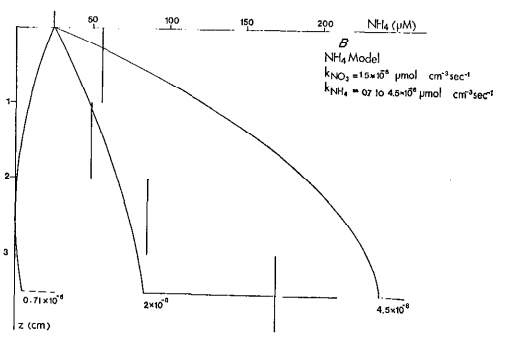


Fig. 5. Solution of diagenetic equation of ammonium for a set of k_{NH_4} values. Vertical bars are experimental concentrations. A—Lower layer; B—upper layer.

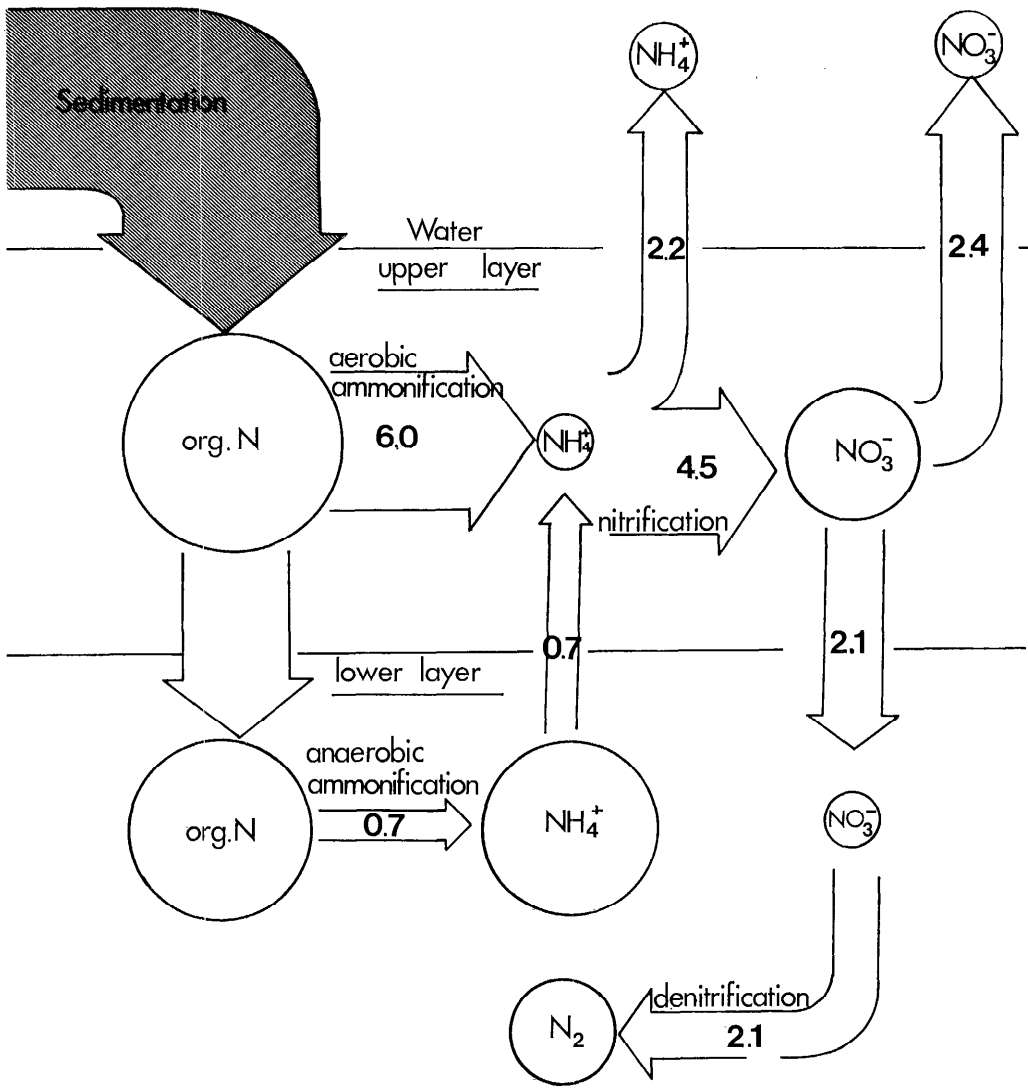


Fig. 6. Schematic representation of nitrogen transformations within the two layers of sediment and its fluxes across boundary between the two layers and sediment–water interface.

bic heterotrophic activity and nitrification. If we consider a $\Delta C:\Delta N$ ratio equal to 8 for this upper layer, the stoichiometry of the coupled reactions 1 and 2, and of the reaction 4, the value of k_{O_2} can be expressed by

$$k_{O_2} = 8k_{NH_4} + 2k_{NO_3}. \quad (5)$$

The remaining parameters must now be chosen to fit simultaneously the three experimental profiles (SO_4^{2-}, NO_3^-, NH_4^+). As far as oxygen is concerned, no experimental profile is available. However, some constraints can be formulated: oxygen concentration at the water–sediment interface

Table 4. Rates of microbiological activities derived from direct measurements published.

Reaction	Rate from in situ measurements (10^{-6} µmol cm^{-3} s^{-1})	Origin and type of sediment	Reference
Sulfate	0.01 - 0.8	Black Sea, surface silt sediment	Sorokin 1962
reduction	0	Black Sea, 10 cm depth sediment	Sorokin 1962
	0.06	Sta-Barbara Basin (USA), upper 10 cm	Kaplan et al. 1963
	0.001 - 0.09	Bay of Kiel (FRG), 0 to 30 cm	Hartmann & Nielsen 1969
	0.64 - 1.6	Limfjord (DK), surface sediment (model system)	Jørgensen & Fenchel 1974
	5.1 - 11.7	Aarhus Bay (DK), surface sediment	Jørgensen & Fenchel 1974
	0.07 - 2.7	Long Island Sound sediment	Goldhaber et al.1977
Ammonification (upper layer)	2 - 19	Raw + activated sludge (15°C)	Jaworski et al. 1963
Ammonification (lower layer)	11.5	Anaerobically digesting sludge (30°C)	Dep. Sci. Ind. Res.1962
Nitrification	11	Sluice Dock Ostend, Belgium, 0 to 5 cm, sandy sediment	Billen 1975
	2.5 - 5.5	North Sea, Belgium, 0 to 5 cm, sandy sediment	Billen 1975
	0.001 - 0.01	Rybinsk reservoir (USSR), 0 to 10 cm, sandy sediment	Kuznetsov 1968
Denitrification	0.9 - 15.8	North Sea, Belgium, muddy sediment	Billen unpublished

is supposed to be 100% saturation, i.e. 340 µM. It must be higher than about 1% saturation (3.4 µM) all over the upper layer and less than this value in the lower layer, for the upper layer has been assumed to be aerobic and the lower layer anaerobic.

Figures 2–5 show the solutions of the equations of Table 1 for selected values of the parameters. We can see that the theoretical curves are very sensitive to small variations of the parameters; the range of allowed values is thus very narrow. The best fit is obtained for the following values:

$k_{O_2} = 5.0 \times 10^{-6}$ µmol cm^{-3} s^{-1}
$k'_{O_2} = 1.5 \times 10^{-3}$ s^{-1}
$k_{SO_4} = 2.5 \times 10^{-8}$ s^{-1} (first-order)
$k'_{SO_4} = 2.0 \times 10^{-7}$ µmol cm^{-3} s^{-1} and $K_m = 2.0$ µmol cm^{-3} (Michaelis-Menten kinetics)
$k_{NO_3} = 1.5 \times 10^{-6}$ µmol cm^{-3} s^{-1}
$k_{NH_4} = 2.0 \times 10^{-6}$ µmol cm^{-3} s^{-1}

The value of k_{O_2} is too low by a factor of 3.5 to satisfy relation 5. This is probably because other oxidants can be used in the upper layer [MnO_2, NO_3^-, $Fe(OH)_3$] and have not been taken into account by the model. If these oxidants are used successively, as in the Scheldt Estuary (Billen and Smitz 1975), a multilayer model would be necessary to describe the phenomena. However, experimental results are not yet sufficient to allow such a model to be elaborated.

Discussion

The six values of the kinetic constants used in the model have been determined only by fitting the theoretical profiles of dissolved species in pore water to the experimental ones. Comparison with direct measurements of microbiological activity in sediments must now be made to see if these values are realistic. Direct measure-

ments of microbiological activities in sediments published in the literature are usually expressed in terms of rate of production or consumption by unit volume of sediment. For purposes of comparison, the values of our kinetic constants have been converted in terms of activity by unit volume (Table 3). The results of direct measurements of microbiological activity published in the literature are reported in Table 4. Although few measurements are available for some reactions, the values postulated from the model appear in all cases quite realistic. The values of the various mass transfer fluxes were calculated from the equations and the results are represented in Fig. 6. As in the case of silica (Vanderborght et al. 1977), the contribution of the upper layer is much more important than that of the underlying sediment. It is probable that the thickness and the influence of the disturbed layer is more important in coastal regions than in the deep ocean, because the existence of this layer is related to appreciable shear stresses or intense biological activity. However, many estimates of fluxes from the pore waters of the sediments are probably underestimates because of the difficulty of recovering this layer during coring. Also, this layer may play an important role in early diagenetic processes, especially for organic matter; it can be assumed that most decomposition of organic matter takes place in this well aerated layer.

References

BERNER, R. A. 1971. Principles of chemical sedimentology. McGraw-Hill.

BILLEN, C. 1975. Evaluation of nitrifying activity in sediments by dark ^{14}C-bicarbonate incorporation. Water Res. **10**: 51–57.

———, AND J. SMITZ. 1975. A mathematical model of microbial and chemical oxidation-reduction processes in the Scheldt estuary. *In* Math. Model Sea, Rapp. Synth. Comm. Polit. Sci.

CAPPENBERG, T. E. 1974. Interrelations between sulfate-reducing and methane-producing bacteria in bottom deposits of a fresh-water lake. 2. Inhibition experiments. Antonie Van Leeuwenhoek J. Microbiol. Serol. **40**: 297–306.

CHAN, Y. K., AND N. E. CAMPBELL. 1973. A rapid gas extraction technique for the quantitative study of denitrification in aquatic systems by N-isotope ratio analysis. Can. J. Microbiol. **20**: 275–281.

CHEN, R. L., D. R. KEENEY, J. C. KONRAD, A. J. HOLDING, AND D. A. GRAETZ. 1972. Gas production in sediments of Lake Mendota, Wisconsin. J. Environ. Qual. **1**: 155–157.

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH. 1962. Water pollution research, 1961. HMSO, London.

EMERY, K. O. 1960. The sea off southern California. Wiley.

GOLDHABER, M. B., R. C. ALLER, J. K. COCHRAN, J. K. ROSENFELD, C. S. MARTENS, AND R. A. BERNER. 1977. Sulfate reduction, diffusion, and bioturbation in Long Island Sound sediments. Report of the FOAM group. Am. J. Sci. **277**: 193–237.

———, AND I. R. KAPLAN. 1974. The sulfur cycle, p. 569–655. *In* E. D. Goldberg [ed.], The sea, v. 5. Wiley.

HARRISON, A. G., AND H. C. THODE. 1958. Mechanism of the bacterial reduction of sulfate from isotope fractionation studies. Trans. Faraday Soc. **54**: 84–92.

HARTMANN, M., AND H. NIELSEN. 1969. ^{34}S-Werte in rezenten Meeresedimenten und ihre Deutung am Beispiel einiger Sedimentenprofile aus der westlichen Ostsee. Geol. Res. **58**: 621–655.

JAWORSKI, N., G. W. LAWTON, AND G. A. ROHLICH. 1963. Aerobic sludge digestion, p. 93–101. *In* Advances in biological waste treatment. Proc. 3rd Conf. Biol. Waste Treatment. Pergamon.

JØRGENSEN, B. B., AND T. FENCHEL. 1974. The sulfur cycle of a marine sediment model system. Mar. Biol. **24**: 189–201.

KAPLAN, I. R., K. O. EMERY, AND S. C. RITTENBERG. 1963. The distribution and isotopic abundance of sulfur in recent marine sediments of southern California. Geochim. Cosmochim. Acta **27**: 297–331.

KUZNETSOV, S. I. 1968. Recent studies on the role of microorganisms in the cycling of substances in lakes. Limnol. Oceanogr. **13**: 211–224.

MARTENS, C. S., AND R. A. BERNER. 1974. Methane production in the interstitial waters of sulfate-depleted marine sediments. Science **185**: 1167–1169.

POSTGATE, J. R. 1951. The reduction of sulphur compounds by *Desulfovibrio desulfuricans*. J. Gen. Microbiol. **5**: 725–738.

RAMM, A. E., AND D. A. BELLA. 1974. Sulfide production in anaerobic microcosms. Limnol. Oceanogr. **19**: 110–118.

REES, C. E. 1973. A steady state model for sulfur isotope fractionation in bacterial reduction

process. Geochim. Cosmochim. Acta **37**: 1141–1162.

SOROKIN, Y. I. 1962. Experimental investigation on bacterial sulfate reduction in the Black Sea using ^{35}S. Mikrobiologiya **31**: 402–410.

VANDERBORGHT, J. P., AND G. BILLEN. 1975. Vertical distribution of nitrate concentration in interstitial water of marine sediments with nitrification and denitrification. Limnol. Oceanogr. **20**: 953–961.

———, R. WOLLAST, AND G. BILLEN. 1977. Kinetic models of diagenesis in disturbed sediments. Part 1. Mass transfer properties and silica diagenesis. Limnol. Oceanogr. **22**: 787–793.

VOSJAN, J. H. 1975. Ekologische en fysiologische aspecten van bacteriële sulfaatreductie in het Waddengebieg. Thesis, Rijksuniv. Groningen.

WHEATLAND, A. B., M. S. BARRETT, AND A. M. BRUCE. 1959. Some observations on denitrification in rivers and estuaries. Inst. Sewage Purif. J. Proc. **2**: 149–159.

Submitted: 13 November 1975
Accepted: 18 February 1977