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IIASA Professional Paper
July 1978

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ABSTRACT

This report includes information about mathematical models of biogenic compound transformations and biochemical oxygen consumption (BOC). These models were constructed in the State Oceanographic Institute (Moscow, USSR). Mathematical models of the nitrogen and phosphorus compound transformation and BOC are presented in this report. These models attempt to give a detailed description of the complex processes, including physical and chemical reactions and biochemical interactions, that determine the transformation rates of chemical compounds and oxygen consumption in different water solutions. The main attention was given to the representation of the experimental observations in a batch microsystem because this stage is necessary for intelligent mathematical modelling of the biochemical transformation processes in natural conditions to characterize the water quality. The published experimental data for batch systems were used to identify the rate constants at separate stages and to reconstruct the dynamics of organic, mineral biogenic compounds, biomasses and to estimate the BOC both at individual stages and as a whole. The models can satisfactorily reflect the transformation dynamics of chemical compounds, microorganisms and oxygen consumption in different water solutions (lake and sea water and sewage). The simulations have showed that despite of all difficulties in a descriptions of chemical matter transformation there are a definite number of main elements and they are quite enough for the detailed mathematical simulations of water system behavior and for the prediction of some essential peculiarities of ecosystems important for water quality characterization. The given models may be used as ready blocks connected with the corresponding hydrophysical blocks during model construction for research of the natural water chemical-ecological system.

A Study of the Transformation of Chemical Compounds And Biochemical Oxygen Consumption Dynamics In the Chemical and Ecological Water Quality Simulation

A.V. Leonov

Until recently, water pollution studies concentrated mainly on estimating the concentrations and effects of man-made pollutants. Certain natural water components that limit the development of organisms of the lowest trophic levels increase as a result of man-made pollution. This may have serious ecological consequences. Among man-made pollutants, organic matter and biogenic element compounds are the most important. The latter greatly influence the behavior of water ecological systems. They determine the kinetics of the transformation of organic matter and the biochemical oxygen consumption (BOC) by their affect on the organism population of the lowest trophic levels. Quantitative information on the transformation kinetics of organic matter and biogenic element compounds is needed for investigating the two most topical problems of modern hydrochemistry: the formation of the biological productivity reservoir base, and its self-purification from pollution. These investigative trends are closely connected with the study of eutrophication and the processes determining water quality.

Studies of the transformation of pollutant in water were limited to the measurement of BOC and the concentrations of biogenic element compounds (carbon, nitrogen, and phosphorus). Clearly, these separate measurements, along with a knowledge of the levels of various pollutants in reservoirs, are not enough to form an opinion on the mechanisms of pollutant transformation. This information is needed for developing methods of water quality prognosis. Such investigations must be supplemented by data on the transformation kinetics of the compounds being considered.

The first kinetic models for estimating the oxidative transformation of organic matter and biogenic compounds and BOC were based on purely chemical considerations. Simple first order reactions [14,18,38] or consecutive first order reactions [1,34] were used for that purpose. Although the ways in which various chemical compounds are transformed differ, numerous experiments demonstrate that microbiological transformation plays a decisive role in decreasing the total chemical component concentrations in natural water. In the first kinetic models, the organism population of the lowest trophic levels--the main transformers of chemical compounds in waters--were not taken into consideration.

The transformation of chemical matter is by an extremely complex system of interrelations between chemical compounds and organism populations. The interaction of these populations also influences the kinetics of the transformation of chemical compounds. Biochemical interactions are one of the most important types of interrelations [20]. However, information about these interactions is limited only to empirical data and qualitative descriptions. More is known about prey-predator interactions among populations for which the use of mathematical models constructed on Volterra-Lotka's principles [33,40] has become generally recognized.

The models mentioned in the literature are only concerned with separate parts of the complex transformation of chemical compounds within ecological systems. At present, researchers face the problem of constructing complex mathematical models of complete ecological-biochemical systems. Initial experience with constructing these models [2,12] has shown that classical simple models of the separate chemical and biological parts of the system do not have the simulation ability needed for studying the processes determining water quality and the transformation of chemical compounds. Analysis of transient processes enables investigators to learn much more about the dynamics of the ecosystem, which is important in predicting the kinetics of the transformation of compounds.

Simulation defects of such models have been encountered for several reasons including the lack of probable change in the organism population and certain features of the transformation of matter and population development resulting from the heterogeneous composition of chemical compounds when replacement of limiting substances becomes possible. In spite of these defects, the models can be used on the computer for studying specific features of the transformation of chemical matter under widely different environmental conditions not possible in the laboratory. Modeling allows one to test existing theoretical knowledge on the transformation of chemical matter, and to determine the transformation kinetics of various stages of the conversion.

Simulation models of the transformation of compounds containing biogenic elements (nitrogen and phosphorus), of BOC and of the behavior of the nonphotosynthetic ecological-biochemical microsystem are considered in this paper.

MODEL OF NITROGEN COMPOUND TRANSFORMATION AND BOC DYNAMICS

Current models of the transformation of nitrogen compounds constructed on the basis of chemical [1,4,34] and ecological [9,26] principles show only general aspects of the process. They do not present features of the complex dynamics of nitrogen compounds as a whole and cannot be used for mathematical simulation.

Experimental investigations of the transformation of nitrogen compounds are partially generalized in reviews [22,29]. The variety of organic nitrogen compounds (e.g., proteins, peptides, amino acids, amines, amides, heterocyclic compounds) explains the complexity of the chemical composition of these compounds and the many possible valent nitrogen states (from -3 to 5) in nitrogen mineral compounds [32]. The complexity of biochemical transformation of nitrogen compounds is connected with the activity of almost all types of microorganisms and aquatic plants. Although different types of microorganisms are responsible for separate elements of the nitrogen cycle, they act together simultaneously on all interface surfaces and water bodies. Thus from an ecological point of view the interaction of nitrogen compounds with organism populations is complex.

The concentration of nitrogen compounds in a natural waterbody may change as a result of the simultaneous biochemical processes such as follows:

- Accumulation, release, and consumption of organic nitrogen by heterotrophic microorganisms and water plants;
- Fermentation hydrolysis of proteins and polypeptides in solution and particulates;
- Biological transformation of organic particulate and living nitrogen matter;
- Release of ammonium in the deamination processes in dissolved organic matter and cell compounds;
- Oxidation of ammonium, nitrite, and intermediate products by autotrophic and heterotrophic nitrifying bacteria;
- Ammonium, nitrite, and nitrate assimilation by autotrophic and heterotrophic microorganisms;
- Reduction of the nitrate and nitrite by denitrifying bacteria, particularly in the bottom sediments;
- Fixation of atmospheric nitrogen by water plants and bacteria [22,29].

The literature contains information on the separate stages of all parts of these complex biochemical transformations. However, two processes--the consumption of nitrogen components by microorganisms and nitrification--have been studied a great deal, particularly with respect to the problems of the biological productivity of water and the oxidation level of nitrogen compounds. The latter is also an important aspect of eutrophication water investigations.

In the oxidation of mineral nitrogen compounds, two exothermic stages are carried on by the two types of chemoautotrophic microorganisms [13]:

- *Nitrosomonas* $NH_4^+ + 1.5\ O_2 \rightarrow NO_2^-$ (+ 59.4 kcal/mol)
- *Nitrobacter* $NO_2^- + 0.5\ O_2 \rightarrow NO_3^-$ (+ 18 kcal/mol).

Some intermediate stages develop rapidly; thus, as a rule, intermediate oxidation products (e.g., hydroxylamine, dihydrooxyammonium, nitroxyl, hyponitrite) are not found [15]. When constructing various models of the transformation of nitrogen compounds one should not consider these rapid stages.

The block scheme of the system for the transformation of nitrogen compounds and its relationship to BOC is presented in Figure 1. This scheme is based on numerous investigations of the transformation of nitrogen compounds.

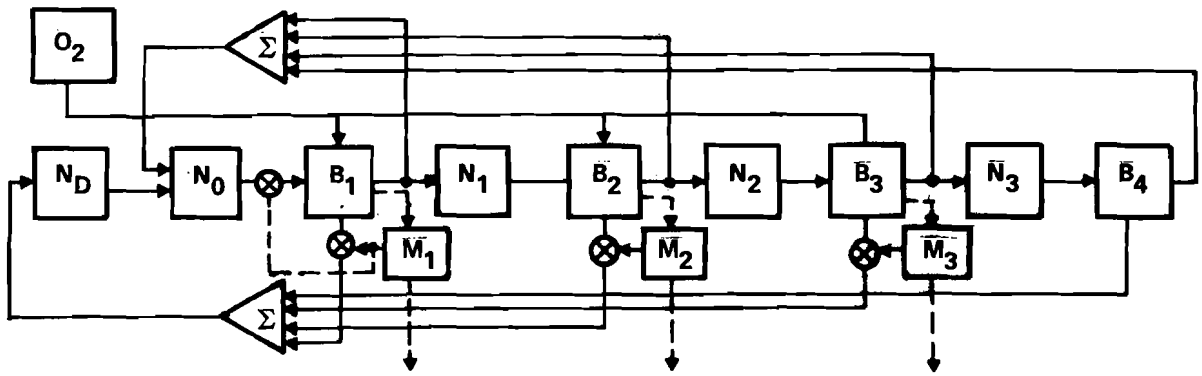

Figure 1. Block scheme of the system for the transformation of nitrogen compounds and its relationship to BOC [2].

Key: N_o,N_D: concentration of organic and detrital nitrogen respectively;

N_i: concentration of mineral nitrogen compounds:

i = 1, ammonium; i = 2, nitrite; i = 2, nitrate;

B_i: microorganism concentration:

i = 1, heterotrophs; i = 2, ammonium-oxidizing chemoautotrophs; i = 3, nitrite-oxidizing chemoautotrophs; i = 4, algae;

O_2: oxygen;

M_i: concentration of autometabolic--limitation of biomass microorganism growth at the approach to M-concentration:

i = 1, for heterotrophs; i = 2, for ammonium-oxidizing chemoautotrophs; i = 3, for nitrite-oxidizing chemoautotrophs; i = 4, for algae.

The principles of biogeocoenosis simulation were considered in the design of the model. The rates of substrate uptake (P_i), of metabolite release (L_i), and of the elimination (S_i) of organisms through natural mortality and consumption by predators were taken into consideration in the equations for kinetics of microorganism growth. When simulating open natural ecological systems for conditions close to the steady state, simple equations for estimating the quantitative values of P_i, L_i, and S_i may be used. As a rule these values are considered either constant or proportional: $P_i = d_iN_i$; $L_i = G_iP_i$; $S_i = f_i \cdot$(predatory concentration) where d_i, G_i, f_i are proportional coefficients. For describing population dynamics over the broad range of substrate concentration changes observed for high population growth in the laboratory, or in the event of pollution discharges in nature, the Michaelis-Menten-Monod equation are usually used: $P_i = \mu_iN_{i-I}/(K_{Mi} + N_{i-I})$, where μ_i,K_{mi} are constants. In this case the limitation on population growth by a single substrate is assumed. This equation may be modified for heterogenic reactions. The following equation, which is of a Longmuir-Hinshelwood type, is more convenient for simulating the transformation of multicomponent systems and was used in this work: $P_i = \mu_iN_{i-I}/(I + D_iN_{i-I})$ where μ_i and D_i are constants.

In the laboratory incubation of water samples, unlike under natural conditions, the ecological microsystems have to move through a transient phase to reach a new steady state; this transient phase depends on the experimental conditions. An analysis of the characteristics of change shows that changes occur in the structure and in the concentration of all system elements as well as in trophic and metabolic organism activity [12]. Thus for mathematical simulation it is necessary to describe in detail the mechanisms for the microbiological transformation of chemical matter.

If the population density changes by a few orders of magnitude the trophodynamics of the microorganisms will be greatly affected. N.D. Ierusalimsky [8] considers this relationship as autometabolic inhibition, which he takes into account by adding

to the denominator in the equation for P_i the coefficient such as $(I + m_i M_i)$ or $m_i M_i$, depending on the nature of the inhibitor, where m_i is the coefficient and M_i the concentration of the inhibitor.

Values for $P_i B_i$ are determined by experiment for changes in the uptake rate of substrate, N_{i-I}, thus making it easier to construct the simulation model in spite of the indefinite information about the nature and dynamics of the inhibitors.

Values for L_i and for the activity coefficient r_i (the amount of liberated matter after a specific quantity of substrate has been consumed) are also determined by experiment for N_{i-I} and liberated product N_i with consideration given to the values of $P_i B_i$. An equation was used to describe r_i in which the amount of matter released by the organisms increases when P_i is increased (with a limit of I), and decreases when P_i is reduced with a limit of some minimal value--$\lim_{P_i \to 0} r_i \to I - n_i$.

There are no reliable data about the rate of organism elimination S_i. Although they could be obtained from differentiable experimental data for the concentration dynamics of detritus, heterotrophic, and chemoautotrophic microorganisms, no such data currently exist. For mathematical modeling the following criteria were used for improving the adequacy of the equations for S_i: (1) In the steady state the value of $S_i = q_i$ is constant but it changes during the transient processes. (2) There is a limit to the value of $S_i = q_i + V_i(I - n_i)$ when $N_{i-I} \to 0$, $P_i \to 0$; this value for chemoautotrophic bacteria is very small. (3) The rate of predatory elimination of organisms increases with improvements in the nutrient concentration and with increase in B_i. (4) The rate of compulsory elimination decreases nearly to zero when the nutrient is at a low level for a long period of time.

By these criteria, it is possible to simulate population dynamics including the interaction of organisms with predators (similar to that in the case of the "prey-predators" scheme [8]).

Also the behavior of chemoautotrophs can be simulated without destroying their transformation in a wide variety of environments. The equation does not consider concrete mechanisms for elimination of organisms, "decodes" which currently are too hypothetical.

The dead organisms and those eliminated by predators are included in the detritus concentration. The biomass of predator organisms that directly excrete an appreciable quantity of nitrogen compound was not taken into account in this case. But in this paper only nitrogen compounds, ammonium-, nitrite- and nitrate-forming microorganisms, such as heterotrophs, Nitrosomonas, and Nitrobacter that convert nitrogen compounds were taken into account.

The rate of biochemical oxygen consumption during separate stages and as a whole in the transformation of nitrogen compounds was calculated by multiplication of the specific rate of release of oxidized nitrogen compounds (L_i), the stoichiometric coefficients (Y_i), and the biomass values (B_i).

The mathematical model for the transformation of nitrogen compounds is given in the following system of equations [2,3, 12,13]:

$$\frac{dB_i}{dt} = (P_i - L_i - S_i)B_i$$

$$\frac{dN_o}{dt} = \sum_{i=1}^{3} c_i L_i B_i + \ell N_D - P_1 B_1$$

$$\frac{dN_i}{dt} = f_i L_i B_i - P_{i+1} B_{i+1}$$

$$\frac{dM_i}{dt} = j_i L_i B_i - k_i M_i$$

$$\frac{dY}{dt} = \sum_{i=1}^{3} y_i L_i B_i$$

$$\frac{dN_D}{dt} = \sum_{i=1}^{4} S_i B_i - \ell N_D$$

$$P_i = \frac{a_i N_{i-1}}{(1 + D_i N_{i-1})(1 + m_i M_i)}$$

$$r_i = \frac{n_i P_i}{1 + G_i P_i} + \left(1 - \frac{n_i}{G_i}\right)$$

$$S_i = q_i + g_i M_i + V_i r_i$$

$$L_i = r_i P_i \quad ,$$

where a_i, c_i, D_i, f_i G_i, g_i, j_i, k_i, ℓ, m_i, n_i, q_i, V_i, y_i are coefficients and Y is the biochemical oxygen consumption.

The model was used for analyzing the transformation of nitrogen compounds in lake, sewage, and sea waters.

The experimental data of K.K. Votintsev [7] were used as the basis for analyzing the transformation of nitrogen compounds in lake water. Figure 2 gives the simulation results (curves) and K.K. Votintsev's [7] experimental data (points) for the transformation of nitrogen compounds. The following output parameters were used for modeling, [3,12,13]:

$B_1 = 8 \times 10^{-5}$; $B_2 = 4 \times 10^{-4}$; $B_3 = 7 \times 10^{-3}$; $B_4 = 0$; $P_4 = 0$;

$N_0 = 1.5$; $N_1 = 0.001$; $N_2 = 0.02$; $N_3 = 0.04$; $M_{B1} = M_{B2} =$

$M_{B3} = 0$; $Y = 0$; $a_1 = 13.6$; $a_2 = 3.4$; $a_3 = 2.7$; $a_4 = 0$;

$D_1 = 0.14$; $D_2 = D_3 = 1$; $r_1 = r_2 = r_3 = 0.7$; $m_1 = 700$;

$m_2 = m_3 = 0$; $q_1 = 1$; $q_2 = q_3 = 0.05$; $g_1 = 75$; $g_2 = g_3 = 0$;

$j_1 = 0.03$; $j_2 = j_3 = 0$; $k_1 = 0.4$; $k_2 = k_3 = 0$; $y_1 = 4$

$y_2 = 2.28$; $y_3 = 3.34$; $f_1 = f_2 = f_3 = 0.999$; $c_1 = c_2 = c_3$

$= 0.001$.

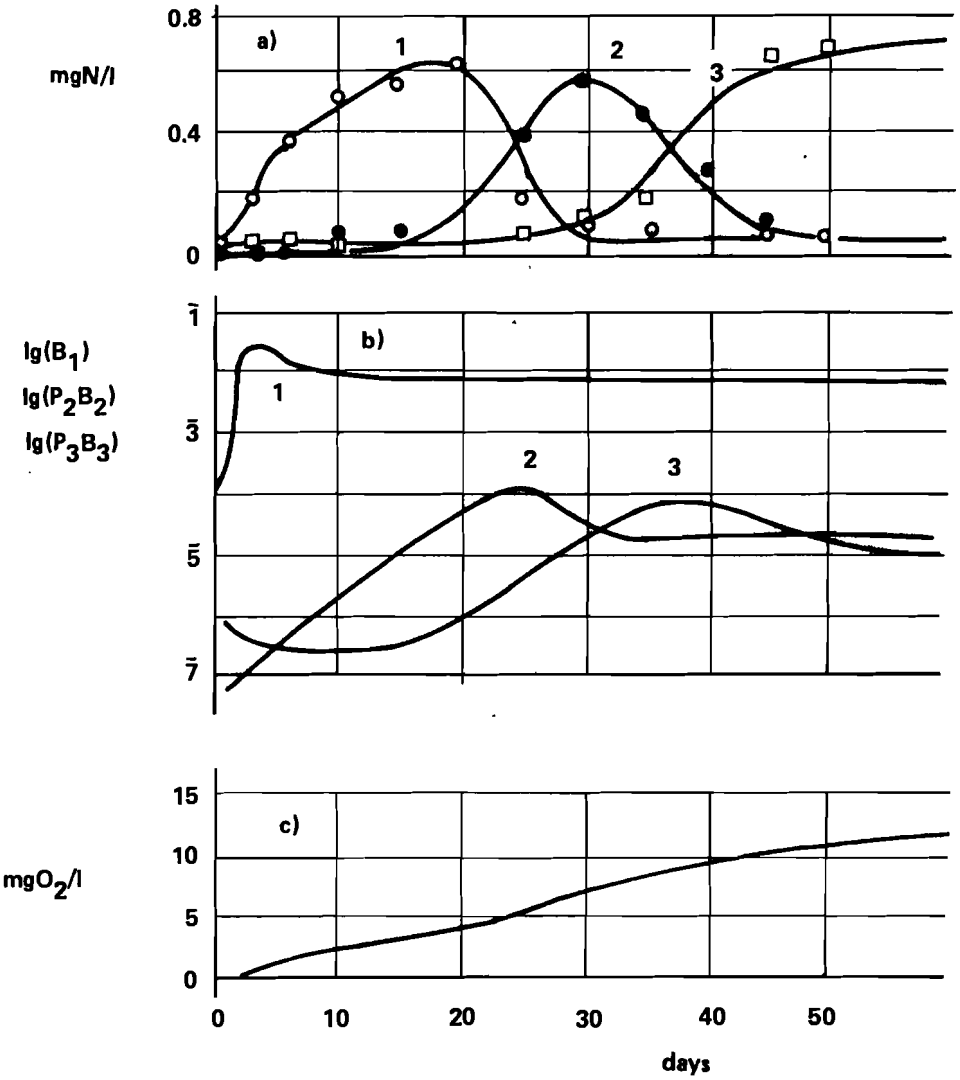

Figure 2. Simulation of nitrogen compound transformation (curves) [3,12] in lake water (Votintsev's K.K. [7] experimental data (points).

(a) 1, ammonium; 2, nitrite; 3, nitrate.

(b) 1, heterotrophs; 2,3, the transformation activity of ammonium- and nitrite-oxidizing chemoautotrophs respectively.

(c) Total BOC

The model accurately represents the transformation of mineral nitrogen compounds within a closed microsystem and also shows the corresponding changes in heterotrophic biomass, and in the transformation activity of the population of ammonium- and nitrite-oxidizing chemoautotrophs. The above values from the simulation exercise are in line with experimental data on dynamics of chemical nitrogen compounds. The biomass heterotrophic change shown in curve 1 of Figure 2b is typical of natural waters: there is a sharp maximum in the first days of the water incubation followed by a steady state concentration that exceeds the initial amount by more than an order of magnitude.

The simulation results for the dynamics of BOC (Figure 2c) are in accordance with established laws for the step-wise oxidation of mineral nitrogen compounds [24]. The BOC values are typical for waters with high concentrations of organic matter.

The experimental data of DeMarco et al [25] on the transformation of organic nitrogen, ammonium, nitrite, and nitrate and the numbers of chemoautotrophic bacteria, were used to analyze the transformation of nitrogen compounds in sewage. The model corresponds completely with the experimental observations on the transformation of the chemical component including those for reappearance of ammonium after 14 days of water incubation (Figure 3) [12,13]. The input parameters used in this variant of the mathematical simulation are as follows:

$B_1 = 0.04$; $B_2 = 0.065$; $B_3 = 0.5$; $B_4 = 0$; $P_4 = 0$; $N_0 = 2.7$;

$N_1 = 10.8$; $N_2 = N_3 = 0$; $M_{B1} = 0.02$; $M_{B2} = 0.0001$; $M_{B3} = 0.01$;

$Y = 0$; $a_1 = 100$; $a_2 = 7$; $a_3 = 10$; $a_4 = 0$; $D_1 = D_2 = D_3 = 5$;

$r_1 = 0.7$; $r_2 = r_3 = 0.95$; $m_1 = 700$; $m_2 = m_3 = 0$; $q_1 = q_2 = 1$;

$q_3 = 0.3$; $g_1 = 75$; $g_2 = g_3 = 0$; $j_1 = 0.03$; $j_2 = j_3 = 0.001$;

$k_1 = 0.4$; $k_2 = k_3 = 0.1$; $y_1 = 4$; $y_2 = 2.28$; $y_3 = 3.43$;

$f_1 = f_2 = f_3 = 0.999$; $c_1 = c_2 = c_3 = 0.001$.

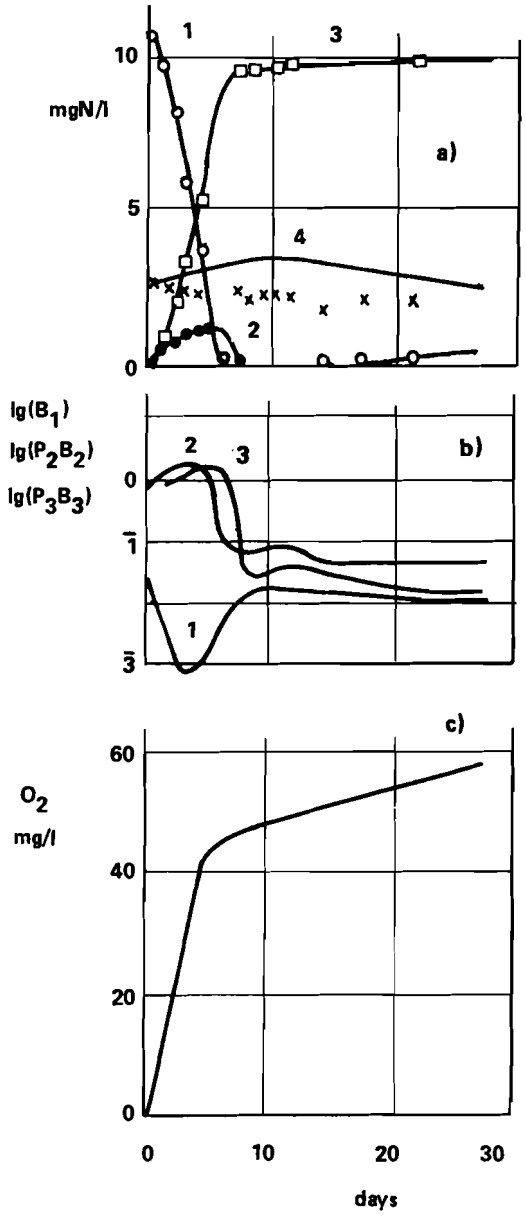

Figure 3. Simulation of nitrogen compound transformation (curves) [12,13] in sewage (De Marco et al [25] experimental data (points):

(a) 1, ammonium; 2, nitrite; 3, nitrate, 4, organic + particulate nitrogen.

(b) 1, heterotrophs; 2,3, transformation activity of ammonium- and nitrite-oxidizing chemoautotrophs, respectively.

(c) BOC total.

The heterotrophic bacteria concentration (curve 1, Figure 3) decreases sharply, reaching a minimum level in three to five days; after 14 days it reaches a steady state. The transformation activity of the chemoautotrophic population (curves 2 and 3, Figure 3b) is high during the first days of water incubation since the substrate concentration--i.e. ammonium and nitrite--is high enough. The integral BOC curve is of a autocatalytic-linear type [10] and there are no subsequent stages of oxygen consumption for the ammonium and nitrite oxidation because these two processes develop rapidly and simultaneously.

The analysis of the simulation results presented in Figure 3 indicates that the oxidative activity of the chemoautotrophic organisms is high and the amount of nitrogen found in biomasses is small (in the cell composition it is less than 5%). The mineral nitrogen compounds are utilized by chemoautotrophic organisms as energy sources according to available information [15] concerning the oxidative activity of intercellular enzymes of chemoautotrophs. Thus for simulating the transformation of nitrogen compounds in sewage the amount of metabolic release of the chemoautotrophic bacteria is assumed to be rather high (about 95%). This value makes possible good agreement of mathematical modelling results with the experimental data on this process.

For simulating the transformation of nitrogen compounds in sea water the experimental data of Brand and Rakestraw [15] were used where the changing dynamics of ammonium, nitrate, nitrite and the particulate organic nitrogen concentration were studied in detail. The following input data were used in obtaining the simulation results presented in Figure 4:

$B_1 = 1 \times 10^{-4}$; $B_2 = 3 \times 10^{-8}$; $B_3 = 1 \times 10^{-8}$; $B_4 = 0.15$; $N_0 = 0.23$;

$N_1 = 0.01$; $N_2 = N_3 = 0$; $N_D = 0.01$; $N_{B1} = M_{B2} = M_{B3} = M_{B4} = 0$;

$Y = 0$; $a_1 = 70$; $a_2 = 300$; $a_3 = 400$; $a_4 = 25$; $D_1 = 0.5$; $D_2 =$

$D_3 = 2$; $D_4 = 100$; $m_1 = 400$; $m_2 = m_3 = m_4 = 0$; $q_1 = 0.6$;

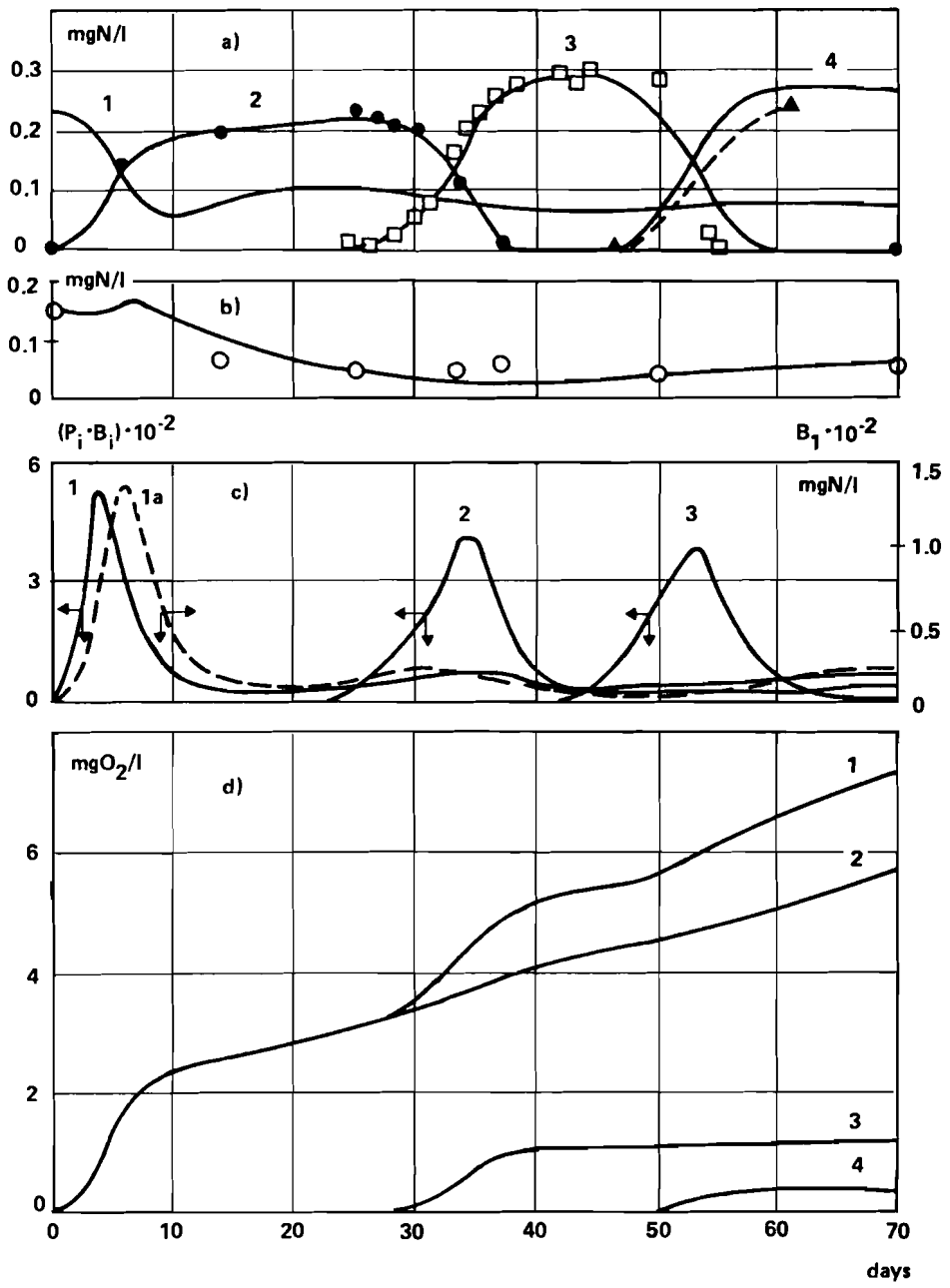

Figure 4. Simulation of nitrogen compound transformation (curves) [2,12] in sea water (Brand, Rakestraw [21] for experimental data (points):

(a) 1, organic nitrogen; 2, ammonium; 3, nitrite; 4, nitrate.

(b) particulate nitrogen.

(c) 1,2,3, transformation activity of heterotrophs, ammonium- and nitrite-oxidizing chemoautotrophs population, respectively. 1a, the heterotrophs' biomasses.

(d) the oxygen consumption curves: 1, BOC general; 2,3,4, BOC by heterotrophes, by ammonium- and by nitrite-oxidizing chemoautotrophs, respectively.

$q_2 = q_3 = 0.05$; $q_4 = 0.06$; $g_1 = 80$; $g_2 = 100$; $g_3 = 1000$; $g_4 = 0$;

$V_1 = -0.1$; $V_2 = 0.05$; $V_3 = 0.1$; $V_4 = 1$; $j_1 = 0.03$; $j_2 =$

$j_3 = 0.001$; $j_4 = 0$; $k_1 = 0.05$; $k_2 = k_4 = 0$; $k_3 = 0.01$;

$y_1 = 13.35$; $y_2 = 3.42$; $y_3 = 1.14$; $y_4 = 0$; $f_1 = 1$; $f_2 =$

$f_3 = 0.99$; $f_4 = 0$; $c_1 = 0$; $c_2 = 0.1$; $c_3 = 0.01$; $c_4 = 0.9$;

$\ell = 0.2$; $n_1 = 0.4$; $n_2 = n_3 = 0.93$; $n_4 = 0.82$; $G_1 = 0.15$;

$G_2 = 2.15$; $G_3 = 1.72$; $G_4 = 10$.

Curve 1 of Figure 4a shows the change in the level of organic nitrogen. (This corresponds to data available in the literature on similar types of curves.) Using the experimental data for particulate organic nitrogen it is possible to simulate the transformation of mineral nitrogen compounds, with a guaranteed upper limit of biomass. The character of the changes of the heterotrophic bacteria biomass is typical of similar curves described in the literature.

A maximum rate of consumption of organic nitrogen (curve 1, Figure 4) is achieved when the heterotrophic bacteria concentration is not yet at its highest value. (These data correspond with available information concerning the change in microorganism activity during development stages.)

The fraction of nitrogen released from the nitrogen consumed depends on the changes in the specific rates of nitrogen consumption; for heterotrophic bacteria it is from 0.6 to 0.86 and for chemoautotrophic bacteria--in an extremely broad interval--from 0.1 to 0.99. The residual concentration of organic nitrogen after 70 days is 29%, resulting from an equilibrium between the entrance phase and the oxidation phase of the organic matter. The total residual concentration (dissolved organic nitrogen plus particulate nitrogen) after 70 days is 24%. These values

are in accordance with estimates of mineralization in sea water resulting from the destruction of dissolved organic matter (DOM) during long periods of incubation [19]. This level of the residual concentration of organic matter was achieved without dividing the organic matter into unstable and stable parts during the process of biochemical destruction.

From the simulation results it is possible to estimate the oxygen consumption by the heterotrophic, and by the ammonium- and the nitrite-oxidizing chemoautotrophic bacteria (see curves 2-4 of Figure 4d). (This is difficult to do in experimental BOC investigations.) The integral BOC values (curves 1, Figure 4d) are typical for sea water, with the addition of organic matter resulting from the destruction of the particular fraction. The oxygen consumption rate by heterotrophic bacteria in the linear part of the BOC curve (curve 2, Figure 4d) is 0.061 mg O_2/ℓ days. As B.A. Skopintsev [17] noted "the oxygen consumption for the period of 70 to 180 days is 0.01-0.03 mg O_2/ℓ days at 16-20 °C; this characterized the oxygen losses for the oxidation of stable organic matter". This value is higher for unstable organic matter. The BOC rates are similar to those achieved in mathematical experiments without taking into account the algal behavior, and the organic nitrogen added as a result of the destruction on the linear part showed the oxygen loss to the oxidation of the "stable" organic fraction.

Thus the simulation results show that the presented model reflects the transformation dynamics of the nitrogen compounds, the biological populations, and the oxygen consumption in various water solutions at different experimental conditions. The kinetics curve for the change in the concentration of DOM, of the mineral nitrogen compounds, and of the BOC represented by the model, corresponds to that obtained during the experimental study of the process.

The mathematical model presented here may be used for the analytical study of the transformation processes of nitrogen compounds in the water ecological systems.

MODEL OF PHOSPHORUS COMPOUND TRANSFORMATIONS AND BOC DYNAMICS

Phosphorus is one of the most important biogenic elements and it often limits the development of the organism population of the lowest trophic levels in natural waters. The mineral phosphorus content determines the rates of primary productivity, the transformation kinetics of organic matter of natural and man-made origin, and the dynamics of BOC [4,5]. The study of phosphorus compound kinetics and its transformation mechanisms is necessary to determine the macrokinetic tasks [36] needed to construct models of water ecological systems [6] and especially to study water eutrophication [30].

Practically all microorganism types take part in the transformation of phosphorus compounds. The dissolved inorganic phosphorus (DIP), which is consumed by algae and bacteria, is bound in the organic compounds--phosphoric acid ethers included in the composition of living cells as an important biochemical component (phospholipids, ATP). The organic phosphorus of living matter along the food chain is included in the organisms of higher trophic levels--plant and predatory zooplankton and so on. The release of mineral compounds and of dissolved organic phosphorus (DOP) as well as the formation of dead particulate organic matter from the feces of detritus phosphorus (D_p) and the organism bodies take place during the vital functions of the organisms. During the detritus autolysis there is a rapid release of DOP (as much as 30 to 40%) into the solution; it is consumed by the heterotrophic bacteria and is probably hydrolyzed by the intercellular phosphatase to DIP [37]. The latter, however, has not been confirmed by experiments of Hofman [28] and Watt and Hayes [42]. The DOP may be immediately assimilated by phytoplankton as well [23]. A possible role of the zooplankton in the mineralization of the DOP from the DIP has been observed [35,42].

The simple mathematical models described in the literature and constructed on the basis of chemical kinetics deal only with the separate chains of the complex system of organism interaction with phosphorus compounds. Numerous models of DIP utilization

by algae and their influence on primary productivity are known. Another group of models studies the regeneration of inorganic phosphate during the destruction of the detritus (the dead plankton organisms).

The first and the simplest model of the transformation of phosphorus compounds investigated the regeneration of phosphate (phosphatification), which was described as an irreversible reaction of the first order [16]. This model describes the process in a rather small interval of time. Nevertheless it is still being used in hydrochemical practice [14].

The rate constants of phosphatification are near to the first order BOC constants; however, these processes have been separately considered. In the work of Grill and Richard [27] the transformation of phosphorus compounds is described as a consecutive two-stage irreversible first order reaction in which the bacterial phosphorus (B_p) is an intermediate product. The most complete model of Watt and Hayes [42] is based on similar chemical kinetic considerations. It is a consecutive two-stage reversible first order reaction: $\mathrm{DIP} \underset{\beta_2}{\overset{\alpha}{\rightleftarrows}} \mathrm{PP} \underset{\gamma}{\overset{\beta_1}{\rightleftarrows}} \mathrm{DOP}$, where α, β_i, γ are the rate constants of the separate stages, and PP is particulate phosphorus. However, each stage in this kinetics scheme is a sum of independent processes. For instance, the regeneration of DIP (PP→DIP) results from the following processes that take place simultaneously: fermentation from organic compounds; heterotrophic bacterial release; zooplankton release; formation during detritus autolysis. Improving the model leads to quite different results from those obtained with simple models. For example the rate constants regeneration of DIP in Grill and Richard's model [27] differs almost fivefold from those in Watt and Hayes's model [42]. We conclude that comparatively simple models can give wrong information about the dynamics of processes and their results should be considered carefully. Watt and Hayes's model [42] does not show a transient process and this is important when considering population successions, pollution, eutrophication, and temperature changes. Their model does not accurately show

the state of equilibrium in a system under natural conditions because the laboratory experiment on which the model is based does not consider changes in the population. The intensity of the oxidative processes in the laboratory and under natural conditions may differ by an order of magnitude or more according to numerous BOC observation data.

The block scheme of the improved model for the transformation of phosphorus compounds and BOC as discussed above is presented in Figure 5 [2,4,5]. The model contains the following differential equations:

$$\frac{dB}{dt} = (P_B - L_B - S_B)B - P_B' Z_S$$

$$\frac{dZ}{dt} = -(L_Z + S_Z)Z$$

$$\frac{dZ^*}{dt} = P' Z_S - (L_Z + S_Z)Z^*$$

$$\frac{dY}{dt} = K_{10} L_B B + K_{15} P' Z_S$$

$$\frac{dC_\ell}{dt} = K_{11} K_7 B S_B - K_3 P_B B - 0.376\ (K_{10} L_B B + K_{15} P' Z_S)$$

$$\frac{d(DIP)}{dt} = K_6 L_B B - K_1 P_{DIP} B - P'_{DIP} Z_S + K_{14}(DOP) + (1 - K_{16}) L_Z Z_S$$

$$\frac{d(DOP)}{dt} = K_7 D_P - K_2 P_{DOP} B - P'_{DOP} Z_S - K_{14}(DOP) + K_{16} L_Z Z_S$$

$$\frac{dD_P}{dt} = B S_B + S_Z Z_S - K_7 D_P$$

$$\frac{dC_M}{dt} = K_8 L_B B - K_9 C_M$$

$$P_B = \frac{d_{10}}{(1 + M_P)(1 + K_4 C_M)} \; ; \; M_P = \frac{B}{d_1(DIP) + d_2(DOP)} + \frac{1}{d_3 C_\ell}$$

$$P_{DIP} = \frac{d_{10} d_3 d_1 C_1 (DIP)}{Q} \quad ; \quad P_{DOP} = \frac{d_{10} d_3 d_2 C_\ell (DOP)}{Q}$$

$$Q = \left\{ [d_1(DIP) + d_2(DOP)] \; (1 + d_3 C_1) + d_3 C_\ell B \right\} \; (1 + K_4 C_M)$$

$$P_B' = \frac{K_5}{1 + Z_S/d_9 B} \quad ; \quad P_{DIP}' = \frac{K_{12}(DIP)}{1 + d_7(DIP)}$$

$$P_{DOP}' = \frac{k_{13}(DOP)}{1 + d_8(DOP)} \quad ; \quad P' = P_B' + P_{DIP}' + P_{DOP}'$$

$$r_B = \frac{d_4 P_B}{1 + d_5 P_B} + (1 - \frac{d_4}{d_5}) \; ; \; r_Z = \frac{d_6 P'}{1 + d_{11} P'} + (1 - \frac{d_6}{d_{11}}$$

$$L_B = r_B P_B \quad ; \quad L_Z = r_Z P'$$

$$S_B = q_B + V_B r_B \quad ; \quad S_Z = q_Z + (V_Z Z_S)/P'$$

Where

Z^*, Z_S: Concentration of the ^{32}P labeled and general zooplankton phosphorus, respectively;

P_B, P_{DIP}, P_{DOP}: Specific rates of bacterial substrate uptake of general phosphorus, inorganic phosphorus, and organic phosphorus (day^{-1}), respectively;

P_B', P_{DIP}', P_{DOP}': Specific rates of zooplankton substrate uptake of bacterial phosphorus, inorganic phosphorus, and organic phosphorus (day^{-1}), respectively;

M_P, Q: Parameters limiting the specific rates of substrate consumption by bacteria;

L_B, L_Z: Specific rates of metabolite release by bacteria and zooplankton (day^{-1}), respectively;

S_B, S_Z: Specific elimination rates of bacteria and zooplankton (day^{-1}), respectively;

r_B, r_Z: Metabolite release activity of the bacteria and the zooplankton, respectively;

d_i, K_i, q_i, V_i: Coefficients.

The expressions for the specific rates of substrate consumption, and of the metabolic release and elimination of the organisms were obtained following investigations of several alternative schemes.

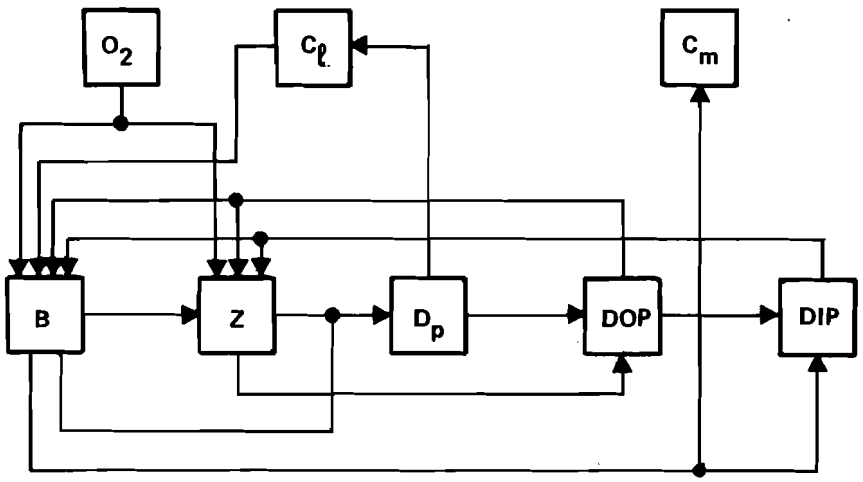

Figure 5. Block-scheme of the system for transformation of phosphorus compounds and its relationship to BOC [4,5].

C_ℓ, C_M, the labile carbonaceous and transformate organic matter, respectively;

O_2, oxygen;

DIP, DOP, dissolved inorganic and organic phosphorus, respectively;

B, Z, D_P, bacterial, zooplankton, and detritus phosphorus, respectively.

The experimental data of Watt and Hayes [42] for the dynamics of general, inorganic, organic, and particulate phosphorus (see points in Figure 6) in freshly collected sea water at a temperature of 18 °C, are compared with the simulation results (curves) [4,5] in Figure 6. The calculations were carried out with the following input parameters:

DIP = 10; DOP = 0.008; C_ℓ = 2; C_M = 0.001; B = 0.05;

Z = 0.05; Y = 0; D_P = 0; d_1 = 0.009; d_2 = 0.0032;

d_3 = 0.01; d_4 = 0.06; d_5 = 0.1; d_6 = 0.45; $d_7 = d_8$ = 0.1;

d_9 = 1; d_{10} = 60; d_{11} = 0.5; $K_1 = K_2$ = 1; $K_3 = K_{11}$ = 40;

K_4 = 0; K_5 = 0.7; K_6 = 1; K_7 = 0.95; K_8 = 0.01; $K_9 = K_{10}$ = 0.1; K_{12} = 0.14; K_{13} = 0.12; K_{14} = 0.2; K_{15} = 0.01;

K_{16} = 0.7; q_B = 0.22; V_B = 0.15; q_Z = 0.1; V_Z = 0.0001.

The initial concentration of inorganic phosphorus (10 μgP/ℓ) was taken as 100%. The model represents the dynamics of the transformation of phosphorus compounds in detail, as can be seen in Figure 6a. There is a discrepancy in the early stages of development between the increase of the bacterial biomass and the changes in the bacterial numbers (curves 5 and 5' of Figure 6b) since during this period the growth in the biomass is greater than the increases in bacterial number; at latter stages this unbalance disappears [8]. Concentrations of all phosphorus components are stabilized after 25 days; however, the consumption of organic carbonaceous matter and oxygen continue (curves 8 and 9, Figure 6c). The general oxygen demand is described by a chemical-kinetic equation of the exponential linear type (dotted line, curve 9, Figure 6c):

$$BOC = 1.10(1 - e^{-0.206t}) + 0.0227t \quad .$$

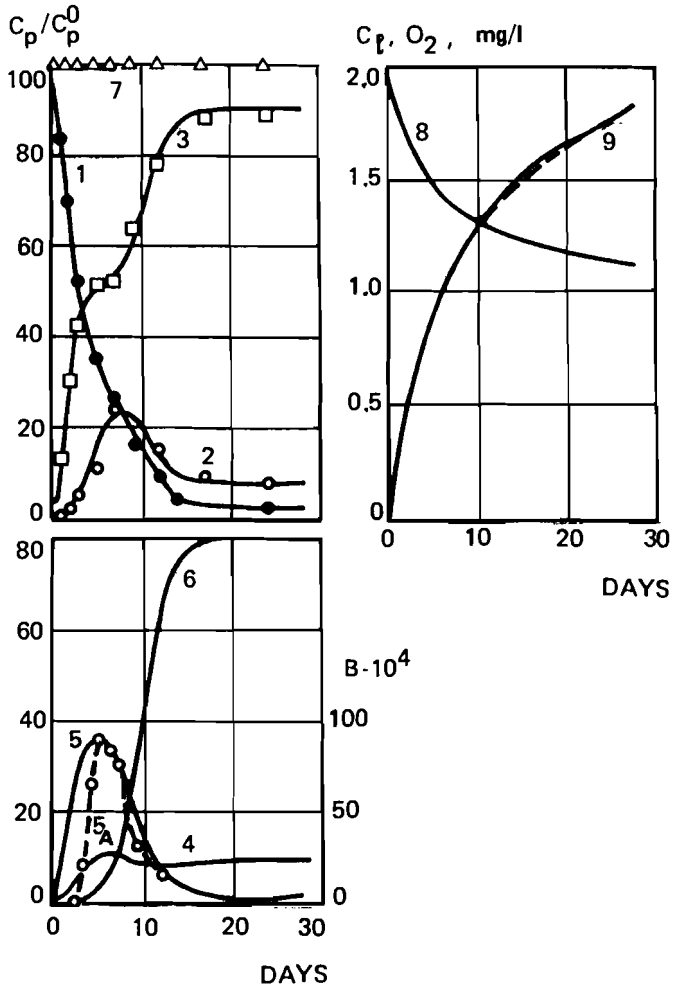

Figure 6. Simulation of phosphorus compound transformation (curves) [4,5] in freshly collected sea water at 18 °C for experimental data (points) by Watt and Hayes [42].

Phosphorus: 1, inorganic; 2, organic; 3, particulate; 4, detritus, 5, bacterial; (5a, dynamics of bacterial number [42]; 6, zooplankton; 7, sum; 8, DOM; 9, total BOC (dotted line is constructed on equation of exponential-linear type).

Kinetic equations of a similar type are often used for describing BOC dynamics in sea water samples at 18 to 20 °C [22]. The rate of oxygen uptake at the first stage is 0.245 mgO_2/ℓ per day--10.8 times higher than that at the linear stage (0.0227 mgO_2/ℓ per day).

Watt and Hayes's experimental data [42] on the transformation of phosphorus compounds at 10, 15 and 20 °C in the dark in sea water previously kept in the laboratory for 14 days were used in

the next calculation runs. The results of these runs are shown in Figure 7 and the values of the input parameters are presented in Table 1.

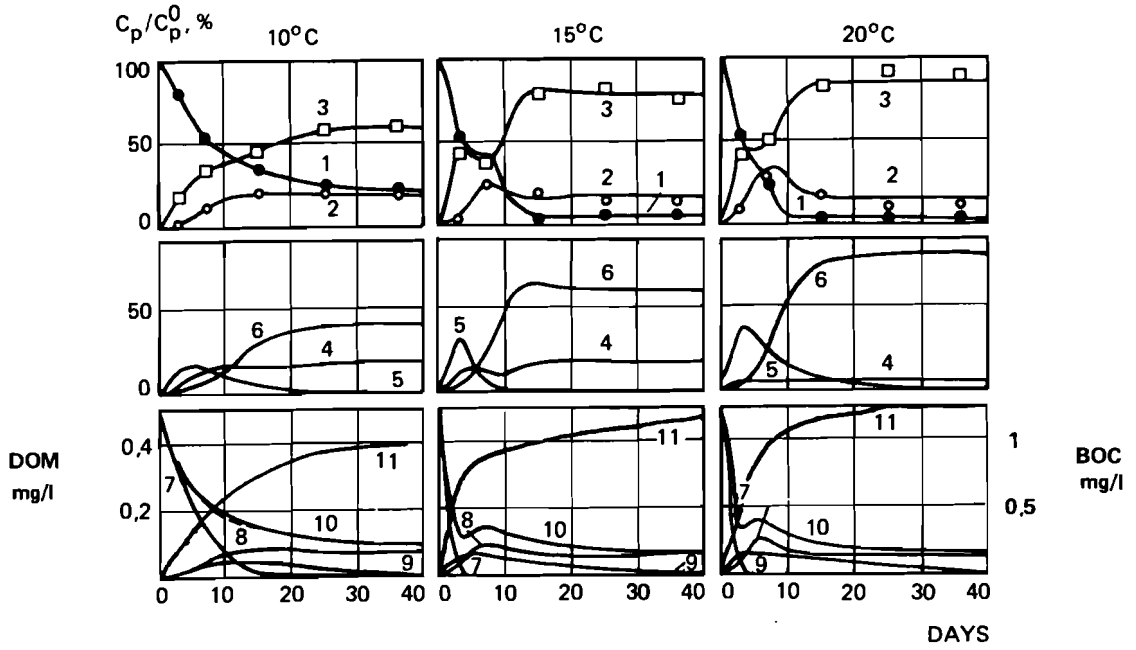

Figure 7. Simulation of phosphorus compound transformation (curves) [4,5] after exposure for two weeks in dark sea water at different temperatures for experimental data (points) of Watt and Hayes [42].

Phosphorus: 1, inorganic; 2, organic; 3, particulate; 4, detritus; 5, bacteria; 6, zooplankton.

Organic matter: 7, labile; 8, phosphorus; 9, transformate metabolic; 10, total DOM; 11 total BOC.

The temperature dependence according to Vant-Goff's law (Q = 2.3) is used only for one parameter, i.e. the rate transformation constant (K_9) of the bacterial organic metabolite which was not determined experimentally. The values of constants d_{10}, K_5, K_7, K_{12}, K_{13} and K_{14}, which are dependent on temperature, were selected so that the simulation results corresponded to the experimental data.

The use of parameter values presented in Table 1 makes it possible to represent the experimental change in concentration of phosphorus compounds to obtain additional information about the component changes of DOM and BOC.

Table 1. The input parameter values used for the phosphorus compound transformation and BOC at 10, 15, and 20 °C [4,5].

parameter	10°	15°	20°	parameter	10°	15°	20°
DIP	10	10	10	K_1	1	1	1
DOP	0.008	0.008	0.008	K_2	1	1	1
C_ℓ	0.48	0.48	0.48	K_3	40	40	40
C_M	0.0001	0.0001	0.0001	K_4	0	0	0
B	0.05	0.05	0.05	K_5	0.738	1.2	0.1
Y	0	0	0	K_6	1	1	1
D_P	0	0	0	K_7	0.27	0.5	2.8
Z	0.05	0.05	0.05	K_8	0.01	0.01	0.01
Z^*	0	0	0	K_9	0.064	0.08	0.1
d_1	0.012	0.012	0.012	K_{10}	0.1	0.1	0.1
d_2	0.0032	0.0032	0.0032	K_{11}	40	40	40
d_3	0.01	0.01	0.01	K_{12}	0.04	0.14	0.4
d_4	0.06	0.06	0.06	K_{13}	0.048	0.065	0.095
d_5	0.1	0.1	0.1	K_{14}	0.12	0.24	0.2
d_6	0.45	0.45	0.45	K_{15}	0.01	0.01	0.01
d_7	0.1	0.1	0.1	K_{16}	0.7	0.7	0.7
d_8	0.1	0.1	0.1	q_B	0.25	0.25	0.25
d_9	1	1	1	V_B	0.15	0.15	0.15
d_{10}	17	50	55	q_Z	0.1	0.1	0.1
d_{11}	0.5	0.5	0.5	V_Z	0.001	0.001	0.001

A characteristic feature of the temperature change is the decrease in bound phosphorus at steady state in the organic, inorganic, and detrite phosphorus and in the DOM, and an increase in the maximum of phosphorus bound in the bacteria and the increase in steady state concentration of zooplankton phosphorus. The oxygen uptake increases with increment in temperature in line with the biological parameters.

There are extreme points on the kinetical curves of DIP and DOM at 15-20 °C; they are not fixed at 10 °C (see Figure 7). This is an important characteristic that allows one to infer biological relationships in the absence of detailed biological data. For hydrochemical investigations, experimental results are usually presented as smoothed average curves; the sharply distinguished experimental points are sometimes excluded and this rather diminishes information of the whole system. Hence, study of these characteristics of kinetic curves gives important information about the behavior of the whole system.

According to the simulation results the dynamics of DOM are typical of the experimental observations made during a long period of sea water incubation. In one case the model represents the dynamics of the element in freshly collected sea water (Figure 6), with an unlimited supply of labile organic matter (2 mg/ℓ) at 18 °C; in the other case it shows the dynamics of the element in two-week-old sea water, with a limited supply of organic matter (0.48 mg/ℓ) at 10, 15, and 20 °C (Figure 7). The initial content of the labile organic carbonaceous matter in the latter case was controlled by the behavior of the other elements and by changes in the concentration of particulate phosphorus. The particulate phosphorus curve is clearly differentiated into two parts, showing the dependence of the behavior of the biological elements (bacteria and zooplankton) in the sea water on the limited supply of labile organic matter at 15-20 °C (Figure 7). This differentiation is less marked at the higher concentration of organic matter (Figure 6). From the model data we can conclude that in sea water with a limited supply of labile organic matter there are restrictions on bacterial development, on the formation of characteristic points on the curve for the kinetics of particulate phosphorus, and on the specific steady state levels of bacterial phosphorus after 15 days.

Changes in the dynamics of DOM concentration during a long incubation period in a dark sea water sample may be described by chemical kinetics equations of an exponential linear type [10]. For instance, the change of DOM content at 10 °C

(Figure 7) is written as follows: $DOM = 0.122 + 0.355e^{-0.195t} - 0.00125t$. This equation shows that the initial rate of DOM destruction is 0.069 mgC/l per day with a rate constant of 0.195 day^{-1}. For long incubation periods (more than 20 days) of the water sample the rate of DOM destruction is very small: 0.00125 mgC/l per day. It is possible to describe the change in DOM concentration at 15 and 20 °C by equations of such type. Since the rate of DOM destruction under these conditions is low and the residual DOM concentration is comparatively high (10-20% of initial content), we conclude that there is stable organic matter (of the humus type) in the water. By means of the simulation a similar situation is obtained even without any information on the presence of such matter in the water. The illusion of presence of organic matter resistant to the biochemical oxidation process is created by the accumulation of the second level organic compounds--metabolites resulting from the release of bacteria and zooplankton. These compounds are subject to destruction as well; however, after 20 days of the water incubation there is dynamic equilibrium in the system between the rates of formation and of destruction of this matter. Owing to this equilibrium, the steady state concentration is always supported. This is an important conclusion for estimating the biochemical stability of natural and man-made matter in the water bodies in the laboratory, using experimental data.

The oxygen consumption dynamics is described by kinetic equations of either exponential-linear or autocatalytic-linear type, depending on the temperature and on the water incubation conditions. For instance, the overall BOC at 10 °C is described by the following autocatalytic-linear equation [10]:

$$BOC = \frac{0.546(e^{0.202t} - 1)}{1 + 0.728e^{0.202t}} + 0.00625t$$

Similar types of curves are often observed in BOC experiments with sea water. They are successfully represented by

chemical-kinetic equations; moreover the constant value is close to that obtained from an analysis of experimental BOC curves. The differentiation of the overall BOC into separate stages and the study of these stages show that the characteristics of the kinetics of the first stage closely resemble the parameter values obtained from analysis of the kinetics curves for the heterotrophic bacterial oxygen consumption.

A maximum value of the kinetics is observed in both cases at a temperature of 20 °C; at 25 °C (the predicted variant) the values of all kinetics BOC parameters are 10 - 30% lower than those at 20 °C [4]. This is a realistic picture of the change in the BOC parameter of the first stage when the data obtained from analyzing the literature on BOC [11] is taken into consideration.

An analysis of the kinetic constants of BOC values from the temperature gives the following estimation of activation energy: the average value $E_{10-20\ °C}$ = 25.8 kcal/mol ($E_{10-15\ °C}$ = 45 kcal/mol; $E_{15-20\ °C}$ = 13.2 kcal/mol). The average value of the activation energy is similar to that obtained from published BOC data [22]. The simulation results show that the rate of the oxygen uptake in the linear stages depends directly on the temperature. The estimated value of the activation energy for this stage is 17.3 kcal/mol. This fact, however, requires additional experimental investigation.

The simulation results can be used to determine the appropriateness of using BOC test data for quantitative and qualitative assessments of the DOM concentration and the destruction dynamics for DOM. The initial rate of the oxygen consumption at 10 °C is 0.064 mgO_2/ℓ day and of the DOM transformation 0.069 mgC/ℓ day. The value of the rate constant (the exponent coefficient) for BOC is 0.202 day^{-1} and for the DOM transformation is 0.195 day^{-1} for the initial period (i.e. the first 15 to 20 days). Consequently, during this period the BOC test satisfactorily reflects the change in the concentration of DOM and the dynamics of the

biochemical destruction in the water sample. The rate of oxygen consumption is 5 times higher than the rate of the DOM decrease over longer incubation periods in the sample of water. In this case, the BOC test does not reflect the concentration change of the DOM; however, it does give a more accurate picture about the dynamics of the biochemical DOM oxidation during longer periods than does direct measurement of the DOM concentration. The trouble is that it establishes only the difference between the process of the oxidative DOM transformation and its entrance at the expense of the liberation of living organisms and lysis of dead organisms at the analytical determination of DOM; but during BOC observations and when the dissolved oxygen decreases, it is only one way that is fixed--the oxygen consumption connected with the DOM oxidation.

The data on the transformation mechanisms of phosphorus compounds in closed ecological systems used in the design of our model have produced similar results as those obtained on the basis of available experimental data for the dynamics of phosphorus compounds, of DOM, and of BOC. The realization of the mathematical model makes it possible to explain the kinetics of both the complete processes and the separate stages in the compound transformations in natural water, and provide new quantitative data about the complex reactions within the system in the transformation processes.

Conclusions

The mathematical models of the transformations of biogenic element compounds and BOC given in this paper attempt to give a very broad simulation of the physical, chemical and biochemical interacting processes that determine the rate of transformation of organic matter and of the oxygen consumption in different water solutions. In this investigation the main attention was given to presenting the experimental observations in closed microsystems because this stage is necessary for modeling the biochemical processes in natural conditions to determine the water quality. The given models may be regarded as complete

blocks that connect with corresponding blocks during model construction, showing the behavior of the whole chemical-ecological system. The dynamics of the separate biogenic element compounds of such a system are considered in the models.

The simple model subsystems were singled out during model construction and a simulation strategy was used to determine the behavior of separate components and model sections from the point of view of how these fragments could be coordinated into a whole at the end of the investigation program [39]. It was taken into consideration that the models would be used to test the validity of the available data to determine individual characteristics of the kinetics and to create a base for further investigations. In spite of a number of difficulties, the simulation exercise has shown there are sufficient number of major elements to be able to model the behavior of a water system.

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