Vertical distribution of nitrate concentration in interstitial water of marine sediments with nitrification and denitrification

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Abstract

Vertical concentration profiles of nitrate and nitrite in interstitial water of sediment in the Sluice Dock at Ostend (Belgium) commonly show a maximum in nitrate concentration at a few centimeters depth where sediments are sandy and poor in organic matter, while in muddy and organic-rich sediments, nitrate is lower in interstitial water than in the overlying water and decreases rapidly with depth. Direct measurements of the activity of autotrophic nitrifying bacteria in the sediments show nitrification in the upper few centimeters of sandy sediments but not in muddy sediments.

A mathematical model is proposed to analyze quantitatively these experimental results, taking into account nitrification, denitrification, diffusion, and sedimentation. Seasonal variations of nitrate concentration in overlying water are slow enough to justify the use of a stationary (steady state) model. When appropriate values are used for the parameters (rate of nitrification, depth of the sedimentary layer in which nitrification occurs, rate of denitrification, diffusion coefficient), some being experimentally determined, the model predicts concentration profiles in good agreement with experimental data.

Quantitative studies of the nitrogen cycle in marine ecosystems are important to an understanding of the basic processes of production in the sea. Since bacteria play an important role in the transformations of nitrogen in sediments and the subsequent diffusion of dissolved nutrients to the overlying water, particularly in coastal regions, there is need for estimates of the rate of microbiological and physicochemical processes occurring in the sediments in connection with biogeochemical cycles. Such dynamic estimates can be deduced from a static description of the vertical distribution of pertinent chemical species in the sediment when an appropriate mathematical analysis of these data is developed (Berner 1972).

Rittenberg et al. (1955) and Berner (1972, 1974) have made such studies of the bacterial degradation of organic nitrogen and diffusion of ammonium. However, less attention has been paid to the repartition of nitrates and nitrites in sediments, although work by Trifonova (cited in Kuznetsov 1968) and Chen et al. (1972) indicates that the nitrate exchange between sediments and water can be a significant part of total nitrogen exchange, whether the sediments act as a nitrate source or sink for the overlying water.

As part of a study of nitrogen transfers in a marine ecosystem (Podamo 1974a,b,c), data were collected on nitrate and nitrite vertical distributions in the pore water of sediments of the Sluice Dock at Ostend, a small artificial lagoon near the Belgian coast. To interpret these data and to deduce the quantitative role of sediments in the nitrogen cycle, a mathematical model of vertical nitrate distribution in pore water is proposed. It is the aim of this paper to show that such a mathematical model can be useful for relating observed nitrate profiles in pore water to the rate of relevant microbiological and physicochemical processes.

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Methods

The Sluice Dock at Ostend is an artificial lagoon (86 ha and about 1.5 m deep), filled with seawater and used for the cultivation...
of oysters. Its biology has been continuously studied since 1938 (Leloup and Van Meel 1965; Polk and Burd 1965; Podamo 1974a,b,c; Mommaerts-Billiet et al. 1974). The sedimentology was surveyed by Wollast and Dchairs (1972), who recognized in the bottom a muddy and sandy zone: in the larger muddy zone, the sediments are rich in clay minerals and organic matter (from 3.5–6% organic matter); in the sandy zone, covering only a tenth of the area, organic content is <3%.

Sediment cores were collected by hand in a rigid plastic tube 5 cm in diameter and about 30 cm long. Cores for chemical analysis were immediately frozen, then sawed into 2- to 0.5-cm lengths.Interstitial waters were extracted by pressure filtration for sandy sediments or by centrifugation for muddy sediments. Samples were either immediately analyzed or kept frozen. Cores for bacteriological experiments were collected in a sheath of transparent plastic inside the rigid corer, so that the sample was easily taken out of the corer without disturbing its stratification. The sheath was then opened and the samples immediately treated.

Nitrate and nitrite were measured by the automated procedure described by Armstrong et al. (1967).

The autotrophic incorporation of bicarbonate by nitrifying bacteria was measured according to the method of Billen (1975b). Two identical 5-cm³ samples of sediments, one untreated and the other treated with 5 ppm of Nserve, a specific inhibitor of nitrifying activity (Goring 1962; Shattuck and Alexander 1963), were incubated in the dark for about 5 h at in situ temperature in the presence of 5 μCi of 14C-labeled bicarbonate. Experiments with enrichment cultures showed that under these experimental conditions Nserve entirely inhibits bicarbonate incorporation by nitrifying bacteria but does not affect incorporation by heterotrophic bacteria (Billen 1975b). After incubation, samples were suspended in 30 ml of filtered seawater, homogenized with an Ultra Turrax to separate bacteria from their solid substrate, and centrifuged at 2,500 rpm for 2 min; the supernatant was then filtered through 0.2-μ Millipore filters. The radioactivity in the material deposited on the filter was measured by liquid scintillation after dissolution in the scintillating medium. Bicarbonate incorporation was calculated from the bicarbonate concentration of the interstitial water determined by standard acid titration. The difference between bicarbonate incorporation by the untreated sample and by the Nserve-treated sample is taken as a relative index of the activity of autotrophic nitrifying bacteria.

To obtain from our measurements an absolute estimate of the rate of nitrification in terms of nitrogen oxidized, the following arguments have been taken into account. Our method of determining incorporated radioactivity is not quantitative because bacterial cells may remain adsorbed on mineral particles in spite of the Ultra Turrax treatment. In contrast, the method of Smith et al. (1972) is much more tedious but gives quantitative measurements. We intercalibrated our method with Smith's with the Sluice Dock sediments and got a fairly reproducible recovery of 2–5% of incorporated radioactivity. These figures were used to estimate a range of total incorporation from our relative measurements. Gundersen and Mountain (1973) stated that nitrifying organisms use about 1 mole of bicarbonate for 5 moles of ammonia oxidized to nitrate. We used this ratio to calculate the rate of nitrate production from the figures for bicarbonate incorporation.

**Experimental nitrate concentration profiles**—Vertical profiles of nitrate concentrations in interstitial waters from the Sluice Dock at Ostend are of two major types. In the first type (Fig. 1a), the concentration of nitrates is lower in the interstitial water of the sediment than in the overlying water and rapidly decreases with depth. Because the concentration gradient at the sediment-water interface is negative, nitrates diffuse from the overlying water into the sediment, which acts as a sink of nitrates for the water. In the second type (Fig. 1b), nitrate and nitrite concentrations are higher in the upper few centimeters of the sediment than
Nitrification in sediments

Nitrate concentration, pM

Fig. 1. Vertical profiles of measured nitrate concentration in pore water of the Sluice Dock sediments. a—Muddy zone; b—sandy zone.

in the overlying water and decrease below that. In this case, the concentration gradient at the sediment-water interface is positive, implying that nitrates diffuse out of the sediments. Profiles from the pore water of the muddy zone are always of the first type; those from the sandy zone are most frequently of the second type, and of the first type only when the nitrate concentration in the overlying water is higher than 100 μmoles liter⁻¹. The data from the two zones are discussed below, in successive sections, with the help of a mathematical model for nitrate concentration in the interstitial water.

Stationary model for the muddy sediments—The rapid decrease of nitrate in the interstitial water of this zone can be attributed to bacterial denitrification—a heterotrophic process in which nitrates and nitrites are used as final electron acceptors in the oxidation of organic matter and transformed into elemental nitrogen. Many groups of heterotrophic bacteria can do this (Painter 1970), so the concentration of nitrates is likely the most important limiting factor affecting the rate of denitrification in organic-rich sediments. This permits us to represent denitrification as a first-order reaction with respect to the concentration of nitrates C in the pore water, with a denitrification rate \( r_d = k_d C \), where \( k_d \) is the first-order rate constant for denitrification.

To establish the diagenetic equation (Berner 1971) for nitrate in pore water, two further assumptions must be made.

1. Nitrates are assumed to diffuse in pore water according to Fick's first law, with a constant diffusion coefficient \( D \). A likely order of magnitude for the diffusion coefficient of this anion is \( D = 10^{-5} \text{ cm}^2 \text{ s}^{-1} \) (Berner 1971). However, as we are concerned with the upper few centimeters of the sediments, turbulences caused by hydrodynamical or biological perturbations cannot be neglected. Recent results (Wollast et al. in prep.) show that apparent diffusion coefficients up to \( 10^{-4} \text{ cm}^2 \text{ s}^{-1} \) can be encountered in the first centimeters of some marine sediments. The order of magnitude for the diffusion coefficient will be taken here as in the range \( 10^{-5} \) to \( 5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \).

2. The sedimentation rate \( \omega \) is assumed to be constant with time. From bathymetric data (Leloup and Van Meel 1965), a value of about 0.5–1 cm yr⁻¹ can be assumed.

The one-dimensional diagenetic equation for nitrates in pore water can then be written as

\[
\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial z^2}\right) - \omega\frac{\partial C}{\partial z} - k_d C, \quad (1)
\]

where \( C \) is a function of both depth \( z \) and
time $t$. When a stationary state is reached, the equation reduces to

$$D\left(\frac{d^2C}{dz^2}\right) - \omega \left(\frac{dC}{dz}\right) - k_d C = 0,$$

(2)

with the boundary conditions $C = C_0$ for $z = 0$ and $C = 0$ for $z = \infty$. The solution of this equation is the decreasing exponential

$$C = C_0 \exp\left\{ -\frac{\omega}{2D} - \left(\frac{\omega^2}{4D^2} + \frac{k_d}{D}\right)^{\frac{1}{2}} \right\} z. \quad (3)$$

If $\omega/4D \ll k_d$ (which means $k_d > 2 \times 10^{-11}$ s$^{-1}$), Eq. 3 can be expressed as

$$C = C_0 e^{-\left(\frac{k_d}{D}\right)^{\frac{1}{2}} z}. \quad (4)$$

The comparison of computed profiles with the experimental ones in Fig. 1b shows that the observed distributions can be simulated by this model with $k_d$ being in the range $2 \times 10^{-6}$ to $4 \times 10^{-5}$ cm$^2$ s$^{-1}$ and $D = 2 \times 10^{-5}$ cm$^2$ s$^{-1}$. This rate of denitrification can be compared with the experimental values for consumption of nitrates by sediments reported by Kuznetsov (1968). According to the law of diffusion, the flux of nitrates crossing the interface from the overlying water into the sediment is

$$\Phi = -D \left(\frac{dC}{dz}\right)|_{z=0},$$

which can be expressed as

$$\Phi = C_0 \left(\frac{k_d D}{D}\right)^{\frac{1}{2}}.$$

For $C_0 = 20 \mu$M, $D = 2 \times 10^{-5}$ cm$^2$ s$^{-1}$, and $k_d = 2 \times 10^{-9}$ to $4 \times 10^{-8}$ cm$^2$ s$^{-1}$, $\Phi = 10^{-7}$ to $6 \times 10^{-7}$ pmole cm$^{-2}$ s$^{-1}$. These values for the nitrate flux are in good agreement with the experimental data of Kuznetsov, which are in the range of $3 \times 10^{-7}$ to $3 \times 10^{-8}$ pmole cm$^{-2}$ s$^{-1}$.

The preceding model is based on the hypothesis that a stationary state is reached in the pore water of the sediments. Because nitrate concentrations in the overlying water vary seasonally, a true stationary state may not be assumed for the nitrate concentration of the pore water. The effect of variations in the upper water composition will now be considered.

**Nonstationary model for the muddy sediments**—If the nitrate concentration in the upper water shows an instantaneous jump from $C_1$ to $C_2$ at time $t = 0$, the time to reach a new stationary state can be calculated. The equation to be solved, if the rate of sedimentation is neglected, is

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial z^2}\right) - k_d C,$$

(5)

with the initial conditions

$$C(z,0) = C_1 e^{-\left(\frac{k_d}{D}\right)^{\frac{1}{2}} z},$$

$$C(0,t) = C_1 \text{ for } t < 0, \text{ and}$$

$$C(0,t) = C_2 \text{ for } t > 0.$$

The solution of this equation can be expressed as the sum of the new stationary state and a transient term:

$$C = C_2 e^{-\left(\frac{k_d}{D}\right)^{\frac{1}{2}} z}$$

$$+ \frac{1}{2} \left( C_1 - C_2 \right) \left\{ e^{-\left(\frac{k_d}{D}\right)^{\frac{1}{2}} z} \text{erfc}\left[ \frac{k_d t}{4Dt} \right] - \frac{z}{(4Dt)^{\frac{1}{2}}} \right\} \right.$$  

$$- e^{\left(\frac{k_d}{D}\right)^{\frac{1}{2}} z} \text{erfc}\left[ \frac{k_d t}{4Dt} \right] + \frac{z}{(4Dt)^{\frac{1}{2}}} \} \quad (6)$$

Concentration profiles have been computed for increasing times after a jump from 150 to 30 $\mu$M of nitrate in the overlying water.
Nitrification in sediments

Although the minimum values for the coefficients $D(10^{-9} \text{ cm}^2 \text{ s}^{-1})$ and $k_d (2 \times 10^{-6} \text{ s}^{-1})$ were used to increase the time to reach the new stationary state, Fig. 2 shows that the maximum no longer exists after 55 h, and a new stationary state is almost reached after 11 days.

Obviously, an instantaneous jump is quite unrealistic. The seasonal variations of nitrate in the water are better approximated by a sinusoidal function of time. The boundary conditions are then

$$C_0 = C(0,t) = (C_0) + (\Delta C_0) \sin \phi t,$$

and $C_{\infty} = C(\infty,t) = 0$.

and the solution of the diagcnctic Eq. 5 is

$$C = (C_0)e^{-\left(\frac{k_d}{D}\right) \frac{h^2}{2}} + (\Delta C_0)e^{-\alpha \sin(\phi t - \beta z)},$$

with

$$\alpha = \left(\frac{1}{2D}k_d + \left(k_d^2 + \phi^2\right)^{\frac{1}{4}}\right)^{\frac{1}{4}},$$

and

$$\beta = \phi \left(2D\left(k_d + \left(k_d^2 + \phi^2\right)^{\frac{1}{2}}\right)^{-\frac{1}{4}}\right).$$

Variations of nitrate profiles have been computed for a sinusoidal variation fitting the seasonal evolution of nitrate concentration in Sluice Dock, expressed by

$$C_0 = 50 + 50 \sin \phi t (C_0 \text{ in } \mu\text{M}),$$

where $\phi = 2 \times 10^{-7} \text{ s}^{-1}$ (1 cycle per year).

Profiles for stationary states corresponding to the same upper water concentration have also been computed according to Eq. 4. The differences between stationary and nonstationary states remain below 2% of the nitrate concentration. Consequently, a stationary model is very good for approximating nitrate concentration profiles in interstitial waters of sediments subjected only to denitrification and diffusion.

Stationary model for the sandy sediments —As indicated above, nitrate in the pore waters of the sandy sediments commonly shows a maximum at a few centimeters depth. The results of the nonstationary model in the preceding section show that this maximum cannot be explained as the persistence of a transient state in response to a variation in the composition of the upper water. The shape of the nitrate profiles in the interstitial water of the sandy sediments therefore implies that nitrates are produced in the upper few centimeters of the sediments. We will now show that nitrification can account for this production.

Although heterotrophic nitrification can take place (Verstrate and Alexander 1973), most nitrification is the result of the activity of autotrophic bacteria deriving their energy from the aerobic oxidation of ammonium. We have made direct measurements of autotrophic bicarbonate incorporation by nitrifying organisms in some freshly collected cores; typical results are shown in Fig. 3. The general pattern in the sandy zone is roughly that of a constant activity in the few upper centimeters, then a sudden reduction to zero with increasing depth. In the muddy zone, on the other hand, the activity is zero at all depths.

These results can easily be explained by the dependence of autotrophic metabolisms on redox conditions. Because nitrifying organisms draw their energy from the oxidation of ammonium to nitrites and nitrates, they cannot function under redox conditions such that ammonium is thermodynamically stable with respect to nitrites and nitrates. A study of nitrification in the Scheldt estuary (Billen 1975a) has shown that an empirical redox limit under which nitrification does not occur is at about 210 mV for pH 7.5, if $Eh$ is measured with a platinum electrode. ZoBell (1935) reported that, in pure cultures of nitrifiers isolated from marine sediments, nitrites appeared only when the redox potential reached $Eh = 250-300$ mV at pH 8.0 (20°C).

It appears therefore, that nitrification can only proceed in sediments where the redox potential is greater than about 200-250 mV. Regardless of how imperfect $Eh$ measurements may be in sediments (Stumm 1966), $Eh$ profiles in the muddy and sandy sediments of the Sluice Dock (Fig. 4) show that redox conditions allow nitrification only in the shallowest depth of the sandy sediments, and not at all in the muddy zone where sediments are highly reducing at all depths. Nitrification in the sediments of
The sand zone will therefore be mathematically expressed by a constant term, \( k_n \), only to be taken into account in the layer above the limit level, \( z_n \), corresponding to the depth where \( Eh \) falls below the value for which oxidation of ammonium is no longer exoenergetic. Denitrification will occur below this depth. The order of magnitude of the nitrifying activity \( k_n \) can be deduced from the measurements of bicarbonate incorporation by nitrifying bacteria. The data of Fig. 3 imply that the nitrification rate is in the range 1 to 8 \( \times 10^{-8} \) pmole cm\(^{-3}\) s\(^{-1}\), in terms of nitrogen oxidized.

The diagenetic equation for this two-layer model is

\[
\frac{\partial C}{\partial t} = \frac{D(\partial^2 C/\partial z^2)}{\partial} - \omega(\partial C/\partial z)
+ ek_n - (1 - \epsilon)k_d C, \tag{8}
\]

with \( \epsilon = 1 \) for \( z < z_n \) (nitrification layer) and \( \epsilon = 0 \) for \( z > z_n \) (denitrification layer). If a stationary state is obtained, the equation is reduced to

\[
D(\partial^2 C/\partial z^2) - \omega(\partial C/\partial z) + ek_n - (1 - \epsilon)k_d C = 0, \tag{9}
\]

with boundary conditions \( C = C_0 \) for \( z = 0 \), and \( C = 0 \) for \( z = \infty \). This equation can be solved by expressing the continuity at depth \( z = z_n \) for concentration and its first derivative. When sedimentation rate can be neglected, the solution is

\[
C = \frac{(kn/2D)z^2}{2} + Az + C_0 \quad \text{for} \quad z < z_n, \tag{10}
\]

\[
C = Be^{-(k_d/D)^{1/2}(z-z_n)} \quad \text{for} \quad z > z_n,
\]

where

\[
A = \frac{k_n}{D} \left[ \frac{z_n^{2}}{2} + \left( \frac{D}{k_d} \right)^{1/2} z_n \right] - C_0,
\]

and

\[
B = \left( \frac{k_n}{2D} \right) z_n^2 + Az_n + C_0.
\]

Theoretical profiles have been drawn for
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Fig. 7. Theoretical nitrate concentration profiles for the two-layer nonstationary model. Sinusoidal variation of nitrate concentration in the overlying water: 1—t = 0; 2—3 months; 3—6 months; 4—9 months.

\[ \text{Stationary state profiles for the same overlying water concentration have also been drawn (Fig. 7). The differences remain below 5\% of the nitrate concentration. The stationary model is thus a good approximation for the two-layer sediment.} \]

Conclusions

The vertical distribution of concentrations of chemical species in the interstitial water of sediments can result from numerous physicochemical and biological phenomena. In this study, we have shown that actual profiles of nitrate concentration in interstitial water can be satisfactorily fitted with the solution of a differential equation taking into account diffusion and denitrification as the only phenomena responsible for nitrate distribution in the muddy zone, and nitrification, denitrification, and diffusion in the sandy zone. In both cases, the seasonal variations of nitrate concentrations in the overlying water are slow enough to allow description of the nitrate profiles in the pore water by a stationary model. The vertical nitrate distribution in sediments can thus be completely described with a few parameters, some of which can be determined: the rate of nitrification and the depth of the layer in which this process takes place, the rate of denitrification (considered as first order with respect to nitrate concentration); the diffusion coefficient of nitrate in pore water; and the sedimentation rate, often negligible with respect to the other factors.

Dynamic parameters such as the total rate of nitrification or denitrification and the flux of nitrate across the sediment-water interface can be deduced from the static distribution of nitrate in sediment pore waters, using the equations of the model. Therefore this model will be useful in studying nitrification and denitrification in marine sediments, their seasonal variations, and their role in the nitrogen cycle of marine ecosystems.

References


Kuznetsov, S. I. 1968. Recent studies on the role of microorganisms in the cycling of sub-
Nitrification in sediments


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Errata

In the article by Tett et al. (Vol. 20, No. 4), the correct symbol for the apparent subsistence quota in Table 1 (p. 588) is \( K_0 \). The first sentence of the second paragraph on p. 596 should read as follows. For the second group, comprising data from 26 March–26 April—the period of decline of the standing crop—the correlation coefficient was -0.55 (17 df), and the intercept \( ccf_{max} \cdot (1 + t/\mu'_{max}) \) was 0.044 (SE 0.007) and the intercept \( (1/K_0)(1 + t/\mu'_{max}) \) was 176 (SE 30).