Mathematical Modelling, Vol. 3, pp. 523–533, 1982
Printed in the USA.

0270-0255/82/060523-11$03.00/0

AN ECOPHYSIOLOGICAL MODEL OF NITRIFICATION IN THE SCHELDT ESTUARY

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Communicated by J. C. J. Nihoul

Abstract—A model of nitrification in the Scheldt Estuary by planktonic microorganisms is constructed; this model includes (i) the description of the complex hydrodynamical factors resulting from the mixing of freshwater and seawater; (ii) the influence of environmental parameters (salinity, redox potential, substrate concentration, temperature) on the activity of nitrifying organisms. The model accurately simulates the longitudinal profiles of nitrate and ammonium nitrogen in the estuary.

INTRODUCTION

Nitrification is a very important process in polluted estuaries because it regenerates nitrogenous oxidized species and constitutes the ultimate step of self-purification before reestablishment of oxygen saturation in the stream. It modifies the speciation of inorganic nitrogen and affects its assimilation rate by phytoplankton. After nitrification, the problem of eutrophication in the receiving coastal areas is set differently.

Nitrification is part of a complex set of redox microbiological processes linked to organic load degradation and restoration of oxidative conditions. Previous studies [1, 2, 3] have shown the importance of nitrification in the Scheldt Estuary and stressed the critical role of different environmental parameters (redox potential, salinity, substrate concentration . . .) on the kinetics of the metabolism.

The Scheldt Estuary, 120 km in length, is a partially stratified estuary which is highly polluted upstream by urban and industrial discharges. Following the discharge of important amounts of organic matter by the Rupel River (km 92) and by the town of Antwerp (km 80), heterotrophic activity uses the mineral oxidants present in the water, in the order O_2, MnO_2, NO_3^-, $Fe(OH)_3$, and $SO_4^=$.

Downstream, when heterotrophic activity decreases due to organic load reduction (partly through its microbiological degradation and mainly through flocculation and sedimentation), chemolithographic metabolisms occur, which regenerate the oxidants in the opposite order: $SO_4^=$, $Fe(OH)_3$, NO_3^-, MnO_2. Oxygen ultimatley reappears by reaeration.

Billen and Smitz [4] have developed a mathematical model describing the relation between microbial redox processes and water quality. The basic assumption of this

model is that the mineral redox couples susceptible to be used by bacteria (O_2/H_2O, MnO_2/Mn^{++}, NO_3^-/NH_4^+, $Fe(OH)_3/Fe^{++}$, $SO_4^=/S^=$) are in thermodynamical equilibrium.

With this crude assumption, a first simulation of the redox state and quality parameters of the water under the influence of heterotrophic activity has been obtained; the behaviour of nitrates, however, was not satisfactorily predicted. Since, in a second step, a kinetic limitation of the nitrate production term has been introduced (the NH_4^+/NO_3^- couple was then considered outside the thermodynamic equilibrium); this "second level" model appears to be more reliable, the computed solutions being in good agreement with measured values. This calls for a more realistic model of nitrification process, taking into account the physiology of nitrifying microorganisms.

The purpose of this paper is to present such a model, based on known physiological properties of nitrifying bacteria and on several *in situ* and laboratory experiments [1, 2].

EXPERIMENTAL PROFILES

Longitudinal profiles of salinity, nitrate and ammonium concentration, and nitrifying activities [2] in the Scheldt Estuary have been measured on four occasions corresponding to different seasonal and hydrodynamic conditions (February, April, May, July 1976) (see Fig. 1). The corresponding river discharges measured 90 km from the mouth were, respectively, 110, 51, 39, and 29 m^3/sec.

MODEL

Hydrodynamics of the estuary

It is beyond the scope of this work to present a detailed description or modelling on the complex hydrodynamics of the Scheldt Estuary. A simple one-dimensional model has been adopted. The longitudinal distribution of any cross-section-averaged concentration c can be described by an equation of the form [5].

$$\mathscr{D}c \equiv \frac{\partial}{\partial t}(ac) + \frac{\partial}{\partial x}(auc) - \frac{\partial}{\partial x}\left(\Lambda \frac{\partial}{\partial x}(ac)\right) = P - D, \tag{1}$$

where x is the longitudinal coordinate; a is the mean cross-section (calculated as an exponential function of x [6]; u is the cross-section-averaged residual velocity; Λ is the global dispersion coefficient (including effects of tidal motions and other complex hydrodynamical phenomena typical of a partially stratified estuary); P and D are, respectively, the rates of production and destruction of c as a result of physical, chemical, or biological reactions; c is the cross-section-averaged concentration averaged over some period τ larger than the tidal period.

The computation of the residual velocity u and of the dispersion coefficient Λ is obtained by the hydrodynamic model of the estuary, the precise calibration being made on the chlorinity concentration profile (chlorinity is a conservative parameter which concentration depends on mixing between saline and freshwater).

In the Scheldt Estuary, the upstream water discharge presents slow seasonal changes, and a steady-state assumption is valid for the description of concentrations variations.

KINETICS OF NITRIFYING ACTIVITY

The comparison of nitrate flux from Scheldt sediments [3] and of nitrate production by planktonic nitrification [2] has shown that the latter process, accounting for more than

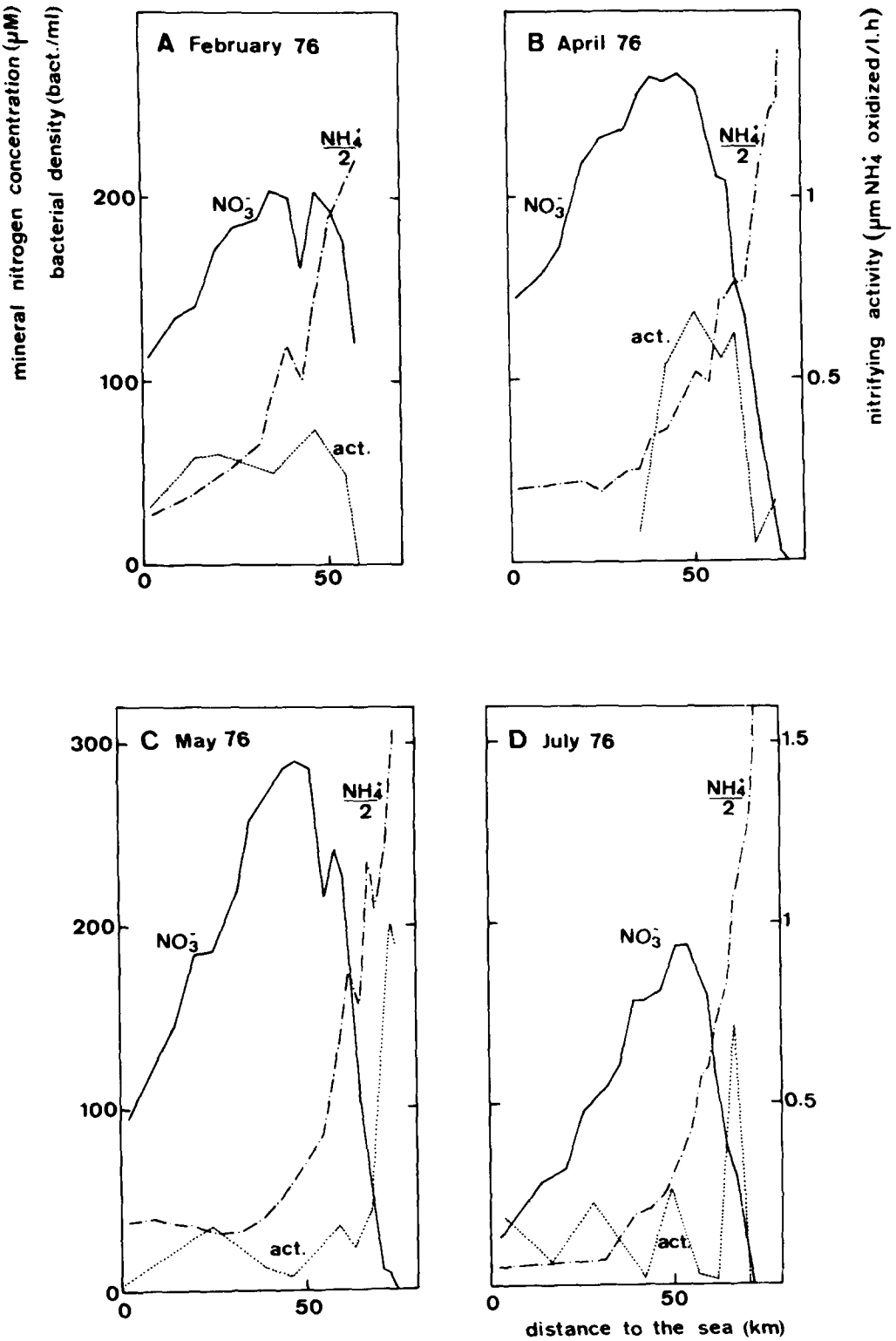

Fig. 1. Measured profiles of the concentrations of nitrate and ammonium and nitrifying activity as a function of the distance to the sea for February (A), April (B), May (C) and July (D), 1976.

Table 1. Nitrate fluxes in the nitrification reach of the Scheldt: (1) from the sediment to the water column; (2) in the water column resulting of nitrification process

	(1) Sediments	(2) Water column
Somville [2]	–	0–0.1 μM NO_3^-/l·h
Somville [3]	0–0.015 μM NO_3^-/l·h	–

90% in the nitrate budget, was by far the most important (Table 1). These observations have led to consider in the model the nitrification process as the result of planktonic nitrification only.

Growth rate of nitrifiers (G) and nitrifying activity (A) are considered as proportional to the number of planktonic nitrifying bacteria (B):

$$G = KB$$
$$A = \alpha KB,$$

where K (sec^{-1}) is the growth constant; α is the quantity of ammonium to be oxidized for duplicating one bacterium, i.e., the reciprocical of the yield constant Y; B is the concentration of nitrifiers (bacteria/l). The value of K is considered to depend on environmental parameters (namely, salinity, ammonium concentration, temperature, redox potential). If $\mathcal{D}$ represents the hydrodynamical operator:

$$\mathcal{D} \equiv \frac{\partial}{\partial x}(au) - \frac{\partial}{\partial x}\left(\Lambda \frac{\partial}{\partial x}(a)\right).$$

The evolution of the nitrifying biomass B resulting from hydrodynamic processes, growth, and mortality effect, can be expressed by

$$\mathcal{D}B = KB - mB \tag{2}$$

and the distribution of ammonium and nitrate are thus expressed by

$$\mathcal{D}(NO_3^-) = \alpha KB \tag{3}$$
$$\mathcal{D}(NH_4^+) = -aKB. \tag{4}$$

K can be expressed by

$$K = kf_1(S) \cdot f_2(NH_4^+) \cdot f_3(T) \cdot f_4(\mathrm{Eh}),$$

where k is the optimal growth constant for nitrifying bacteria, and f_1, f_2, f_3, and f_4 are, respectively, functions of salinity, ammonium concentration, temperature, and redox potential; the value of these functions is one at optimal conditions.

Effect of salinity

Potential nitrifying activities measured on short term experiments by dark ^{14}C-incorporation [2] at different places in the estuary have shown that during progressive mixing of freshwater into saline water masses, the *in situ* population of nitrifying

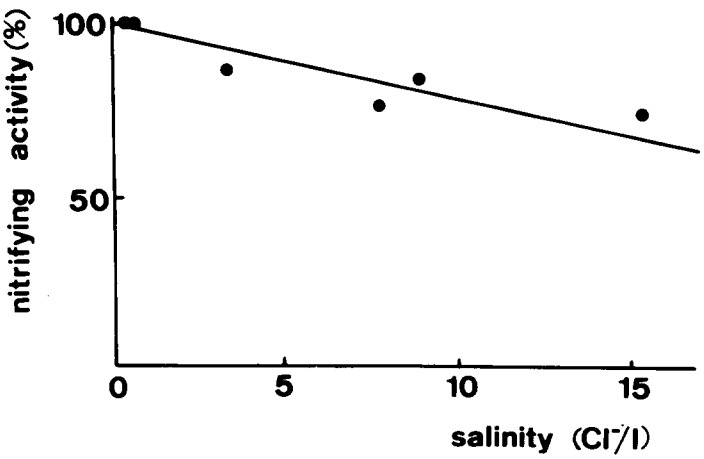

Fig. 2. Relative nitrifying activity of various populations with respect to the maximum activity observed, as a function of the salinity of the water mass from where they originate.

bacteria tends to adapt itself to the prevailing chloride concentration, with, however, a definite delay.

The relation found between salinity of the sample and nitrifying activity, expressed as a percentage of the activity at optimal salinity, is represented on Fig. 2. This experimental relation can be parameterized by

$$f_1(S) = 1 - 0.018S,$$

where f_1 is the fraction of nitrifying activity measured at salinity S (g Cl^-/l) with respect to optimal activity.

Effect of substrate concentration

The relation between the potential nitrifying activity of an enrichment culture of nitrifiers and the ammonium concentration is shown in Fig. 3. This experimental

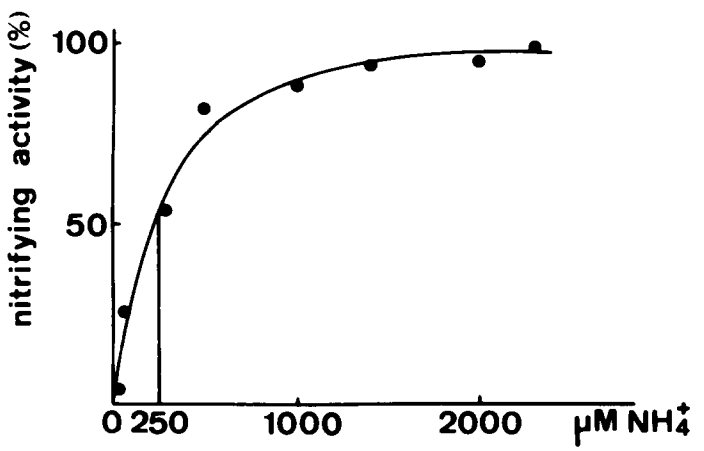

Fig. 3. Relation between potential nitrifying activity of an enrichment culture of nitrifiers and the ammonium concentration.

relationship has been represented by a Michaëlis–Menten–Monod function:

$$f_2 = \frac{[NH_4^+]}{[NH_4^+] \times Km}$$

with Km equal to 250 μM NH_4^+.

Influence of temperature

Carlucci and Strickland [7] have determined that the optimal temperature for marine nitrous bacteria in pure culture was 28 °C. As the temperature of water in the Scheldt Estuary is always lower than 28 °C, the effect of temperature is expressed by $(T - 28)/10$; $f_3 = Q_{10}$, with T expressed in °C. Buswell *et al.* [8], Carlucci and Strickland [7], Wild *et al.* [9], determined Q_{10} values, respectively, in the range 1.7–1.9, 1.7–2.2, and 1.3–3.0 for *Nitrosomonas*. Q_{10} has thus been chosen to the mean value of these results ($Q_{10} = 1.9$).

Redox potential function

Billen [1] showed that nitrification was only possible above a critical potential. At pH 7.5, this critical redox potential (measured with a platinum electrode) above which nitrification is possible was found 220 mV. Accordingly, f_4(Eh) is defined as

$$f_4(\text{Eh}) = 1 \text{ for Eh} \geq 220 \text{ mV}$$
$$= 0 \text{ for Eh} < 220 \text{ mV}$$

Optimal growth constant k

A review of the growth constant k measured in pure culture, in optimal conditions of growth, has been published by Painter [10]. In the present work, k has been chosen between the extreme values of 5×10^{-6} and 25×10^{-6} sec^{-1}, respectively, reported by Lees [11] and Skinner *et al.* [12].

Yield constant

Assuming a cellular water content of 70% and a mean diameter of the cell of 2.5 μ [7], the values of α cited by Alexander [13], Carlucci and Strickland [7], and Loveless and Painter [14] are, respectively, equal to 0.35×10^{-6}, 2×10^{-6}, 1.4×10^{-6}, and 1.7 to 4.2×10^{-6} μmole NH_4^+/bacterium. α has then been choosen adaptable within the range 0.35 to 4.2×10^{-6} μmole NH_4^+/bacterium.

Mortality

The measurements of nitrifying bacteria concentration in the Scheldt Estuary (Fig. 4) show an important decrease near the mouth. Therefore, we have investigated the mortality of nitrifiers as a function of salinity.

Scheldt water has been incubated at salinities between 0.4 and 25 g Cl^-/l at 20 °C in dark air-tight Winkler bottles, i.e., in anaerobic conditions where growth of nitrifying bacteria is impossible. The nitrifiers concentration was followed by MPN method during eight days incubation. At each salinity, a first-order decrease of the nitrifying population with time was observed. Figure 4 represents the experimental relationship between the

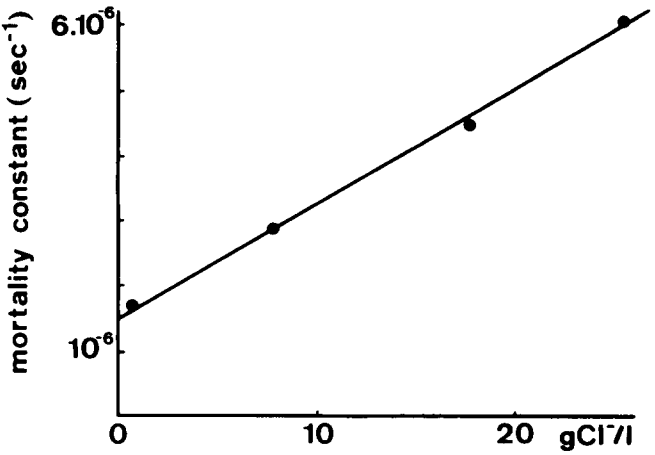

Fig. 4. Relation between the first order constant of mortality for nitrifying bacteria as a function of salinity.

first-order constant of mortality and salinity. This relationship can be written

$$m = m_0 + \beta S$$

with $m_0 = 1.45 \times 10^{-6}\,\text{sec}^{-1}$, $\beta = 0.17 \times 10^{-6}\,\text{sec}^{-1}\,\text{g Cl}^-/\text{l}$, and where S is the salinity (g Cl^-/l). In this equation, m_0 can be interpreted as the residual mortality due to anaerobiosis. Therefore, in the model, the mortality expression used restricts to

$$m = \beta S,$$

since the anaerobiosis mortality effect does not exist in the Scheldt Estuary.

SOLUTION OF THE DIFFERENTIAL EQUATIONS

Boundary conditions

For solving Eqs. (2), (3), and (4), a set limit condition (upstream and mouth water composition) has to be known. In the case of chemical species, ammonium and nitrate, these conditions are obviously the experimental concentrations. In the case of bacterial concentration, boundary conditions can be experimental MPN counts (Fig. 5). It must be noticed that these nitrifiers concentrations are in good agreement with MPN counts reported by various authors in polluted streams: 1–100 bacteria/ml in the Elb River [15], ±3000 bacteria/ml in the Trent River (GB) [16], 2.6–5000 bacteria/ml in the Passaic River (USA) [17].

On the other hand, several workers [18, 19] have pointed out the pour reliability of this largely used numeration method. The work of Tate [18] has shown that the measured bacterial concentrations in soils were 10^3 times too small to explain the *in situ* production of nitrate, assuming maximal efficiency of the microorganisms.

It appears then necessary to check the accuracy of the nitrifiers concentrations by comparing the computed activities ($\alpha K[B]$), based on the possible range of α and K values and the experimental bacterial concentration, with the *in situ* activities measured in the stream [2].

This comparison has shown that the MPN counts obtained in the Scheldt were several

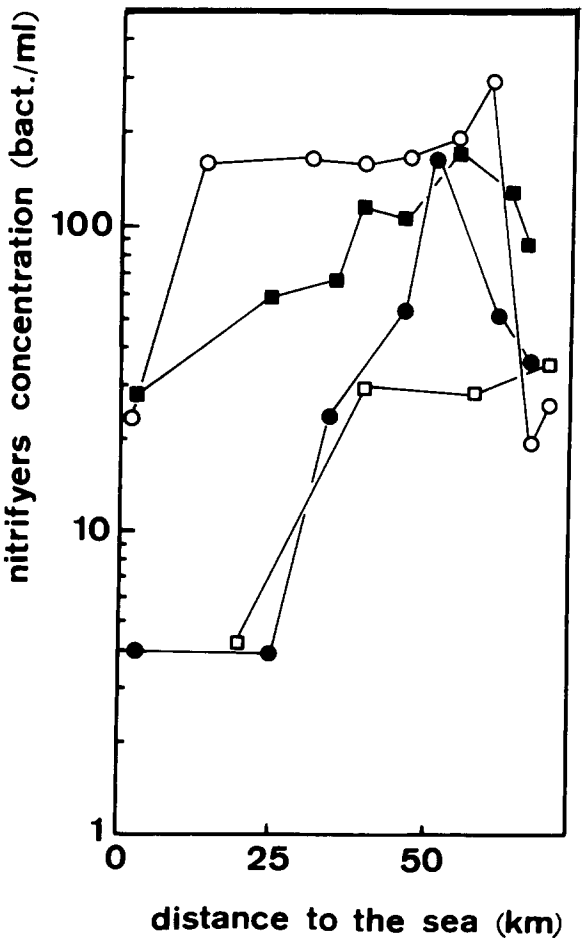

Fig. 5. Longitudinal profiles in the Scheldt estuary of nitrifying (nitrous + nitric) bacteria counted in fresh water medium for February 1974 (□), January (■), April (○) and June (●) 1975.

orders of magnitude lower than what could be expected from the direct activity measurements. It was therefore decided to evaluate nitrifiers numbers directly from the *in situ measured activities*. The limit conditions adopted for the four situations studied (February, April, May, and July 1976) are given in Table 2.

Solution of Eqs. (2), (3), *and* (4)

Owing to the coupling of Eqs. (2) and (3) by means of the ammonium concentration, the first step computes the solution of the bacteria equation [Eq. (2)] using the experimental ammonium profile, previously smoothed.

Table 2. Limit conditions used for the simulation of the situations of February, April, May, and July 1976

	Upstreams			Mouth		
	$NH_4^+(\mu M)$	$NO_3^-(\mu M)$	bact/ml	$NH_4^+(\mu M)$	$NO_3^-(\mu M)$	bact/ml
February 76	440	128	17	54	117	1.7
April 76	560	2	170	81	145	170
May 76	608	2	100	80	88	1
July 76	640	1	100	21	16	1

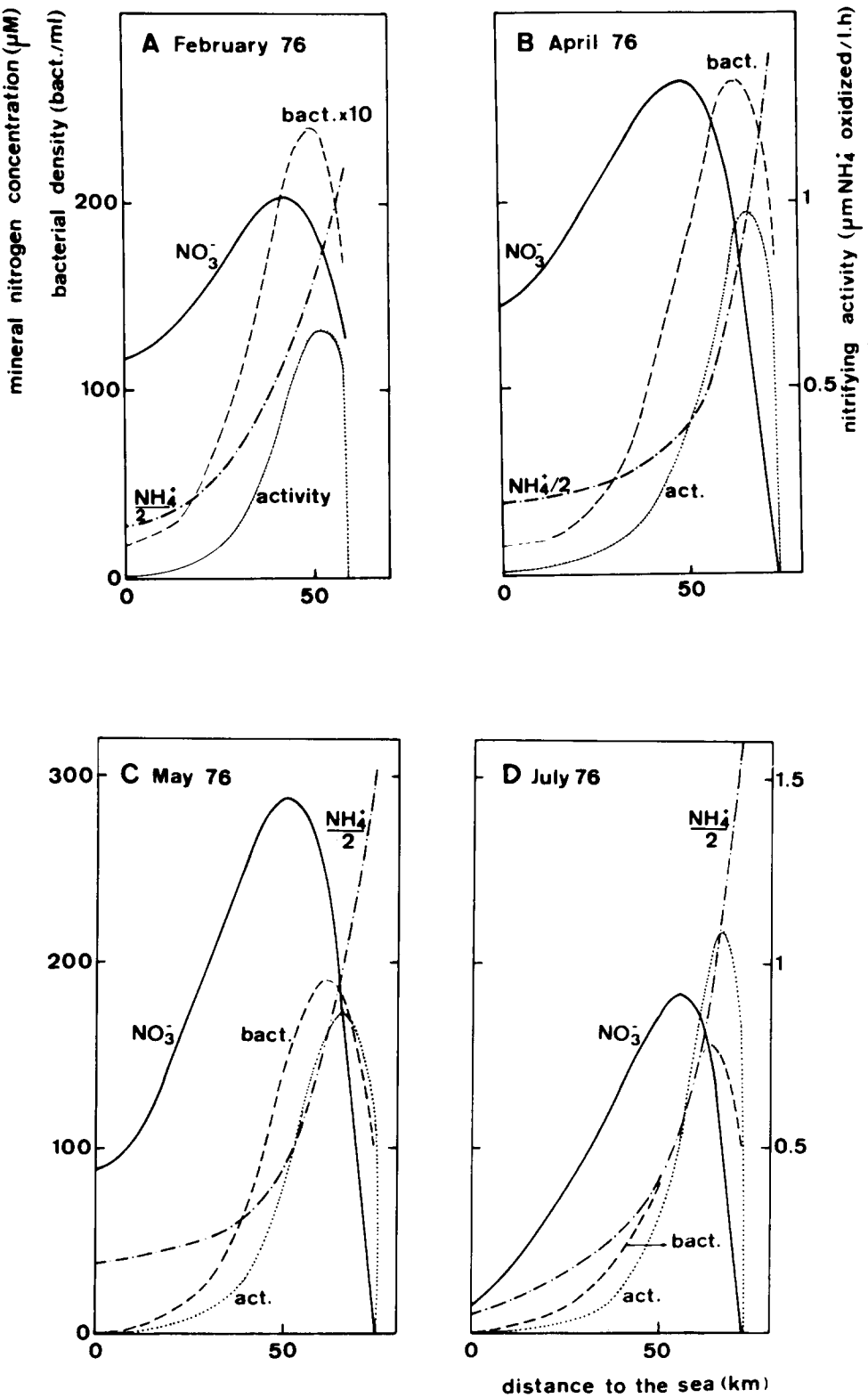

Fig. 6. Calculated profiles of the concentrations of nitrate, ammonium and nitrifying bacteria, and nitrifying activity as a function of the distance to the sea for February (A), April (B), May (C) and July (D), 1976.

Table 3. Values of the constants α and k used for the mathematical simulations (Fig. 6)

Months	k sec^{-1}	α $\mu M\ NH_4^+$/bact
February 1976	25×10^{-6}	3×10^{-6}
April 1976	12×10^{-6}	0.56×10^{-6}
May 1976	7×10^{-6}	0.87×10^{-6}
July 1976	7.5×10^{-6}	0.84×10^{-6}

The complete solution of the problem is calculated by an iterative process adjusting the constant α. The convergence of the process is quadratic and is obtained after a few loops. The values of α and k so determined are in perfect agreement with the literature.

The computed profiles of ammonium, nitrate bacteria, and nitrifying activities are represented on Fig. 6, for the situations of February, April, May, and July 1976. The values of α and k used for these simulation are reported in Table 3.

CONCLUSIONS

The hydrodynamical and biological processes occurring in estuarine environments are difficult to assess due to interactions between numerous parameters: factors related to the mixing of freshwater and seawater, influence of environment factors on microbial kinetics...

A quantitative approach of such problem is possible by the use of mathematical models, assuming a small number of essential parameters.

The unidimensional mathematical model of the nitrification described above has been shown to describe quantitatively the nitrification process in the Scheldt Estuary. With the aid of a limited number of ecophysiological relations, an accurate description of the *in situ* situation has been possible.

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