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A MATHEMATICAL MODEL FOR PREDICTING THE CONCENTRATION OF NITROGEN COMPOUNDS IN SURFACE AND GROUNDWATER STREAMS.

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ABSTRACT

The mechanism of water pollution by nitrogen compounds in natural streams comprises simultaneous processes of hydrodynamic, physico-chemical and biological transformations. The paper presents a generalized model which considers the governing processes simultaneously while reducing the number of required parameters. This is done by showing the existence of universal parameters which govern the biological and mass transfer processes, by considering the total mineral nitrogen as the substrate, by an adoption of the Monod model in describing denitrification and by adding the balance of dissolved oxygen.

The final part of the paper describes the use of the model as a tool for solving field problems involving the prediction of pollution hazards and possibilities of pollution control.

INTRODUCTION

The mechanism of water pollution by nitrogen compounds comprises three distinct processes, namely: hydrodynamic mass transport, chemical and biological mass transfer within the water and physical mass transfer at interface surfaces.

The present study put forward the objective of integrating the existing knowledge into a generalized physically consistent mathematical model for predicting the concentration of various nitrogen compounds in open streams and in groundwater.

Hypotheses

The proposed model is based on the following hypotheses:

a) The bacteriological processes of nitrification and denitrification are controlled by two universal parameters: pH and Temperature.

b) The substrate in the nitrification process is the total nitrogen contained in both ammonia and ammonium. However, due to the relationship of chemical equilibrium between them, it is possible to refer just to one of them as a substrate and thus simplify the formulation of the model and the required input to it, with a proper modification of the model's parameters.

c) The Monod model which has been used to describe the rate of growth of nitrifying bacteria can also be applied to describe the rate of growth of denitrifying bacteria as well.

d) The transition from denitrification to nitrification and vice versa is gradual and goes through a zone (between zero and some minimal concentration of dissolved oxygen in which both processes occur simultaneously.

e) The processes of volatilization of ammonia and reaeration can be described by a common model of gas transfer.

f) An effective depth of distribution can be assigned to the state variables of pollution over which these variables can be averaged so as to enable the coupling of water quality and water flow simulation models.

SCOPE AND MATHEMATICAL DESCRIPTION OF THE MODEL

The biological processes covered by the model are presented in fig. 1.

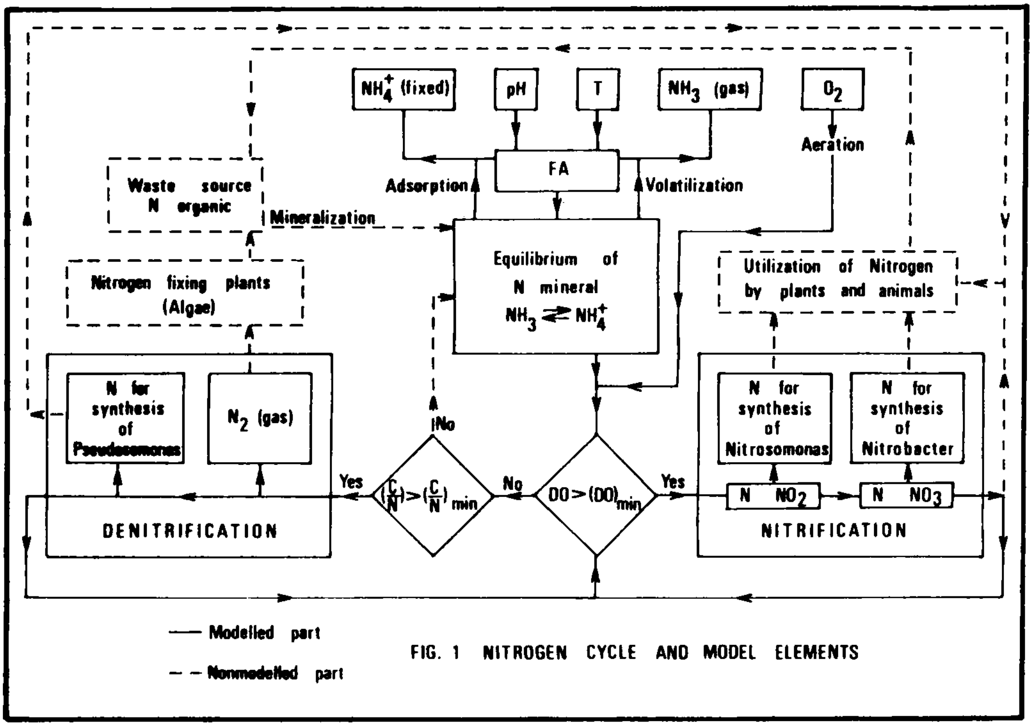

FIG. 1 NITROGEN CYCLE AND MODEL ELEMENTS

The model is represented by the following set of equations:

$$\frac{\partial \bar{N}_k}{\partial t} = \left\{ \frac{\partial}{\partial x_i} \left[D^{(k)}_{ij} \frac{\partial \bar{N}_k}{\partial x_j} \right] - \bar{v}_i \frac{\partial \bar{N}_k}{\partial x_i} \right\} (1-\delta_{k8}) + \bar{F}_k + b_{kj}\bar{N}_j \qquad (1)$$

$$i,\ j = 1,\ 2;\ k = 1,\ 2,\ \ldots 8,\quad \delta_{mn} = \begin{cases} 1 & \text{for } m=n \\ 0 & \text{for } m\neq n \end{cases}$$

The overbar denotes here an average over an 'effective mixing depth'.

N_k is the concentration of the k-th component of the system, namely:

$N_1 = N_{1\alpha} + N_{1\beta}$ total concentration of the unoxidized mineral nitrogen

$(N_{1\alpha} = N_{NH}$, $N_{1\beta} = N_{NH_4^+})$

$N_2 = N_{NO_2^-}$,

$N_3 = N_{NO_3^-}$

$N_4 = X_1$ concentration of Nitrosomonas bacteria

$N_5 = X_2$ concentration of Nitrobacter bacteria

$N_6 = X_3$ concentration of Pseudosomonas bacteria

$N_7 = DO_{Sat}-DO$ dissolved oxygen deficit

N_8 adsorbed ammonium nitrogen (mass per unit volume of solution)

V_i is the velocity of the liquid phase

$D^{(k)}_{ij}$ is the dispersion coefficient of the k-th component, defined by

$$D^{(k)}_{ij} = \begin{cases} A^{(k)}\left[(a_1-a_2)\bar{v}_i\bar{v}_j / \bar{v} + (a_2\bar{v} + D^{\star}_d)\delta_{ij} \right] / f(Pe,\ \delta) & \text{in an aquifer} \\ n\bar{v} \cdot R_H^{5/6}\ \delta_{1i}\ \delta_{1j} & \text{in a stream (the coordinate } X_1 \text{ taken along the flow direction)} \end{cases} \qquad (2)$$

a_1 and a_2 are the longitudinal and transversal dispersivities of the aquifer, respectively, $D^{\star}_d$ denotes the coefficient of molecular diffusion and $f(Pe,\ \delta)$ is a dimensionless function of the peclet number (Pe) and a geometric characteristic of the pore space (δ). n is the Manning coefficient, whereas R_H is the hydraulic radius.

$$F_k = a_{kl} \times \frac{\mu_{ml}}{Yl} \cdot \frac{N_8 N_{l+3}}{k_l+N_l} - B_k\bar{N}_k; \qquad \ell = 1,\ 2,\ 3\ (\text{for } N_l) \qquad (3)$$

a_{kl} is the matrix of the biological process defined by: (see next page) (4)

KN_7 as on the next page (4) with $(DO)^{(2)}_{min}$ instead of $(DO)^{(1)}_{min}$ and $(DO)^{(2)}_{min}$ are theshold values above which the first and second stages of the nitrification process, respectively, are not affected by the concentration of dissolved oxygen.

$$a_{kl} = \begin{bmatrix} -(1+\gamma Y_1)HN_7 & 0 & 0 \\ HN_7 & -(1+\gamma Y_2).KN_7 & 0 \\ 0 & KN_7 & -(1+\gamma Y_3)(1-HN_7) \\ Y_1.HN_7 & 0 & 0 \\ 0 & Y_2.KN_7 & 0 \\ 0 & 0 & Y_3.(1-HN_7) \\ 3.43HN_7 & 1.14\ KN_7 & 0 \\ 0 & 0 & 0 \end{bmatrix} \qquad (4)$$

$$HN_7 = \begin{cases} 1 & \text{for } N_7 < DO_{Sat} - (DO_{min}^{(1)} \text{ or } DO > (DO)_{min}^{(1)} \\ DO/(DO)_{min}^{(1)} & \text{for } DO_{Sat} - (DO)_{min} < N_7 < DO_{Sat} \text{ or } 0 < DO < (DO)_{min}^{(1)} \\ 0 & \text{for } N_7 = DO_{Sat} \text{ or } DO=0 \end{cases} \qquad (5)$$

μ_{ml} is the maximum rate of bacterial growth defined by:

$$\mu_{ml} \begin{cases} 135 \times 10^{-0.788(pH-7)} \equiv \mu_{ml} \text{ for Nitrosomonas} \\ 520 \times 10^{-1.486(pH-7)} \equiv \mu_{m_2} \text{ for Nitrobacter} \end{cases} pH > 7 \\ \phantom{\mu_{ml}} \ 920 \times 10^{-0.994(pH-6)} \equiv \mu_{m_3} \text{ for Pseudosomonas } (pH > 6) \qquad (6)$$

K_l is the saturation constant defined by:

$$K_l = \begin{cases} 140 \times 10^{-0.8037(pH-7)} \equiv k_1 \text{ for Nitrosomonas} \\ 580 \times 10^{-1.684\ (pH-7)} \equiv k_2 \text{ for Nitrobacter} \end{cases} pH > 7 \\ \ 920 \times 10^{-0.994\ (pH-6)} \equiv k_3 \text{ for Pseudosomonas } (pH > 6) \qquad (7)$$

Y_l is the yield constant for bacterial growth on the substrate N_l and γ is the Nitrogen utilization coefficient for the cellular synthesis of bacteria.

B_k is the vector of bacterial mortality defined by:

$$B_k = (0,\ 0,\ 0,\ b_1,\ b_2,\ b_3,\ 0,\ 0) \qquad (8)$$

where b_l is the rate of decay of bacteria related to the substrate N_l.

b_{kj} is the matrix of interphase mass transfer defined by:

$$b_{kj} = R \times FA\delta_{1k}\ \delta_{1j} + R\delta_{7k}\ \delta\delta_{7j} + \begin{cases} \lambda_a(\gamma_a\ \delta_{1j}+\delta_{8j})(\Phi\delta_{1k}+\delta_{8k}) & \text{in an aquifer} \\ 0 & \text{in a stream} \end{cases} \qquad (9)$$

where: FA is the equilibrium ratio between N_l and N_1 defined by:

$$FA = (1+10^{10-0.03T_c^o} - pH^{-1}) \qquad (10)$$

R is a universal coefficient of gas transfer between the liquid and the gaseous phases defined by:

$$R = \frac{D}{\varepsilon_d 2} \qquad D = \begin{cases} D_d^{\star} + a_2\bar{v} & \text{in a phreatic aquifer} \\ D_d + f(n,\bar{v},R_H) & \text{in a stream} \end{cases} \qquad (11)$$

where D is a vertical transfer coefficient in the liquid phase, d is an 'effective' mixing depth and ε is a dimensionless conversion factor which expresses the local flux at the surface in terms of averages over the mixing depth.

λ_a is the first order kinetic rate constant of adsorption; Φ is the ratio of sorbed surface area to the total surface area of the void space; γ_a is the partition coefficient which relates N_1 to N_8.

APPLICATIONS

An application of the model to data obtained from a variety of experiments made it possible to derive a functional form of the universal biological parameters. These in turn were used in verifying the model by proving its capability to reproduce data from other experiments under given initial and boundary conditions. An evaluation of the range of validity of the various presently existing models for simulating water pollution by nitrogen compounds was also made.

In order to study field problems of pollution the model was computer programmed. At this stage the program handles only one dimension in space and steady flow conditions.

In surface water the program was applied to the study of flow in an open stream allowing for the supply of pollutants at a given point either continuously or during a finite period of time. From the study of the two cases it was concluded that a properly planned intermittent discharge of pollutants to a stream can avoid the onset of anaerabic conditions. In groundwater two problems were studied:

a) Concentration distribution of nitrogen compounds in a semi-infinite thick phreatic aquifer under conditions of a steady and uniform flow and fixed concentrations at the boundary.

b) Concentration distribution of nitrogen compounds in a steady radial divergent or convergent flow field with a given concentration at the source or on a circle around it, respectively.

In both cases it was found that the vertical region of interest can be subdivided into 3 zones:

a) The surface layer zone which is a few millimeters thick and in which the dissolved oxygen is always at the level of saturation. In this zone the biological process includes nitrification only.

b) The intermediate zone in which aeration is still possible. It is the domain of the effective depth of dissolved oxygen.

In this domain the biological processes include nitrification and/or denitrification according to the concentration of dissolved oxygen.

c) The bottom zone in which anaerobic conditions prevail. The biological process in this zone includes denitrification only.

For sufficiently high values of R (gas transfer coefficient), the abundance of dissolved oxygen causes a quick transfer from substrate to nitrate while at low R values denitrification may occur.

It was found that the relative weights of the hydrodynamic and biological processes in determining the concentration distribution of nitrogen compounds can be characterized by a dimensionless parameter s, $(s = \frac{a_1\mu_{m1}}{v})$. This parameter expresses the ratio between the hydrodynamic dispersivity and a properly defined biological dispersivity. The spread of the nitrogen compounds increases as s increases. Thus, for sufficiently high values of s, (e.g. s in the order of several hundreds) the biological process can be neglected, and vice versa.

In study b) solutions were obtained for both the surface layer and the intermediate zone.

In the surface layer zone, the abundance of dissolved oxygen causes the concentration profile of the substrate to approach a steady distribution. On the other hand the profile of nitrate advances in time always containing a front part in which nitrification is the dominant process. The length of this part increases as time goes on. The concentration of nitrate in it is higher than at the source and the maximum concentration moves with the average velocity.

In the intermediate zone hydrodynamic transport can be considered as the dominant process.

CONCLUSIONS

1. The transformation of nitrogen compounds in surface or groundwater streams can be predicted by a unified mathematical model which rests on universal parameters and on considering the total mineral nonoxidized nitrogen as the substrate. The major advantage of such a model is the simultaneous consideration of the governing processes, while reducing the number of required parameters. Moreover, in order to determine these parameters it is enough to know the temperature and pH of the solution.

2. The pollution of an aquifer, caused by the spread of nitrogen compounds from a given areal or point source usually raises two questions:

a) The time of arrival of the first trace at a given distance from the source.

b) The areal concentration distribution in the aquifer.

The first problem can be handled by considering the surface layer only.

The second problem can be handled by considering the intermediate zone (zone of effective depth) and/or the bottom zone of the aquifer according to the location of the source of pollution.

3. Because of the limited time scale of the biological process in some cases it may be sufficient for practical purposes to split the duration of the entire process of nitrogen transformations into distinct parts, with only one dominant process being considered in each of them.

The generalized model can serve as a tool for planning the regime of waste disposal to a water course so as to avoid nuisances due to anaerobic conditions.

It can also serve as a tool for controlling groundwater quality in areas of waste disposal.

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