Экология / 2. Экологические и метеорологические проблемы больших городов и промышленных зон.

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## A structured approach to the construction of models of transformation of substances in the aquatic environment

Water quality models are varied and have the different degree of complexity. Balance models and monomolecular models are relatively simple and often used, but they can account only the processes of biochemical decomposition of substances and their income from external sources. When predicting the contents in the aquatic environment substances, which are linked together by processes of mutual transformation, the use of such models is not enough. In this situation, need to build more complex models, which can take account the sequential transformation of substances. The phenomenon of mutual transformation of substances is important for the processes of self-purification and secondary pollution of water bodies. For example, the process of mutual transformation of substances underlies cycles as nitrogen cycle, phosphorus and carbon. Modelling of processes that are more complex requires the analysis of the factors influencing the process, of identifying of their importance and of the possibility to neglect some of them in the process the modelling. The analysis should be based on data of nature observations and be conducted on basis of statistical methods, theory of sensitivity and of factor analysis. After determining the set of significant factors, it is necessary to carry out stages of identification and verification of the model. The final stage is to check the model adequacy. The level of complexity of the model always represents a compromise between the real process and the abstraction of mathematical model. In principle, the components of water quality models can be grouped in the following categories: hydraulic or hydrodynamic, including the processes of transport and mixing of substances in the aquatic environment; chemical compounds; bacteria; phytoplankton and zooplankton; macrophytes and higher trophic levels. The order of these components approximately inversely to the scale knowledge and of ability to describe these processes. Question the model complexity depends on the level of knowledge about the process. From this point of view is preferred, the first three are the most studied component categories: hydrodynamic, chemical compounds and bacteria. However, in some cases it is

necessary to include in consideration of the plankton components and higher trophic level. A structured approach to build of model allows to develop and to complicate the model by increasing the level of knowledge about the process.

Consider the use of a structured approach to the construction of mathematical models of water quality on the example of modelling of transformation of nitrogen compounds in the aquatic environment. The main components of the nitrogen cycle are mineral forms of nitrogen in the form of compounds of ammonia nitrogen ($NH_4$), nitrite nitrogen ($NO_2$) and nitrate nitrogen ($NO_3$); nitrogen contained in phytoplankton and zooplankton; organic nitrogen in suspended and soluble forms; free nitrogen and nitrogen of sediments. When modelling the amount of nitrogen in all components is accounted for in terms of pure nitrogen.

The basis of the nitrogen cycle is the nitrification process. It involves the oxidation of ammonia nitrogen to nitrate nitrogen. The nitrification process of the nitrogen takes place in two stages, at both stages is required for aerobic conditions. In the first stage, the oxidation of ammonia nitrogen to nitrite nitrogen is carried out nitrifying bacteria Nitrosomonas. The oxidation reaction takes place exothermically and is described by the equation.

$$NH_4^+ + OH^- + 1,5O_2 \rightarrow H^+ + NO_2^- + 2H_2O + 54,9\kappa cal$$

In the reaction, on the one weight part of nitrogen is consumed three weight part of oxygen and allocated to 54.9 kcal of heat energy. In the second stage, nitrification bacteria Nitrobacter oxidize the nitrites to nitrates. The reaction also proceeds exothermically, but in this case, on the one weight part of nitrogen is consumed only one weight part of oxygen and allocated to 18 kcal of heat energy. The reaction equation has the form

$$NO_2^- + 0,5O_2 \rightarrow NO_3^- + 18\kappa cal$$

Thus, the nitrification process consumes four weight parts of oxygen per part by weight of nitrogen. Taking into account atomic weights of nitrogen and oxygen, this means that for oxidation of 1 mg of nitrogen required is 4.57 mg of oxygen.

For simplicity, below we consider the dot models of process of the transformation of nitrogen-containing substances in which all the characteristics of the water body are averaged.

**Model 1**. The model is a simplified representation of the nitrification process, namely, the ignored role of bacteria and changes in their density. In this case, it is assumed that each stage of the nitrification process is first order reactions. Schematically this process can be represented in the form

$$NH_4 \xrightarrow{K_1} NO_2 \xrightarrow{K_2} NO_3 \qquad (1)$$

A mathematical model, which describes of nitrification process in aerobic conditions, takes into account the law of conservation of matter if there is two stages of this process would be represented in the form

$$\begin{aligned} \frac{dN_1}{dt} &= -k_1 N_1 & N_1(0) &= N_{10} \\ \frac{dN_2}{dt} &= -k_2 N_2 + k_1 N_1 & N_2(0) &= N_{20} \\ \frac{dN_3}{dt} &= k_2 N_2 & N_3(0) &= N_{30} \end{aligned} \qquad (2)$$

where $N_1$, $N_2$, $N_3$ – concentrations of ammonium nitrogen, nitrite and nitrate in terms of pure nitrogen, mg/l; $k_1$, $k_2$ – decomposition coefficients of ammonium and nitrite nitrogen, 1/day.; $N_{10}$, $N_{20}$, $N_{30}$ – initial concentrations of these mineral forms of nitrogen, respectively, mg/l; t – time of the process of nitrification, days

The system of equations has a solution

$$\begin{aligned} N_1 &= N_{10} \cdot e^{-k_1 t} & N_1(0) &= N_{10} \\ N_2 &= N_{20} \cdot e^{-k_2 t} + N_{10} \cdot \frac{k_1}{k_2 - k_1} \cdot \left( e^{-k_1 t} - e^{-k_2 t} \right) & N_2(0) &= N_{20} \\ N_3 &= N_{30} + N_{20} \cdot \left(1 - e^{-k_2 t}\right) + N_{10} \cdot \left( 1 - \frac{k_2 \cdot e^{-k_1 t} - k_1 \cdot e^{-k_2 t}}{k_2 - k_1} \right) & N_3(0) &= N_{30} \end{aligned} \qquad (3)$$

The decomposition coefficients on the results of field observations are taken: for reservoirs $k_1$ = 0.16 1/day, $k_2$ = 0.28 1/day.; for watercourses $k_1$ = 0,069 1/day, $k_2$ = 10.8 1/day.

Of all mineral forms of nitrogen, the most strictly standardized content in water nitrite nitrogen. Therefore, of particular interest is to determine which values can reach its concentration as result nitrification process. The maximum concentration of nitrite nitrogen can be determined from the condition

$$\frac{dN_2}{dt} = -k_2 N_2 + k_1 N_1 = 0 \Rightarrow k_1 N_1 = k_2 N_2 \qquad (4)$$

By simple calculations from the condition (4) can determine the time ($t_c$) during which the concentration of nitrite nitrogen reached its maximum.

$$t_c = \frac{1}{k_2 - k_1} \ln \left( \frac{k_2 \cdot \left( k_1 N_{10} - \left( k_2 - k_1 \right) \cdot N_{20} \right)}{k_1^2 \cdot N_{10}} \right) \qquad (5)$$

In the case where the nitrite nitrogen formed in the water body only through the transformation of ammonia nitrogen ($N_{20}$ = 0), the expression (5) is simplified and the time and value of maximum concentration of nitrite nitrogen can be determined by the formula

$$t_c = \frac{1}{k_2 - k_1} \ln \left( \frac{k_2}{k_1^2} \right) \qquad N_{2\max} = N_{10} \cdot \left( \frac{k_2}{k_1} \right)^{-\frac{k_2}{k_2 - k_1}} \qquad (6)$$

According to the expressions (6), for reservoirs the time during which the concentration of nitrite nitrogen reaches its maximum, is about five days, and the maximum concentration of nitrite nitrogen reaches the value of $0.27 \cdot N_{10}$. If we assume that the initial content of ammonium nitrogen was at the upper limit of water quality standard ($N_{10}$ = 0,389 g/m$^3$), the concentration of nitrite nitrogen reaches the value of 0,27·0,389 = 0,105 that exceeds the water quality standard for nitrite nitrogen, equal to 0,02 g/m$^3$, to 5 times. This calculation shows, how important is the account of nitrification in the reservoirs when the forecast of water quality.

For rivers, the picture is somewhat different. According to the expressions (6) time during which the concentration of nitrite nitrogen reaches its maximum, is about 0,5 days and the maximum concentration of nitrite nitrogen reaches $0{,}006 \cdot N_{10}$. In this case, the nitrification process is considerably faster and the maximum concentration of nitrite nitrogen is significantly less too. If execute a similar previous calculation for rivers, the maximal concentration of nitrite nitrogen will equal 0,006·0,389 = 0,0024, which is almost ten times less than water quality standard for nitrite nitrogen. This means that for rivers of violation of water quality only at the expense the process of nitrification will not occur.

The proposed model adequately describes the process of nitrification for 4 days. Longer forecasts can lead to considerable error, particularly when predicting nitrate concentrations.

**Model 2.** This model is based on the previous model, but allows taking into account the role of bacteria in the nitrification process. For this purpose, equations that taking into account the dynamics of changes in biomass of bacteria, which feed on the considered forms of nitrogen, were introduced into model. In our case, it is the Nitrosomonas, feed on ammonia nitrogen, and Nitrobacter for which a nutrient substrate is nitrite nitrogen. To describe the change of biomass of bacteria use model Michaelis – Menten – Mono. The equation of Michaelis – Menten – Mono are the fundamental equations of the theory of enzyme kinetics, taking into account the peculiarities of development of living organisms. The biomass of bacteria is quantitatively evaluated by two factors: the concentration and density of bacteria. The concentration of bacteria characterizes number of cells per unit volume. The density of bacteria characterizes the dry weight of bacteria per unit volume. The growth of biomass usually results in increased cell numbers, cell mass and size of the body. Because bacteria are unicellular organisms, their biomass increases at the expense of reproduction. Bacteria grow in the process of dividing into two, so the rate of growth is the number of doublings per unit time. This value is called the rate of cell division and is determined by the formula

$$\nu = \frac{1}{t} \cdot \frac{\lg(N) - \lg(N_0)}{\lg(2)} \qquad t_0 = 0 \tag{7}$$

where, **t** is the time of division, $\mathbf{N_0}$ – initial concentration of bacteria, **N** is the concentration of bacteria at time **t.**

The concept of concentration of bacteria and the speed of their division are commonly used in studying the cellular structure of living organisms in such Sciences as biology, genetics, and medicine. In the process of transformation of substances bacteria play the role of mediator, so it is more convenient to use the notion of density of bacteria (biomass) and the biomass growth rate. The growth rate of biomass μ similar to the notion of coefficient of decomposition substance and is numerically equal to the increase in units of dry mass bacteria per time unit.

$$\frac{dX}{dt} = \mu \cdot X \Rightarrow \mu = \frac{1}{t} \ln\left(\frac{X_t}{X_0}\right) \qquad t_0 = 0 \tag{8}$$

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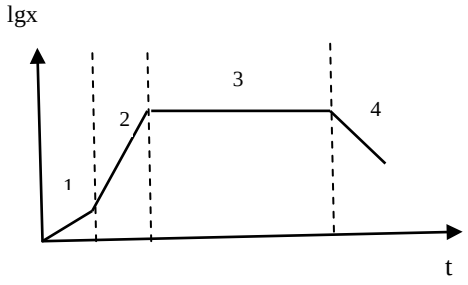
In conditions of exponential growth bacteria, the following formula describes link growth rate μ and the rate of cell division ν bacteria.

$$\mu = \nu \cdot \ln(2)$$

The exponential growth of bacteria is observed in the most favorable for their development conditions. It was established experimentally that if there are no inhibitors that suppress the growth of bacteria, enough of all the essential nutrients, physic-chemical conditions are suitable for bacteria the rate of increase of biomass of bacteria is proportional to their biomass. It means that bacteria grow by exponential low. To ensure favorable conditions bacteria need regular replenishment of their food base. In the absence of external coming of the substrate, the biomass goes through 4 phases of development. This is lag phase (initial phase), log phase (exponential growth), stationary phase and death phase. Growth curve of the biomass has in this case an S-shape. The lag phase encompasses the period between the introduction of bacteria and maximize the speed of their growth. In this phase bacteria adapts to new conditions and the growth rate increases. Characteristics of the lag phase depend on the properties of bacteria and the environment. The better the nutrient medium suitable for bacteria, the shorter the lag phase. Therefore, the duration of the lag phase describes the suitability of the environment for the sustenance of bacteria. Ideally, the adaptation occurs almost immediately. Thus, the duration of the lag



phase characterizes the suitability of the environment for the sustenance of bacteria. Ideally, the adaptation occurs almost immediately. In reality, the duration of the lag phase may be different. Bacterial culture, for which the lag phase is missing, is called ideal culture. Than the shorter lag phase, the bacterial culture closer to the ideal culture. When building mathematical models for the growth of biomass is assumed that the bacterial environment is ideal.

The log phase, corresponding to the exponential biomass development, covers the period of time when the growth rate of biomass constant and equal to its maximum, that is, $\mu = \mu_{max}$. The exponential phase is only possible under favorable conditions, the most important of which is unlimited nutrient substrate and its diversity.

Stationary phase covers the period when the biomass is constant. The transition from the previous phase to the stationary phase occurs gradually. First, the decrease substrate for bacteria and the decrease in living space leads to a decrease in the rate of growth. The reduction in living space leads to the poisoning of the bacteria by products of metabolism and negative mechanical impact of the cells on each other. As reducing, the amount of nutrient substrate the growth rate is reduced from $\mu_{max}$ to zero. During the stationary stage, processes growth of bacteria and their natural decay are balanced.

The decay phase is characterized by the excess of the dying away of bacteria in comparison with their of reproduction. It is the least studied phase. Now concept of the cell death by exponential low is accepted.

A complex life cycle of bacteria requires a special approach when modeling. In the basis of models of the dynamics of biomass of growth is the theory of enzyme kinetics and principle of minimum. According to this principle, the rate of a complex reaction is determined by the speed of the slowest simple reaction. Speed other simple reactions that constitute the mechanism of a complex reaction, are irrelevant. In relation to bacterial cells, the minimum principle is expressed by the principle of Liebig. According to the Liebig law, the speed of development of the organism is determined only limiting factors, that is, those external factors that are at the minimum. The speed of enzymatic reactions in the rate-limiting factor is determined by the equation of Michaelis – Menten

$$V = \frac{V_{\max} \cdot S}{k_m + s} \qquad (9)$$

where $V_{max}$ is the maximum reaction rate; **S** is the value of the limiting factor; $k_m$ is the Michaelis constant, equal to the value of the limiting factor, in which speed of enzymatic reactions $V = 0,5\ V_{max}$.

It is experimentally proved that the factor limiting the rate of growth of bacterial cells is the concentration of nutrients. Therefore, the growth of the bacterial mass in resource-limited settings is determined by the need of the bacteria for nutrients and the consumption rate of the substrate. The bacteria need nutrients quantitatively assessed using the economic factor Y. This factor is numerically equal to the increase in biomass due to the consumption of a unit of substrate and shows what portion of consumed substrate is used to increase the biomass.

$$Y = \frac{dX}{dS} \tag{10}$$

The economic factor is always less than one or equal to one. When the value $Y = 1$ the entire substrate is to increase the biomass, when $Y < 1$ part of the substrate is lost to unproductive allocation of metabolic products. Mono shows that under unchanging external conditions Y = const.

The rate of consumption of substrate is characterized by a metabolic coefficient or specific rate of metabolism. Specific metabolic rate q is numerically equal to the amount of substrate consumed by the unit biomass per unit time.

$$\frac{dS}{dt} = q \cdot X \tag{11}$$

The value of the metabolic coefficient and the value of the economic coefficient are linked relation, which is easy derived from expressions (8), (10) and (11).

$$q = \frac{\mu}{Y} \tag{12}$$

From the expression (12) implies that if the economic coefficient is equal to one, the speed of processing of the substrate is equal to the biomass growth rate and the entire substrate is consumed on biomass growth. If the economic factor is less than one, then the substrate is processed faster than one absorbed by the biomass and the recycled portion of the substrate is in the form of metabolic products. In addition, a direct proportionality of metabolic coefficient and growth factor leads to the fact that metabolic coefficient reaches its maximum simultaneously with the speed of growth, i.e. exponential growth phase of the biomass.

Applies the principles of enzyme kinetics for bacteria. In this case, the enzymatic reaction is the recovery of bacteria of the substrate, the rate of this

enzymatic reaction is the rate of processing of the substrate, that is, metabolic coefficient, and the limiting factor is the concentration of substrate. If bacteria feed on several substrates, the limiting factor will be the concentration of a substrate, which is the minimum. The equation of Michaelis – Menten (9) for the metabolic coefficient has the form

$$q = \frac{q_{\max} \cdot S}{k_s + S} \tag{13}$$

where $\mathbf{k_s}$ is a constant of half-saturation, numerically equal to the substrate concentration at which the coefficient of metabolism is half of its maximum; **S** is concentration of limiting substrate; $q_{max}$ is the maximum specific rate of metabolism corresponding to the exponential phase of biomass development.

In models the transformation of nitrogenous substances, the rate of bacterial growth is of more concern than the metabolic coefficient, so we write the equation (13) relative to the speed of bacteria growth. On the base of expression (12) taking into account, that the economic coefficient is constant under constant ambient conditions, we obtain the equation of Mono.

$$\mu = \frac{\mu_{\max} \cdot S}{k_s + S} \tag{14}$$

Using the expression (8), (11), (12) and (14), we write the system of equations of the Michaelis – Menten – Mono, describing the rate of biomass growth of bacteria and consumption of the substrate depending on the substrate concentration.

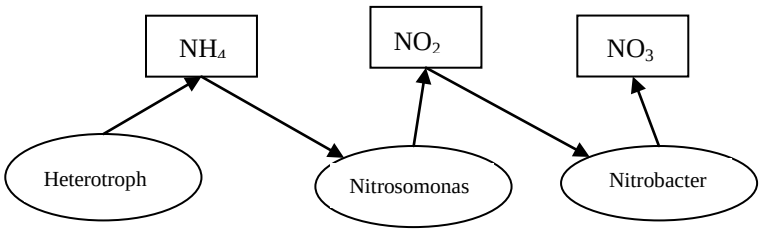
$$\frac{dS}{dt} = \frac{\mu_{\max}}{Y} \cdot \frac{S}{k_s + S} \cdot X \qquad \textit{for substrate}$$

$$\frac{dX}{dt} = \mu_{\max} \cdot \frac{S}{k_s + S} \cdot X \qquad \textit{for biomass}$$

Complete the second equation of the system by the member, taking into account the process of dying bacteria. Because this process is not limited by the availability of substrate, it can be assumed that the rate of decay is directly proportional to biomass. This means that the process of decay of biomass follows the reaction of the first order. The equation will take the form of

$$\begin{cases} \dfrac{dS}{dt} = \dfrac{\mu_{\max}}{Y} \cdot \dfrac{S}{k_s + S} \cdot X \\ \dfrac{dX}{dt} = \mu_{\max} \cdot \dfrac{S}{k_s + S} \cdot X - k_d X \end{cases} \tag{15}$$

We can compose mathematical model of nitrification process based on model (2) and equations (15). This model will be taking into account dynamics development of the nitrifying bacteria. The model diagram presented below




In the first stage of nitrification involves bacteria Nitrosomonas. They use ammonia nitrogen as a substrate, and excrete nitrite nitrogen as a product metabolism. Nitrobacter bacteria play the main role on the second stage of nitrification. They consume nitrite nitrogen and produce as a product of the metabolism nitrate nitrogen. In the model traditionally first written the equations for the substrate, and then the equations for the biomass of bacteria. The model has the form

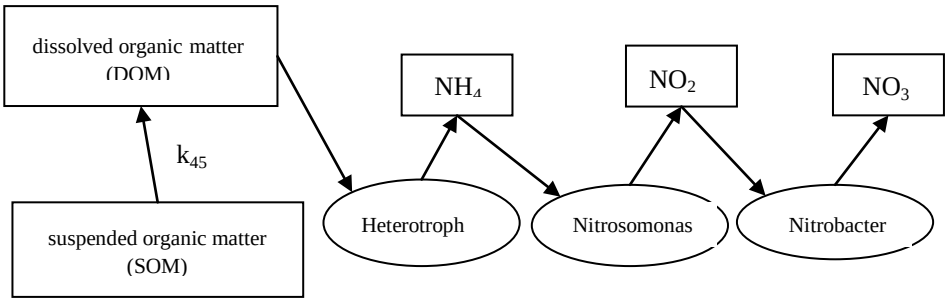
$$\begin{aligned}
&\frac{dN_1}{dt} = -\frac{\mu_{\max 11}}{Y_{11}} \cdot \frac{N_1}{k_{S11} + N_1} \cdot X_1 && N_1(0) = N_{10} \\
&\frac{dN_2}{dt} = \frac{\mu_{\max 11}}{Y_{11}} \cdot \frac{N_1}{k_{S11} + N_1} \cdot X_1 - \frac{\mu_{\max 22}}{Y_{22}} \cdot \frac{N_2}{k_{S22} + N_2} \cdot X_2 && N_2(0) = N_{20} \\
&\frac{dN_3}{dt} = \frac{\mu_{\max 22}}{Y_{22}} \cdot \frac{N_2}{k_{S22} + N_2} \cdot X_2 && N_3(0) = N_{30} \qquad (16) \\
&\frac{dX_1}{dt} = \mu_{\max 11} \cdot \frac{N_1}{k_{S11} + N_1} \cdot X_1 - k_{d1} X_1 && X_1(0) = X_{10} \\
&\frac{dX_2}{dt} = \mu_{\max 22} \cdot \frac{N_2}{k_{S22} + N_2} \cdot X_2 - k_{d2} X_2 && X_2(0) = N_{20}
\end{aligned}$$

where $N_1$, $N_2$, $N_3$, $N_{10}$, $N_{20}$, $N_{30}$ are concentrations of mineral forms of nitrogen and their initial values, g/m$^3$; $X_1$, $X_2$, $X_{10}$, $X_{20}$ are densities biomass Nitrosomonas and Nitrobacter and their initial values, g/m$^3$; $\mu_{max11}$ is maximum growth rate of Nitrosomonas when they consume ammonium nitrogen, 1/day; $\mu_{max22}$ is maximum growth rate of Nitrobacter when they consume nitrogen nitrite, 1/day; $Y_{11}$ is economic coefficient Nitrosomonas when they consume ammonium nitrogen; $Y_{22}$ is economic coefficient Nitrobacter when they consume nitrogen nitrite; $k_{S11}$ is constant of half-saturation for Nitrosomonas when they consume ammonium nitrogen, g/m$^3$; $k_{S22}$ is constant of half-saturation for Nitrobacter when

they consume nitrite nitrogen, $g/m^3$; $k_{d1}$, $k_{d2}$ are mortality coefficients of Nitrosomonas and Nitrobacter, respectively, 1/day

Inclusion in modelling of nitrification bacteria has led to a substantial complication of the model. Equation models are nonlinear, their number increased from two to five; increased the number of constants which to be need determined in the process model identification from two to ten. In order to reduce the number of identifiable parameters, the study of variability of some parameters was performed. The study showed that the values of parameters such as economic coefficient, the rate of bacterial growth and constant of half-saturation mainly determined by the type of bacteria, temperature and pH of the aquatic environment. Because the kind of bacteria does not change, and the temperature and pH of the aquatic environment vary in relatively small limits, the six parameters can be excluded from the identification process of the model. Their values can be taken according to the literature data. Now it is not enough information about the process of dying out of the bacteria. We can assume that the rate of death of bacteria can vary substantially depending on environmental conditions. Sensitivity analysis the model to this parameter was used for determinate necessity to identify the model by the rate of decay of the bacteria. The results showed that the model is little sensitive to the rate of decay of bacteria, so parameters $k_{d1}$ and $k_{d2}$ may be excluded from the identification procedure. Usually the values of these parameters are taken $k_{d1} = k_{d2} = 0$. Thus, the procedure for model identification is reduced to determining two parameters – the initial concentrations of bacteria. The solution of this system of equations is possible only by numerical methods. Verification of the model adequacy showed that the model describes well the process within 10 days.

**Model 3**. This model is based on the model 2. This model permits to take into account of the role of nitrogen in form dissolved organic matter, nitrogen in form suspended organic matter and the role of heterotrophic bacteria in nitrification process. The model diagram presented below.



In the beginning of the cycle is lying nitrogen, that included in the composition of suspended organic matter (SOM). This nitrogen is transformed into nitrogen dissolved organic matter (DOM). The process consists from two processes: deposition of a part of the suspended matter in bottom sediments and dissolution of the remaining portion, and can be evaluated according to the laws of first order reactions. Dissolved nitrogen is a substrate for Heterotroph bacteria, which, as a product of metabolism, are isolated in an aqueous environment, the ammonium nitrogen. Further, the nitrification process is in the previous scenario. The model consists of eight equations, the first five equations are inanimate nitrogen compounds, and the remaining three equations describe the change of biomass of bacteria.

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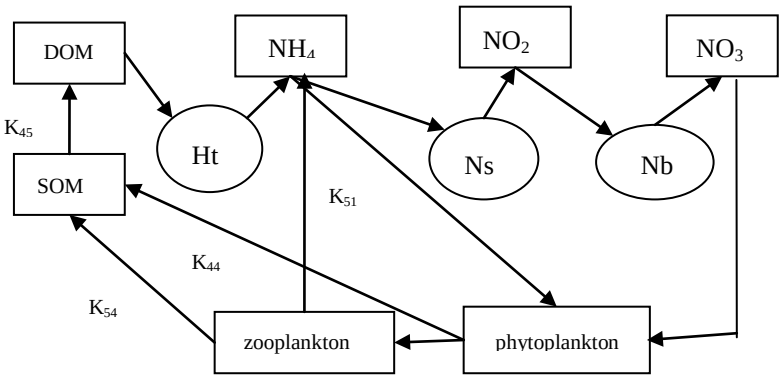
\begin{aligned}
&\frac{dN_1}{dt} = \frac{\mu_{\max 34}}{Y_{34}} \cdot \frac{N_4}{k_{S34} + N_4} \cdot X_3 - \frac{\mu_{\max 11}}{Y_{11}} \cdot \frac{N_1}{k_{S11} + N_1} \cdot X_1 && N_1(0) = N_{10} \\
&\frac{dN_2}{dt} = \frac{\mu_{\max 11}}{Y_{11}} \cdot \frac{N_1}{k_{S11} + N_1} \cdot X_1 - \frac{\mu_{\max 22}}{Y_{22}} \cdot \frac{N_2}{k_{S22} + N_2} \cdot X_2 && N_2(0) = N_{20} \\
&\frac{dN_3}{dt} = \frac{\mu_{\max 22}}{Y_{22}} \cdot \frac{N_2}{k_{S22} + N_2} \cdot X_2 && N_3(0) = N_{30} \\
&\frac{dN_4}{dt} = -k_{45} \cdot N_4 && N_4(0) = N_{40} \\
&\frac{dN_5}{dt} = k_{45} \cdot N_4 - \frac{\mu_{\max 35}}{Y_{35}} \cdot \frac{N_5}{k_{S35} + N_5} \cdot X_3 && N_5(0) = N_{50} \\
&\frac{dX_1}{dt} = \mu_{\max 11} \cdot \frac{N_1}{k_{S11} + N_1} \cdot X_1 - k_{d1} X_1 && X_1(0) = X_{10} \\
&\frac{dX_2}{dt} = \mu_{\max 22} \cdot \frac{N_2}{k_{S22} + N_2} \cdot X_2 - k_{d2} X_2 && X_2(0) = N_{20} \\
&\frac{dX_3}{dt} = \mu_{\max 35} \cdot \frac{N_5}{k_{S35} + N_5} \cdot X_3 - k_{d3} X_3 && X_3(0) = X_{30}
\end{aligned}
\qquad (17)
$$

where $N_1$, $N_2$, $N_3$, $N_4$, $N_5$, $N_{10}$, $N_{20}$, $N_{30}$, $N_{40}$, $N_{50}$ are concentrations of mineral forms of nitrogen, nitrogen of suspended and dissolved organic matter and their initial values, g/m$^3$; $X_1$, $X_2$, $X_3$, $X_{10}$, $X_{20}$, $X_{30}$ are densities biomass Nitrosomonas, Nitrobacter, Heterotroph respectively, and their initial values, g/m$^3$; $\mu_{max11}$ is maximum growth rate of Nitrosomonas when they consume ammonium nitrogen, 1/day; $\mu_{max22}$ is maximum growth rate of Nitrobacter when they consume nitrogen nitrite, 1/day.; $\mu_{max35}$ is maximum growth rate of Heterotroph when they consume nitrogen of dissolved organic matter, 1/day; $Y_{11}$ is economic coefficient Nitrosomonas when they consume ammonium nitrogen; $Y_{22}$ is economic coefficient Nitrobacter when they consume nitrogen nitrite; $Y_{35}$ is economic coefficient Heterotroph when they consume nitrogen of dissolved organic matter;

$k_{S11}$ is constant of half-saturation for Nitrosomonas when they consume ammonium nitrogen, g/m$^3$; $k_{S22}$ is constant of half-saturation for Nitrobacter when they consume nitrite nitrogen, g/m$^3$; $k_{S35}$ is constant of half-saturation for Heterotroph when they consume nitrogen of dissolved organic matter; $k_{d1}$, $k_{d2}$, $k_{d3}$ are mortality rates of Nitrosomonas, Nitrobacter and Heterotroph, respectively, 1/day.`

The study of the model sensitivity to the new parameters showed that she is very sensitive to changes in the speed of bacterial growth Heterotroph. For example, a decrease in the rate of growth of Heterotrophs is almost twice as inhibits the growth of nitrates. In addition, there is the sensitivity of the model to changes in initial biomass density of Heterotrophs. The increase of this parameter up to 10 times leads to the achievement of the maximum content of ammonium nitrogen and nitrite nitrogen for a few days earlier. Overall, this model better describes the nitrification process than the previous two. Except for the first ten days, the calculated data are in good agreement with measured data for two months.

**Model 4**. The model includes the model 3, but describes not only the transition of suspended organic matter in dissolved organic matter, the mineralization and nitrification of nitrogen containing substances with emphasis on the role of heterotrophic and nitrifying bacteria, but the role of plankton in the process of transformation and cycling of nitrogen in the aquatic ecosystem.




Accounting for the role of zooplankton and phytoplankton has allowed us to close the loop of the nitrogen cycle in the aquatic ecosystem. The phytoplankton uses for their growth two types of substrate – ammonia nitrogen and nitrate nitrogen. At the same time, it is food for zooplankton and, after death, it replenishes the suspended organic matter. Zooplankton feeds on phytoplankton, in the process of excretion excretes ammonia nitrogen, when death and defecation restock suspended organic matter. Since phytoplankton and zooplankton are living organisms, the processes of their development are subject to the laws of kinetics

Michaelis – Menten – Mono. The processes of decay of both types of plankton, defecation and excretion of zooplankton obey the law of the first order. The flow of the products of metabolism of plankton in the form of dissolved organic matter is insignificant in comparison with other elements of the nitrogen cycle, so they can be neglected. Since the phytoplankton in the process of life does not emit products of metabolism, and all of the consumed substrate (ammonium nitrogen and nitrate nitrogen) is only on the increase in the biomass of phytoplankton, for him, the economic coefficient is equal to 1. In this model, phytoplankton and zooplankton play a dual role. On the one hand, they are live organisms and their growth is subject to the laws of Michaelis - Menten – Mono. On the other hand, the phytoplankton itself is a substrate for zooplankton. Both types of plankton in the processes of decay behave as non-living organisms. With this in mind, the model has the form

$$
\begin{aligned}
\frac{dN_1}{dt} &= \frac{\mu_{\max 35}}{Y_{35}} \cdot \frac{N_5}{k_{S35} + N_5} \cdot X_3 + k_{51} X_5 - \frac{\mu_{\max 11}}{Y_{11}} \cdot \frac{N_1}{k_{S11} + N_1} \cdot X_1 - \frac{\mu_{\max 41}}{Y_{41}} \cdot \frac{N_1}{k_{S41} + N_1} \cdot X_4 \\
\frac{dN_2}{dt} &= \frac{\mu_{\max 11}}{Y_{11}} \cdot \frac{N_1}{k_{S11} + N_1} \cdot X_1 - \frac{\mu_{\max 22}}{Y_{22}} \cdot \frac{N_2}{k_{S22} + N_2} \cdot X_2 \\
\frac{dN_3}{dt} &= \frac{\mu_{\max 22}}{Y_{22}} \cdot \frac{N_2}{k_{S22} + N_2} \cdot X_2 - \frac{\mu_{\max 43}}{Y_{43}} \cdot \frac{N_3}{k_{S43} + N_3} \cdot X_4 \\
\frac{dN_4}{dt} &= k_{d5} \cdot X_5 + k_{d4} \cdot X_4 - k_{45} \cdot N_4 \\
\frac{dN_5}{dt} &= k_{45} \cdot N_4 - \frac{\mu_{\max 35}}{Y_{35}} \cdot \frac{N_5}{k_{S35} + N_5} \cdot X_3 \\
\frac{dX_1}{dt} &= \mu_{\max 11} \cdot \frac{N_1}{k_{S11} + N_1} \cdot X_1 - k_{d1} X_1 \\
\frac{dX_2}{dt} &= \mu_{\max 22} \cdot \frac{N_2}{k_{S22} + N_2} \cdot X_2 - k_{d2} X_2 \\
\frac{dX_3}{dt} &= \mu_{\max 35} \cdot \frac{N_5}{k_{S35} + N_5} \cdot X_3 - k_{d3} X_3 \\
\frac{dX_4}{dt} &= \mu_{\max 41} \cdot \frac{N_1}{k_{S41} + N_1} \cdot X_4 + \mu_{\max 43} \cdot \frac{N_3}{k_{S43} + N_3} \cdot X_4 - k_{d4} X_4 - \mu_{\max 54} \cdot \frac{X_4}{k_{S54} + X_4} \cdot X_5 \\
\frac{dX_5}{dt} &= \mu_{\max 54} \cdot \frac{X_4}{k_{S54} + X_4} \cdot X_5 - k_{d5} X_5 - k_{51} X_5
\end{aligned}
\qquad (17)
$$

Initial conditions: $N_i(0) = N_{i0}$, $X_i(0) = X_{i0}$ ($i = 1 \div 5$).

In the system (17) is used such new notation: $X_4$, $X_5$, are the densities of biomass of phytoplankton and zooplankton, g/m$^3$; $X_{40}$, $X_{50}$ are the initial densities of the biomass of phytoplankton and zooplankton, g/m$^3$; $\mu_{max41}$ is maximum growth rate of phytoplankton when he consumes ammonia nitrogen, 1/day; $\mu_{max43}$ is maximum growth rate of phytoplankton when he consumes nitrogen-nitrate, 1/day,

$\mu_{max54}$ is maximum growth rate of zooplankton when he consumes phytoplankton, 1/day; $Y_{41}$ is the economic coefficient of phytoplankton when he consumes ammonia nitrogen; $Y_{43}$ is the economic coefficient of phytoplankton when he consumes nitrate nitrogen; $Y_{54}$ is the economic coefficient of zooplankton when he consumes phytoplankton; $k_{S41}$ is constant of half-saturation for phytoplankton in nutrition by ammonium nitrogen, g/m$^3$; $k_{S43}$ is constant of half-saturation for phytoplankton in the diet of nitrate nitrogen, g/m$^3$; $k_{S54}$ is constant of half-saturation for zooplankton when feeding on phytoplankton; $k_{d4}$, $k_{d5}$ are mortality rates of phytoplankton and zooplankton, 1/day; $k_{51}$ is a coefficient of excretion of zooplankton, 1/day. The values of economic coefficients $Y_{41} = Y_{43} = 1$.

The proposed model is complex, but it describes well the simulated process and is adequate for the period in a few months. The drawback of the previous model, which is manifested in the deviation of calculated data from field during the first ten days, in the model is neutralized.

The drawback of all considered models is that they do not take into account the spatial characteristics of the water body. Such models are good to use for bodies of water with strong mixing conditions. In other cases, it is necessary to modify the proposed model by using the turbulent diffusion equation or the equation of convective transfer.