

Chapter II

I

A mathematical model of microbial and chemical oxidation-reduction processes in the Scheldt estuary

by

G. BILLEN and J. SMITZ

Based on work by Y. ADAM³, G. BILLEN^{1,2}, M. HOENIG¹, Cl. JOIRIS¹, J. LEFEVRE²,
Y. RUNFOLA³, J. SMITZ³.

1. Laboratoire de Chimie industrielle, U.L.B.
2. Laboratorium voor Ekologie en Systematiek, V.U.B.
3. Groupe de Mécanique des Fluides géophysiques, U. Lg.

Introduction

The deterioration of chemical and biological properties of natural waters by domestic pollution is not the direct consequence of the presence of an organic load in the water, but is rather the result of heterotrophic bacterial activity which modifies oxidation-reduction characteristics of the water while degrading this charge. Because other oxidants than oxygen can be used by heterotrophic microorganisms (anaerobic respirations), a complete oxidation-reduction budget is necessary to describe correctly the evolution of the chemical composition of the water under microbiological influence. The classical models of river pollution, using oxygen as the only chemical state variable, are confronted with serious difficulties as soon as anaerobic microbial metabolisms occur.

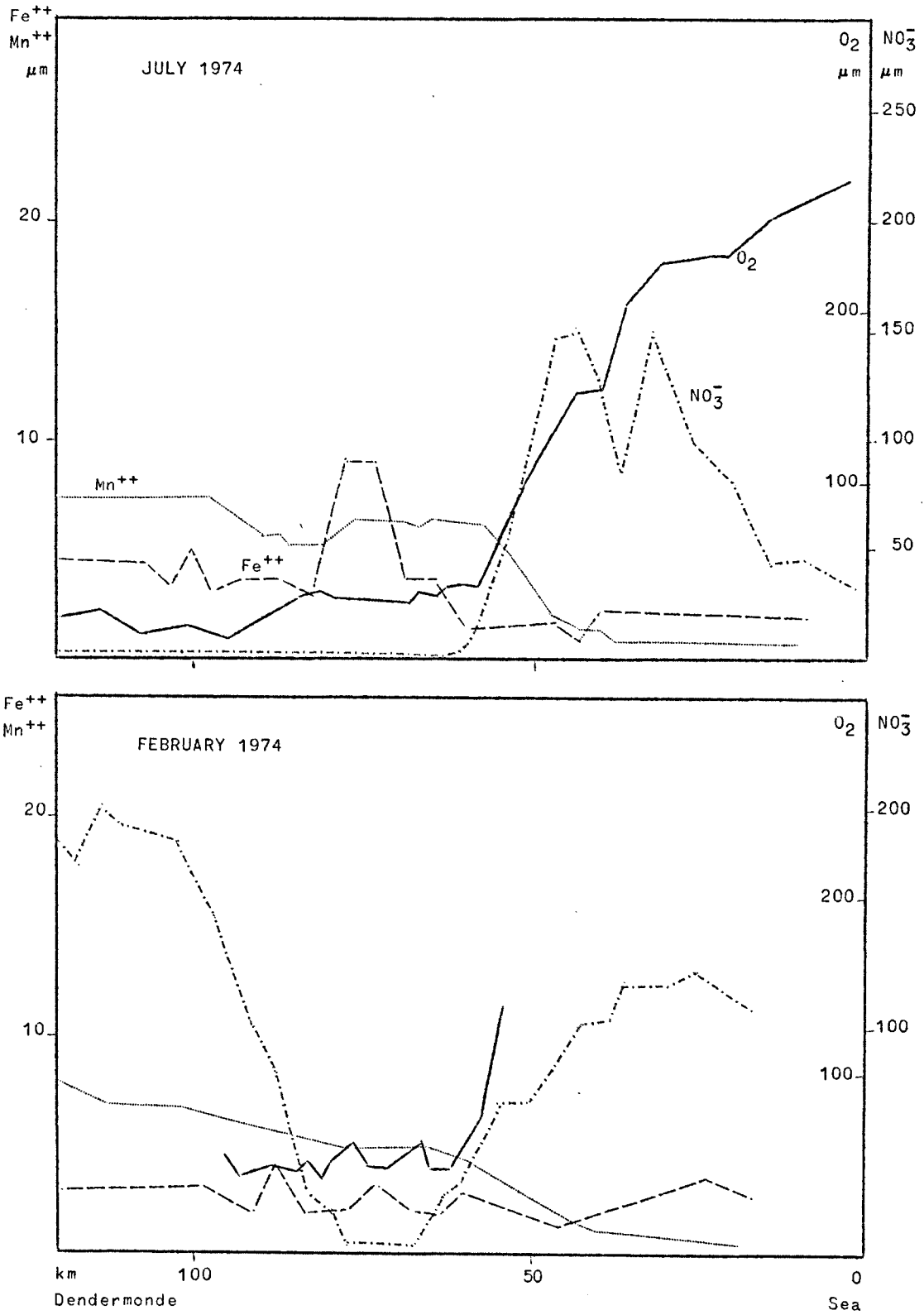


fig. 1.

Longitudinal profiles of oxidation-reduction compounds in the Scheldt Estuary.

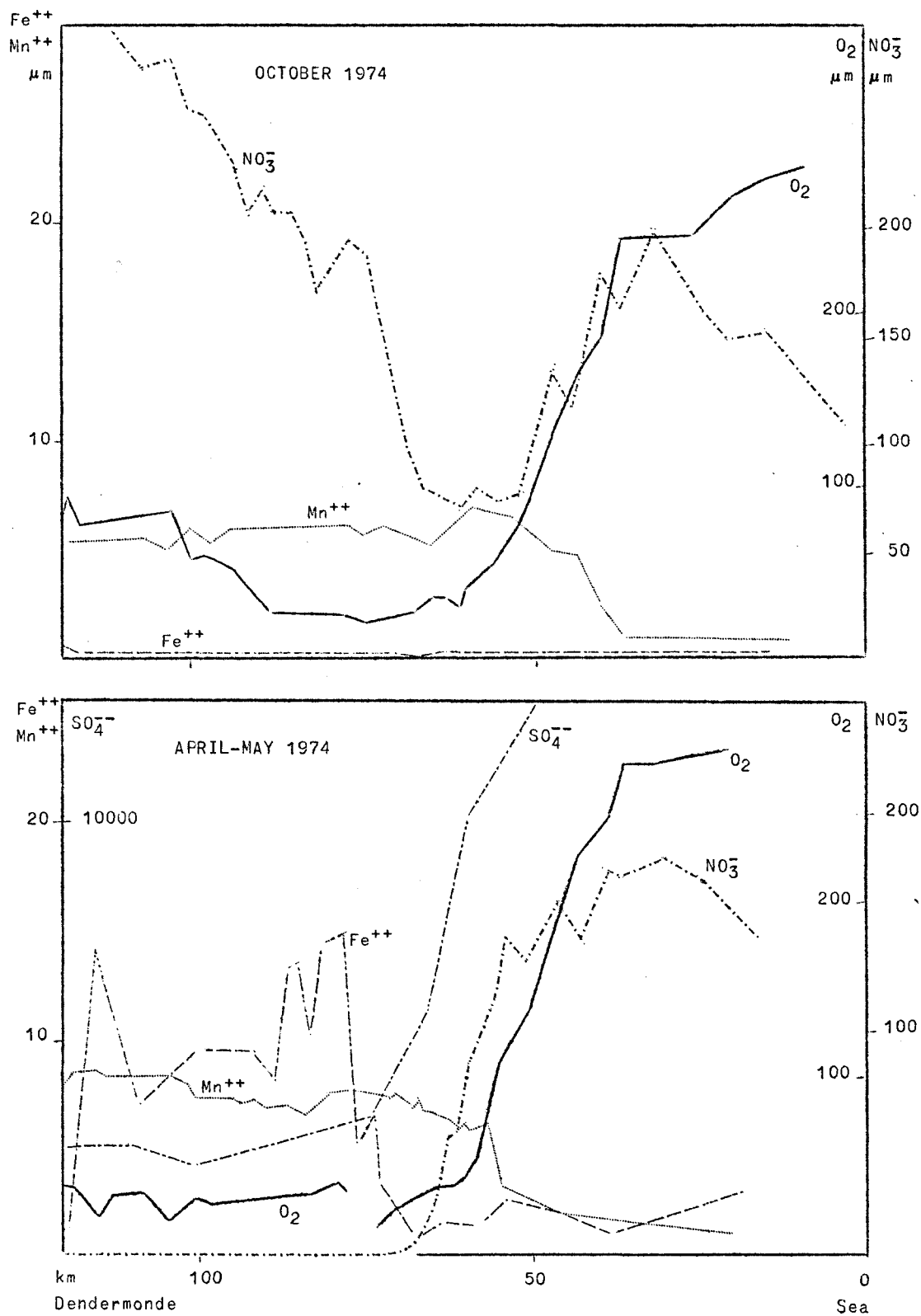


fig. 1.

Longitudinal profiles of oxidation-reduction compounds in the Scheldt estuary.

This work presents an oxidation-reduction model of the influence of bacterial activity on water composition, applied to the case of the Scheldt estuary. Basically the same phenomena occurs in natural water systems sustaining an intense heterotrophic activity, such as bottom water of stratified basins [Richards (1965)] or interstitial water of sediments [Thorstenson (1970)]. With a few modifications, the same model could be applied to these cases.

1.- Experimental results

Typical longitudinal profiles of concentration of several oxidation-reduction compounds are shown in fig. 1 for winter and summer situations. Note abrupt transitions between zones where a given substance is reduced or oxidized. According to these profiles, it is possible to define an upwards zone (with chlorinities less than 2 g Cl/l) where oxidants (O_2 , Mn^{4+} , NO_3^- , Fe^{+++} , SO_4^{--}) are successively reduced, and a downwards zone (with chlorinities higher than 2 g Cl/l) where oxidants are regenerated in the opposite order. The reductive stage proceeds less far in the winter than in the summer : for instance, reduced iron does not appear in the winter.

Dark ^{14}C -bicarbonate incorporation, an index of heterotrophic bacterial activity has been determined along several longitudinal profiles of the Scheldt (fig. 2). Again, two zones can be distinguished : intense heterotrophic activity occurs upwards, approximately down to the point where 2 g/l chlorinity is reached, and abruptly vanishes downwards. Bacterial activity is much less intense in the winter than in the summer; an empirical relation with water temperature T and river discharge d has been found : The mean upwards heterotrophic bicarbonate incorporation is proportional to $\frac{1}{d} 10^{T/d}$.

2.- General principles of the model

The above mentioned results are easily interpreted : The Scheldt Estuary is heavily polluted upwards Antwerp by important amounts of

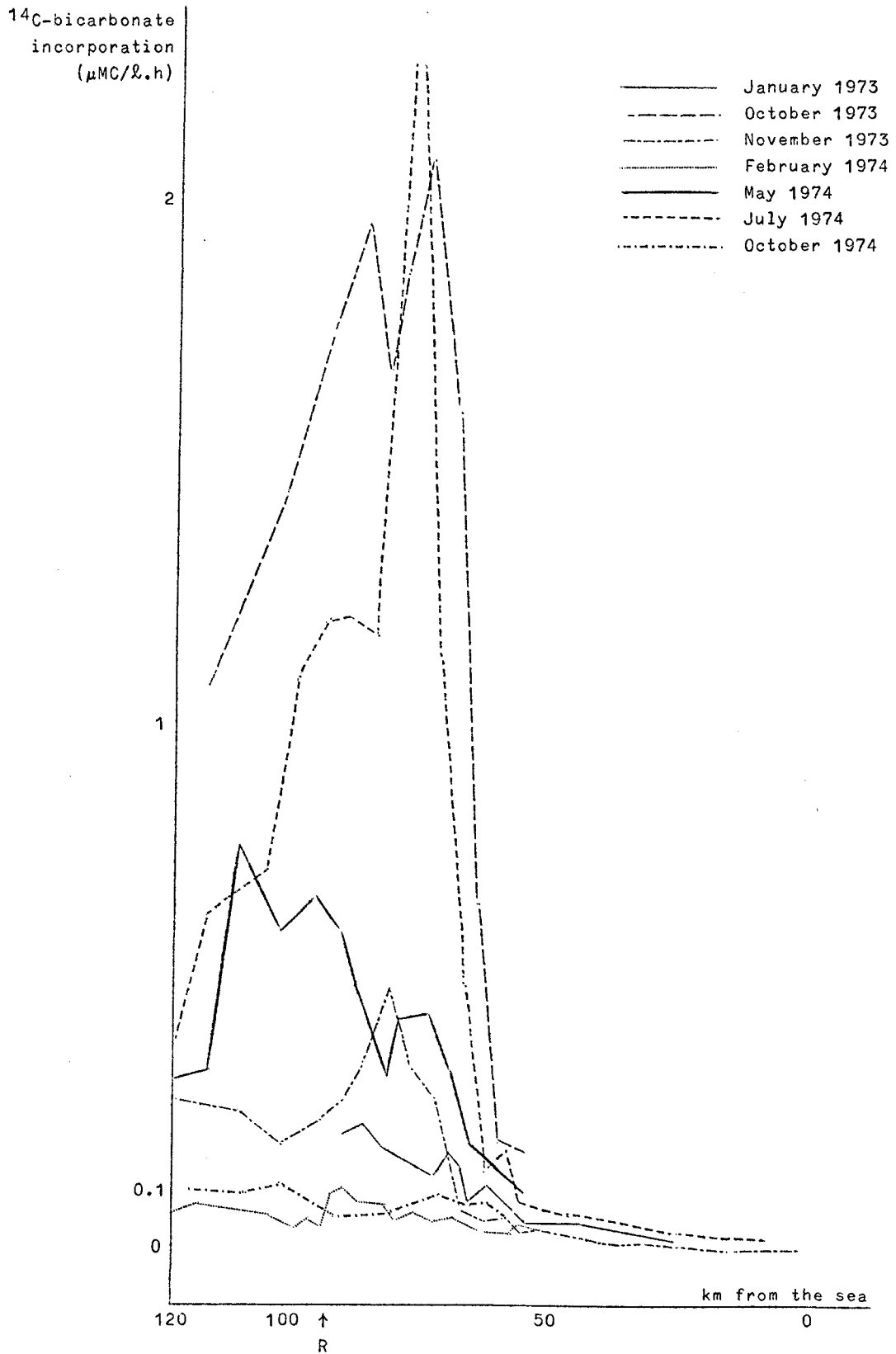


fig. 2.

Dark ^{14}C -bicarbonate incorporation along a profile of the Scheldt, at different seasons.

organic matter. Owing to the intense bacterial activity, the redox potential decreases from Dendermonde (km 120) to about Antwerp (km 80) . Oxygen is rapidly entirely depleted, and other oxidants are used by anaerobic metabolisms. Then, near km 70 , owing to increasing salinity, flocculation and precipitation of the suspended organic matter occur [Wollast (1973)], bacterial activity falls down and a phase of recuperation begins, accelerated by mixing with unpolluted sea water. During this stage, reaeration not only restores the oxygen concentration but also regenerates the previously used oxidizing agents.

All these phenomena will be simulated by a model in which measured values of bacterial activity are introduced as a command parameter modifying the composition of the water without disturbing the thermodynamic internal equilibrium between all the involved oxidation-reduction couples.

The variations in the concentration of the considered chemical compounds are the result of advection, turbulent diffusion or consumption by oxidation reduction processes :

$$(1) \quad \frac{\partial}{\partial t} x_i + u(s,t) \frac{\partial}{\partial s} x_i = D(s,t) \frac{\partial^2}{\partial s^2} x_i - C_i(s,t)$$

where t is the time, s is the longitudinal coordinate, x_i is the concentration of the i^{th} species, u is the residual velocity of the water, D is the turbulent diffusion coefficient, C_i is the rate of oxidation-reduction consumption.

2.1.- Hydrodynamical model

The residual velocity of the water has been calculated as the quotient of the residual outflow [the seasonal variation of which is given by the measurements published by the *Antwerpse Zeediensten* (1966)] to the wet section area [reported by Wollast (1973) to fit a logarithmic fonction of the distance to the mouth].

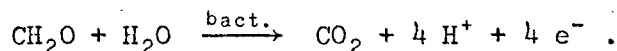
For the turbulent diffusion coefficient, phenomenological values, integrating the effects of the tides were calculated according to the method described by Wollast (1973).

This one dimensional hydrodynamic treatment is admittedly very simplistic. However, its ability to simulate the observed longitudinal profile of chlorinity for each cruise has been shown to be satisfactory.

2.2.- Microbiological model

The oxidation reduction processes, represented by the term C_i , are controlled by heterotrophic bacterial activity in the water. For oxygen, an additional aeration term occurs. It was taken as proportional to the oxygen saturation deficit, with a proportionality coefficient K about $6 \times 10^{-3} \text{ h}^{-1}$, as estimated by Wollast (1973).

The bacterial activity can be viewed as an electron flux imposed to the water system, according to the reaction :



By writing this equation, we assumed that, from an overall point of view, fermentations play no important role, *i.e.* that no accumulation of un-completely oxidized organic compounds (acids, cetones or alcohols) occurs. For organic acids, this has been experimentally confirmed.

This electron flux, $H(s,t)$, provokes one or several of the following reactions to go on :

- a) $4 \text{e}^- + \text{O}_2 + 4 \text{H}^+ \rightleftharpoons 2 \text{H}_2\text{O}$
- b) $8 \text{e}^- + \text{NO}_3^- + 10 \text{H}^+ \rightleftharpoons \text{NH}_4^+ + 3 \text{H}_2\text{O}$
- c) $2 \text{e}^- + \text{MnO}_2 + 4 \text{H}^+ \rightleftharpoons \text{Mn}^{++} + 2 \text{H}_2\text{O}$
- d) $1 \text{e}^- + \text{Fe}(\text{OH})_3 + 3 \text{H}^+ \rightleftharpoons \text{Fe}^{++} + 3 \text{H}_2\text{O}$
- d') $\text{Fe}^{++} + \text{HCO}_3^- \rightleftharpoons \text{FeCO}_3 + \text{H}^+$
- e) $14 \text{e}^- + 2 \text{SO}_4^{--} + \text{Fe}^{++} + 16 \text{H}^+ \rightleftharpoons \text{FeS}_2 + 8 \text{H}_2\text{O}$

so that $H(s,t) = \sum_i v_i C_i(s,t) .$

Some of these reactions are biologically mediated and the presence of the responsible organisms has been demonstrated in the Scheldt (oxygen consumption, denitrification, nitrification, sulfato-reduction), others occur spontaneously although direct biological mediation can occur in certain

circumstances (iron oxidation and reduction, manganese oxidation and reduction). However this distinction in the reaction mechanisms is not essential for the overall balance we are doing.

To portion out the total electron flux $H(s,t)$ imposed to the system by heterotrophic activity between the different microbiological or chemical electron consuming pathways, the assumption is made that an internal thermodynamic equilibrium is achieved in the system for reactions a) to e). This imposes that five simultaneous equilibrium relations of the general form

$$E_h = E_i^0 + RT \log \frac{Ox_i}{Red_i}$$

hold. This is equivalent to saying that the bacteria only use thermodynamically favourable half reactions in their energy yielding metabolism.

Given a set of limit conditions (composition of the water at Rupelmonde and at the sea), the knowledge of the total bacterial activity $H(s,t)$ would allow to calculate the consumption term $C_i(s,t)$ for each oxidant considered, and hence the complete evolution of the water composition along a longitudinal profile of the estuary. Direct introduction of bacterial activity as a command parameter would allow to take implicitly into account a lot of phenomena that it would be difficult to consider explicitly, such as lateral import of organic matter, modification of the bacterial population with salinity, etc. According to Romanenko (1964), total carbon metabolism [and hence electron flux $H(s,t)$] can be evaluated from dark bicarbonate incorporation measurement by simply multiplying it by a constant factor α :

$$H(s,t) = 4 \times (\text{total C metabolism}) = 4\alpha \times (\text{bicarbonate incorporation}) .$$

However, critical examination of the literature [Romanenko (1964), Sorokin (1965), Overbeck (1974)] shows that this factor α can vary greatly with the bacterial species, the growth phase, the quality of the substrate, etc. Because of the lack of a precise value of α , and considering that α can vary because of changes in the bacterial community, we treated it as an adjustable parameter which can have different values from one season to the other.

3.- Mathematical resolution

To summarize preceeding discussion, the problem posed is to calculate the concentrations $X_i(s,t)$ of the considered oxidants and the concentrations $Y_i(s,t)$ of corresponding reduced form, by solving following system of equations :

i) 5 transport-diffusion equations

If $\nabla(s,t)$ represents the operator $\frac{\partial}{\partial t} + u(s,t) \frac{\partial}{\partial s} - D(s,t) \frac{\partial^2}{\partial s^2}$ the equations are :

$$(2) \quad \nabla X_1(X,t) = K(X_{1_{\text{sat}}} - X_1) - C_1(s,t)$$

where the subscript 1 refers to O_2 .

$$(3) \quad \nabla X_j = C_j(s,t)$$

$j = 2,5$ (i.e. NO_3^- , MnO_2 , $Fe(OH)_3$, SO_4^{--})

ii) one-relation on the C_i 's

$$(4) \quad H(s,t) = \sum_{i=1}^5 v_i C_i .$$

iii) 5 logarithmic relations between a sixth variable Eh and the X_i 's and Y_i 's

$$(5) \quad Eh(s,t) = \ell_1(X_1, Y_1) = \ell_2(X_2, Y_2) = \ell_3(X_3, Y_3) = \ell_4(X_4, Y_4) = \ell_5(X_5, Y_5)$$

These logarithmic relations enable to express the concentrations of oxidants as a function of the redox potential Eh . In the general case, the function ℓ_i has the form :

$$Eh = a_i + b_i \log \frac{X_i}{Y_i}$$

(see fig. 3) where Y_i refers to the concentration of the reduced form of the oxidant considered. (Note that if the oxidant or the reductor is a solid species, the corresponding value of X_i or Y_i to be used in the preceeding relation must be unity or zero.)

For the reduced form Y_j , we have

$$(6) \quad \nabla Y_j(s,t) = - C_j(s,t)$$

By summing this equation with the corresponding equation (3) for the X_j 's , we have :

$$(7) \quad \nabla Z_j(s,t) = 0$$

$$\text{if} \quad Z_j \equiv X_j + Y_j .$$

i.e.

$$\nabla(\text{NO}_3^- + \text{NH}_4^+) = 0$$

$$\nabla(\text{MnO}_2 + \text{Mn}^{++}) = 0$$

$$\nabla[\text{Fe}(\text{OH})_3 + \text{Fe}^{++} + \text{FeCO}_3 + \text{FeS}_2] = 0$$

$$\nabla(\text{SO}_4^{--} + 2 \text{FeS}_2) = 0 .$$

The maximum possible value of $X_i(x,t)$ is of course $Z_i(s,t)$. The minimum considered is 10^{-6} moles/l , which is approximated to zero. This divides the redox potential range into three domains for every oxidant :

$$E_h > L_A ,$$

$$X_i(x,t) = Z_i(s,t) ;$$

$$L_B > E_h > L_A ,$$

X_i given by the relation

$$E_h = a_i + b_i \log \frac{X_i}{Z_i - X_i} ;$$

$$E_h > L_B ,$$

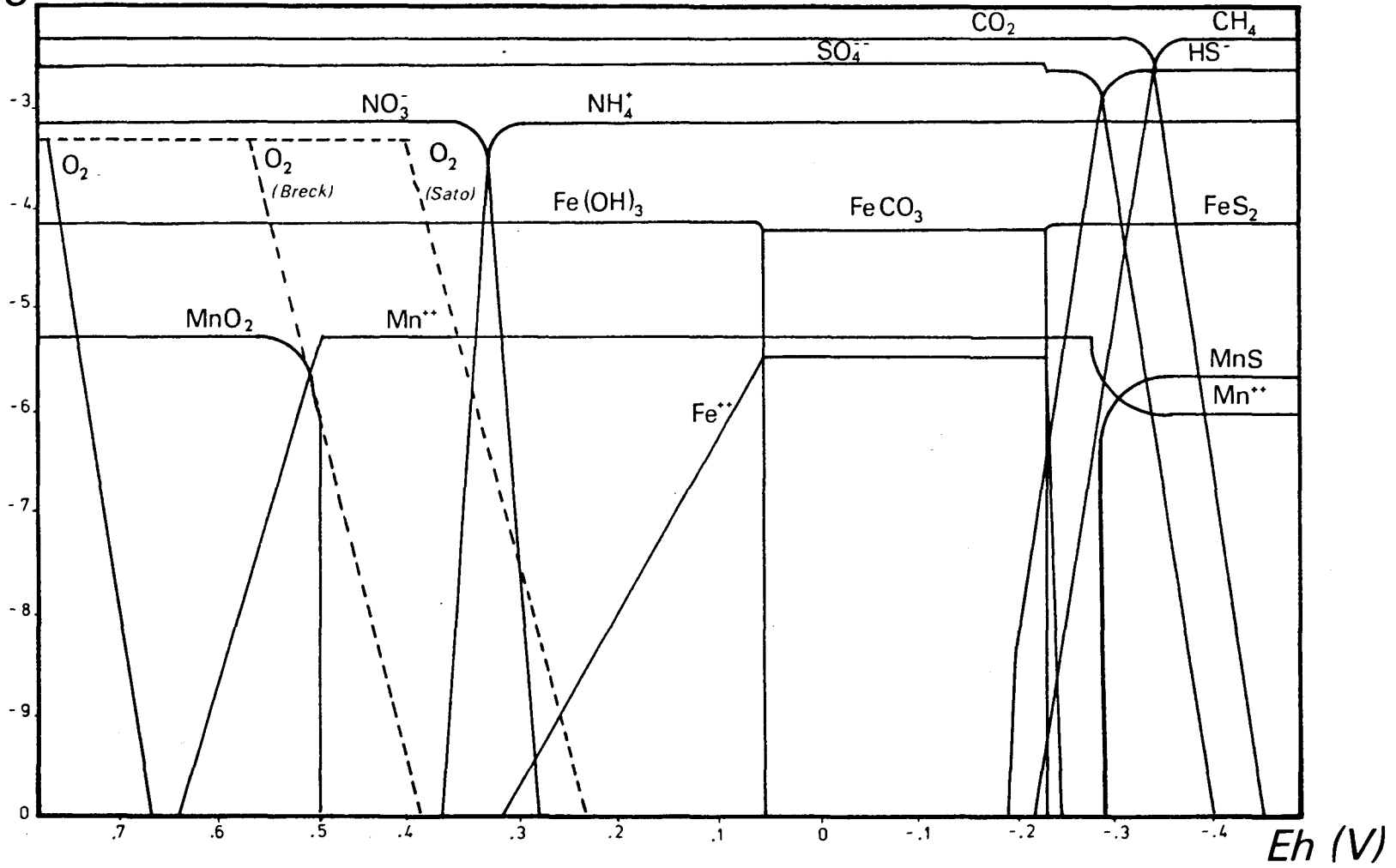
$$X_i = 0 .$$

The numerical method used to solve the system utilizes time and space discretisation and, at each time step, the following sequential procedure is used :

- i) solution of the four equations (7) for $Z_j(s,t)$;
- ii) computation of the limits $L_A(s,t)$ and $L_B(s,t)$ for every oxidant in the E_h domain.
- iii) computation of an associated variable

$$(8) \quad F(s,t) = \sum_{i=1}^5 v_i X_i$$

$\log C$



- 79 -

fig. 3.
Eh-concentration diagram for the water at Ruppelmonde.

for which the following equation holds :

$$(9) \quad \nabla F(s,t) = v_1 K(X_{1_{\text{sat}}} - X_1) - H(s,t)$$

As this equation contains oxygen concentration explicitly, the expression $(X_{1_{\text{sat}}} - X_1)$ is calculated using the value of X_1 at the preceding time step (if X_1 varies slowly) or by an iterative scheme over points 3 and 4.

The discretization of transport-diffusion equations leads to tri-diagonal form :

$$- A_i F_{i+1} + B_i F_i - C_i F_{i-1} = D_i$$

which is then solved by recurrent algorithm [Adam and Runfola (1971), Adam (1975)].

iv) Solution of an implicit relation

$$F(s,t) = \sum v_i X_i = f(Eh, L_A, L_B) .$$

This relation allows to calculate the redox potential $Eh(s,t)$ and the concentration of the oxidants via the logarithmic relations

$$Eh = \ell_i(X_i) .$$

4.- Results and discussion

The present discussion will be limited to the simulation of the profile of February 1974, as an illustration of the capabilities and the limitations of the model used. Most of the discussion will be devoted to the validity of the assumption made that an internal equilibrium is achieved in the system between all the redox species considered.

4.1.- Perfect thermodynamic equilibrium

If it is assumed that perfect internal equilibrium is achieved in the system for reactions a) to e), the following relations must hold :

$$a) \quad Eh = 1.26 - 0.059 \text{ pH} + 0.015 \log O_2$$

- b) $Eh = 0.882 - 0.074 \text{ pH} + 0.007 \log \text{NO}_3^-/\text{NH}_4^+$
c) $Eh = 1.229 - 0.118 \text{ pH} - 0.029 \log \text{Mn}^{++}$
d) $Eh = 1.057 - 0.177 \text{ pH} - 0.059 \log \text{Fe}^{++}$
d') $\log \text{Fe}^{++} - \log \text{HCO}_3^- + \text{pH} = - 0.286$
for $- 0.215 < Eh < 0.053$
e) $Eh = 0.354 + 0.008 \log \text{SO}_4^{--} - 0.067 \text{ pH} + 0.004 \log \text{Fe}^{++}$

These relations are diagrammatically represented in figure 3 for the gross chemical composition of the water at Rupelmonde.

Figure 4 shows the calculated profile obtained with this assumption.

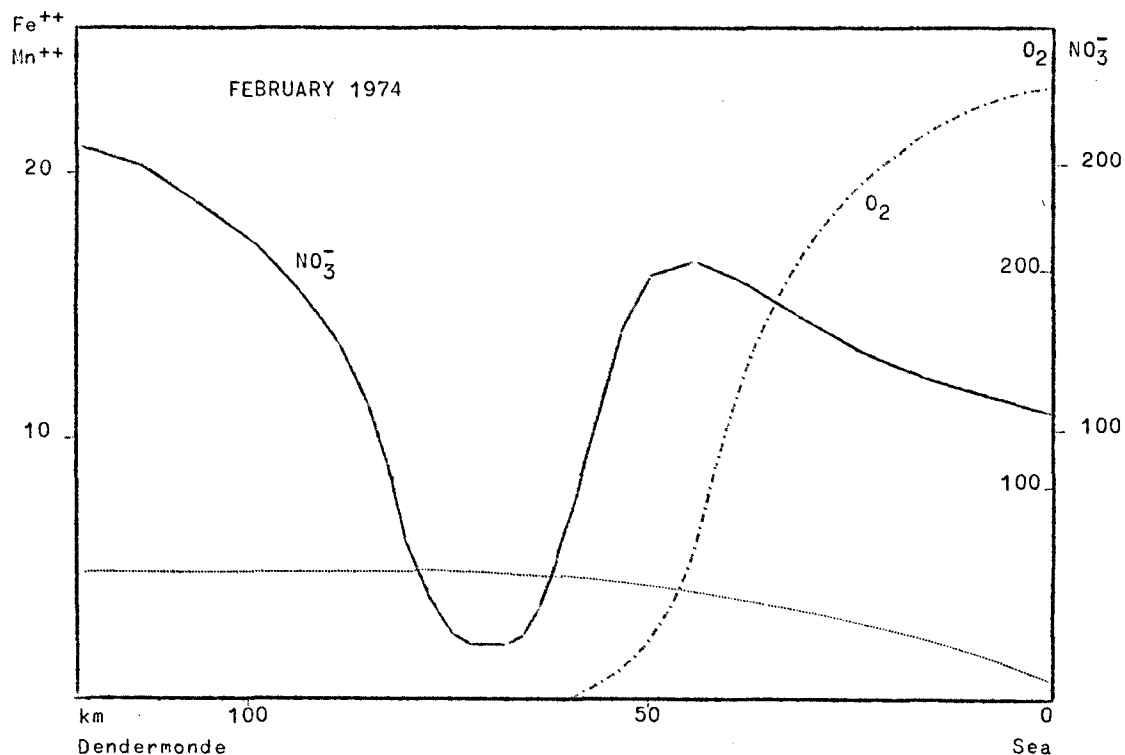


fig. 4.

Calculated profile for February 1974, obtained with a model assuming a perfect internal thermodynamic equilibrium.

Comparison with the experimental profile shows that the general trends of the evolution of the water composition are reproduced by the simulation.

However, oxygen concentration increases much later in the calculated profile. Clearly this is the consequence of our assumption of perfect internal equilibrium. With this assumption, oxygen can only begin to increase after all NH_4^+ and all Mn^{++} have been completely oxidized. To explain the observed profiles, kinetical limitations must be invoked : the rate of the chemical and microbiological reactions involved is not sufficient for an internal thermodynamic equilibrium between the $\text{NH}_4^+/\text{NO}_3^-$, $\text{Mn}^{++}/\text{MnO}_2$, $\text{O}_2/\text{H}_2\text{O}$ redox couples to be achieved.

4.2.- Empirical kinetic model for oxygen

It is possible to obtain a quite good simulation (see fig. 5) of the observed profile by expressing the oxygen consumption as a kinetical

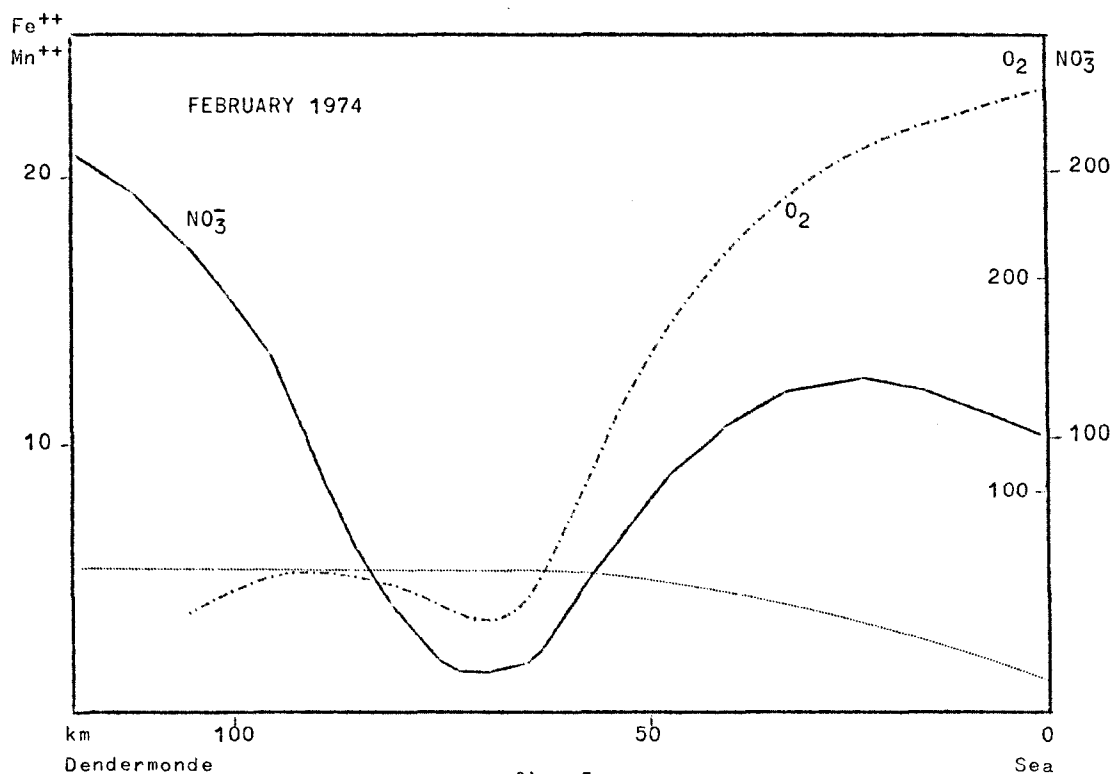


fig. 5.

Calculated profile for February 1974, obtained with a model using an empirical kinetic term for oxygen consumption.

term not immediately depending on Eh, but proportional to the concentration of reduced forms of the other redox couples :

$$\Delta x_i = K(x_{1_{\text{sat}}} - x_1) - k \left(\sum_{j=2}^5 z_j - x_j \right) .$$

In this treatment, only equations b) to e) are considered for assessing Eh and the relation on the C_i 's becomes :

$$H(s,t) = \sum_{j=1}^5 C_j + k \sum_{j=1}^5 (z_j - x_j) .$$

This treatment is not very satisfactory from the point of view of the microbiologist because it is only possible to justify the particular form given to the term representing oxygen consumption by assuming that all heterotrophic activity is sustained by utilization of other oxidants than oxygen, the latter only reacting chemically to regenerate these oxidants. This is of course quite unrealistic, aerobic metabolisms constituting always an important part of heterotrophic activity. However the fact that this model does fit the experimental profiles, while the former does not, indicate that kinetical hindrances in the reactions of O_2 with NH_4^+ and Mn^{++} must be somehow taken into account.

4.3.- Kinetical hindrance to equilibrium

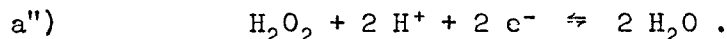
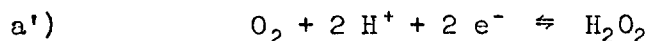
The first model, based on the assumption of thermodynamical equilibrium could not account for two observations :

i) Nitrate formation from ammonium is not completed before the beginning of oxygen concentration increase.

This can be explained by the physiology of nitrifying bacteria. The population of nitrifying bacteria of the Scheldt estuary are probably made of fresh water organisms of terrestrial origin, carried down by the river. As soon as the convenient Eh value is reached, their activity begins. However, because of increasing salinity, they cannot divide rapidly enough to counterbalance their dilution in sea water, so that nitrification cannot be completed [Billen (1975)]. A model of nitrification in the Scheldt estuary, taking into account the physiology of nitrifying bacteria is now in progress [Somville, Billen and Vanderborgh (in preparation)].

ii) oxygen concentration increases before manganese oxidation begins

To explain this discrepancy, slowness of bacterial action cannot be invoked because manganese oxidation is a rapid spontaneous chemical process. In this case, the kinetical hindrance with respect to the equilibrium model probably originates from the mechanisms of Eh control by oxygen. This control has been discussed in detail by Sato (1960) and Breck (1972), (1974). Both authors stressed that the chemical reduction of oxygen is a multistep process in which oxygen peroxide is an intermediate : summarizing



The former of these processes is easy; the latter, involving rupture of an O-O bond, is very slow. A definite non neglectable H_2O_2 concentration can thus exist in natural oxygenated waters. A lot of chemical species (including oxidized forms of iron and manganese) readily react with H_2O_2 , decomposing it back to oxygen and preventing further oxidation of the solution by reaction a''). The steady state so established between O_2 and H_2O_2 is the effective way of control of the redox potential. This implies that relation a) must be replaced by the corresponding Nernst equation for reaction a'). The steady state concentration of H_2O_2 has been estimated by Sato and Breck respectively to 10^{-6} and 10^{-11} moles/l. The two resulting Nernst relations are represented diagrammatically in figure 3 (dotted lines).

Introduction of these relations in the model and comparison with preceeding data (experimental and calculated) will allow to estimate influence of oxygen peroxide process in the control of Eh potential in the Scheldt Estuary.

References

- ADAM, Y., RUNFOLA, Y., (1971). *Numerical Resolution of diffusion equation*, Rapport N.9, Progr. Nat. Environnement Physique et Biologique, Projet Mer.

- ADAM, Y., (1975). *A Hermitian finite difference method for the solution of parabolic equations*, to be published.
- ANTWERPSE ZEEDIENSTEN, (1966). *Stormvloeden op de Schelde*, Ministerie van openbare werken; Bestuur der waterwegen.
- BILLEN, G., (1975). Nitrification in the Scheldt Estuary (Belgium and the Netherlands), *Estuarine and Coastal Marine Science*, 3, 79-89.
- BRECK, W.G., (1972). Redox potentials by equilibration, *J. Mar. Res.*, 30, 121-139.
- BRECK, W.G., (1974). *Redox potentials in the sea*, in *The Sea*, Goldberg ed., vol. 5, Wiley, New York.
- OVERBECK, J., DALEY, R.J., (1973). Some precautionary comments on the Romanenko technique for estimating heterotrophic bacterial production, *Bull. Ecol. Res. Comm.* (Stockholm) 17, 342-344.
- RICHARDS, F.A., (1965). *Anoxic basins and Fjords*, in *Chemical oceanography*, Vol. 1, 611-645, Eds. Riley, S.P. and Skirrow, G., Academic Press, New York.
- ROMANENKO, V.I., (1964). Heterotrophic CO₂ assimilation by bacterial flora of water, *Mikrobiol.*, 33, 779-683.
- SATO, M., (1960). Oxidation of sulfide ore bodies, 1. Geochemical environments in terms of Eh and pH, *Econ. Geol.*, 55, 928-961.
- SOROKIN, Y.I., (1965). On the trophic role of chemosynthesis and bacterial synthesis in water bodies, *Mem. Ist. Ital. Idrobiol.*, 18 Suppl., 187-205.
- THORSTENSON, D.C., (1970). Equilibrium distribution of small organic molecules in natural waters, *Geochim. Cosmochim. Acta*, 34, 745-770.
- WOLLAST, R., (1973). *Origine et mécanismes de l'envasement de l'estuaire de l'Escaut, Rapport de Synthèse*, Recherche effectuée dans le cadre de l'étude de l'envasement de l'Escaut dirigée par le Laboratoire de Recherches Hydrauliques, Borgerhout, Ministère des Travaux Publics.
- WOLLAST, R., (1973). *Circulation, accumulation et bilan de masse dans l'estuaire de l'Escaut*, in *Modèle mathématique de la pollution en mer du Nord, Rapport de synthèse 1972*, Commission interministérielle de la politique scientifique (Belgium).