

# Chemical and Biological Modelling of Water Quality in Rivers

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*The eutrophication of aquatic systems represents one of the most important processes which affect water quality. The physical, chemical and biological phenomena that go on inside an aquatic system are very complex and determine their trophical level. Moreover, some interdependence relations take place between these phenomena which must be taken into account for a complete description of the global process. This paper presents a one-dimension numerical model that can be used to investigate a river water quality. The proposed model is focused on the chemical and biological factors and the state variables are total nitrogen, soluble phosphorus and algal biomass. The model is applied to the case of a river with simplified conditions and the obtained numerical results are compared to the analytical solutions.*

*Keywords: aquatic ecosystem, eutrophication, river, nutrients, modelling.*

Pollution has become a contemporary social – economical issue which in some regions of the world and especially in strong industrialized countries imposes the adoption of some drastic measures for limitation of pollutant discharges into the aquatic systems. Thus, if until a certain limit the addition of nutrients in the aquatic systems doesn't become embarrassing, being able to enrich the aquatic flora, thereby allowing the multiplication and diversification of aquatic fauna, over fertilization of surface waters causes the explosive plants development, which may induce serious water quality problems. This process, called eutrophication, is one of the conventional pollution problems and concerns the evolution of the organic and inorganic substances which have reached the water mass and have integrated into a series of physical and biochemical processes involving the biocenoses of aquatic system [1]. The eutrophication is a normal phenomenon as long as it has a natural evolution and in such case the process is very slow. In the case of natural eutrophication, the enrichment with nutrients is carried out only by natural factors and, during the process, the nutrients concentration can increase and decrease according to weather condition.

Eutrophication caused by human activities (atrophic eutrophication) is characterized by an accelerated evolution and its impact on the water quality becomes very important. In this case, the contribution of nutritive substances is artificially stimulated by human factors, such as the use of agriculture fertilizers, deforestation, animals' growth, urbanization and industrialization [2]. The concept of rivers eutrophication appeared since 1955, but even now the understanding of this process is very limited [3]. Thus, the scientific studies indicate some problems involving water quality in rivers arising from the anthropogenic eutrophication of these ecosystems (excessive growth of primary production, the reduction of macrophytes species numbers, diminution of dissolved oxygen level, pH changes or brown and green water appearance), and these effects have not been explained clearly enough [4]. Starting from the analysis of the main processes involved in the eutrophication phenomenon of aquatic ecosystems, this paper proposes a simplified numerical model that allows the analysis of eutrophication process and water quality in the rivers ecosystems.

## River eutrophication

In order to investigate the eutrophication process, it is necessary to identify the principal interdependences between chemical elements, inorganic substances, bacteria and phytoplankton. The development of bacteria population, in aerobe conditions, in an aquatic ecosystem leads to the transformation of the organic substances in inorganic substances which represent the main food of phytoplankton. By photosynthesis, the phytoplankton population produces biomass and a certain amount of oxygen. Taking into account these factors, the photosynthesis process and surface aeration can be considered the main sources of oxygen in the water. However, the bacteria activity needs oxygen, which is taken from the water and produces the decrease of oxygen level. In this way, anaerobic conditions are avoided, which significantly slowdown water self-purification. Bacterial and algal biomass makes up food for zooplankton and fish. All these elements of this web food are producers of organic material through the processes of excretion and mortality. This quantity of organic material together with the one of external origin becomes food for bacteria population.

Thermal and hydraulic conditions existing in the river have a large influence on water mass biochemical processes described above. Thus, thermal conditions have a direct influence on the concentration of dissolved oxygen in water mass, with consequences for surface aeration process, while the hydraulic conditions influence water quality by flow, speed and depth of flow. The increase of the river flow leads to the increase of dilution rate and a decrease of pollutant concentrations, while an increase in speed will cause a slowdown of self-purification biochemical phenomenon because of lower time of travel. This description of the river ecosystem is simplistic, but it provides necessary information for understanding the changes issues in biochemical, thermal and hydraulic variations as a consequence of human activity. Thus, the biodegradable organic material of anthropogenic nature discharged in aquatic ecosystem causes a diminution of oxygen dissolved in water and in the same time a considerably growth of mineral nutrients. Due to large residence time characteristic for some areas of flowing waters, the content of mineral nutrients may be assimilated

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by algae, leading to their multiplication. As a result of algal bloom, a shadowing phenomenon of depth water mass is produced and that leads to massive death of organisms from this level, a high consumption of oxygen and maintenance of large quantity of mineral nutrients. These represent the water degradation steps, until the eutrophic or hypertrophic state.

Generally, it is found that the algal cells contain nutritive elements in approximately the same proportion indifferent of algal species. The development of algal population occurs if the nutrients are found in sufficient quantities. If the concentration of one or more nutrients will fall below a level that biomass increase will not be able to continue, it's considered that development is limited by nutrients; from this point of view, the nutrients are limiting factors [5]. For surface waters, the most limited nutrient is phosphorus, but there are situations where nitrogen or a combination of phosphorus and nitrogen become limiting factors. When the nutrients concentration in the rivers are about five times lower than half saturation coefficients (nutrient limiting values), the kinetic algal development can be considered of first order variation (*Michaelis-Menten*) [6].

The influence of punctual pollution sources to rivers eutrophication can be analyzed using the diagram proposed by *Thomann* [7]. In this approach, the most important assumption is that for polluted rivers upstream from punctual source only by diffuse sources, if effluents' flow is less than 2% than total debit after the mixture, phosphorus may become limiting algal growing factor for downstream section of river. Otherwise, if effluents' flow is more than 2%, any of these nutrients can become a limitation factor. If the treatment of wastewater before pollutant discharge includes phosphorus removal, it will become the limiting factor in the riverbed. Moreover, the eutrophication process can be increased near the discharge pollutant point in the case of a reduced river flow.

An important factor which influences the consumption of nutrients by planktonic algae in a river ecosystem is the retention time, also called time of travel. Therefore, the eutrophication process in rivers may be manifested in two different ways depending on the river type. Thus, for large and deep water courses with long time of travel whose lower stream is characterized by large amounts of nutrients and the domination of planktonic algae, the eutrophication models of lakes may be applied [8]. However, for rivers with reduced time of travel, the macrophytes and attached algae are dominated, while planktonic algae influence only the water turbidity and less the primary productions growth.

### The eutrophication modeling in river ecosystem

Generally, it is found that the phenomena involved in the process of eutrophication are easier to model for enclosures of relatively stagnant water such as lake ecosystems. However, there are numerous attempts to approach these problems in the case of a river ecosystem type [8]. The essential difference between the two types of ecosystems consists in hydrodynamic and biologic phenomena. On the basis of a comparison with lake system and the behavior of some of the other factors considered above, it is possible to propose a conceptual model of the development of eutrophic condition in rivers. Therefore the water flow model must take into account the following aspects:

- long retention-time rivers respond differently to the short retention - time rivers when exposed to excess nutrients. The former move to dominance by

phytoplankton, whereas the latter tend to dominance by benthic and periphytic algae;

- in short retention - time rivers macrophyte growth becomes limited by light as a result of epiphytic algal growth rather than by nutrients;

- the median soluble reactive phosphorus concentration is likely to be a better predictor of trophic status in short retention-time rivers than the total phosphorus;

- the soluble reactive phosphorus concentration at which the eutrophic/hypereutrophic boundary lies is much higher in short retention-time rivers than in lakes [8].

For the most part of cases, the study of river's water quality using one-dimensional models is satisfactory. These models consider that the state variables have mean values in transversal section and vary with distance along the river axis. The average values are often the best indicators for the river studies, but there are some limits which are related to the impossibility of calculating the concentration of pollutants near the discharge section (because pollutants are not uniformly dispersed in the section). On the other hand, bi-dimensional and three-dimensional models require much more input data but also high computing resources, making the cost of their implementation very high.

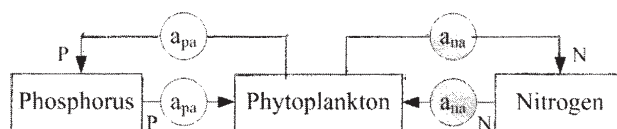


Fig. 1. Interdependences of the model state variables in the case of a river eutrophication process

The proposed numerical model allows estimating the evolution of nutrient content and algal biomass in the case of a river ecosystem and also highlights the influence of nutrients limitative effect on the algal growth rate. The physical model concerns a river with a regular riverbed which is polluted by a punctual source. The state variables of the model are total nitrogen ( $N$ ), soluble phosphorus ( $P$ ) and algal biomass ( $A$ ) and the interdependence relations between these variables are presented in figure 1. For simplicity, we consider the steady-state and we assume that flow velocity is constant and equal to the mean value  $V$ . The governing equations are based on the mass conservation law applied for algal biomass, total nitrogen and soluble phosphorus [9]:

$$E \frac{\partial^2 A}{\partial x^2} - V \frac{\partial A}{\partial x} + [k_c(T, N, P, I) - k_{ra}(T) - \frac{v_a}{H}] A = 0, \quad (1)$$

$$E \frac{\partial^2 N}{\partial x^2} - V \frac{\partial N}{\partial x} - a_{na} k_c(T, N, P, I) A = 0, \quad (2)$$

$$E \frac{\partial^2 P}{\partial x^2} - V \frac{\partial P}{\partial x} - a_{pa} k_c(T, N, P, I) A = 0, \quad (3)$$

where  $x$  represents the river longitudinal space coordinate,  $k_c$  is the growth algal rate ( $\text{day}^{-1}$ ),  $T$  is the water temperature ( $^{\circ}\text{C}$ ),  $I$  is the solar radiation intensity ( $\text{W}/\text{m}^2$ );  $k_{ra}$  is the loss phytoplankton rate which include respiration, excretion, natural mortality ( $\text{day}^{-1}$ ),  $v_a$  is the phytoplankton sedimentation rate ( $\text{m}/\text{day}$ ),  $E$  is the longitudinal massic dispersion coefficient,  $V$  is the mean flow velocity of river ( $\text{m}/\text{s}$ ),  $H$  is the flow depth ( $\text{m}$ ) and  $a_{na}$  and  $a_{pa}$  are the stoichiometric coefficients of eutrophication global reaction, that represents nitrogen - phytoplankton transformation rate, respectively phosphorus - phytoplankton transformation rate. For a long river sector the *Peclet* number ( $Pe$ ) which is the ratio of advection and dispersion intensity  $Pe = xV/E$ , take large values ( $Pe > 10$ )

and in this case the dispersive terms of the equations (1) – (3) are insignificant as compared to the convective terms, hence it is possible to neglect the longitudinal massic dispersion coefficient [6]. The initial conditions of the equations (1) – (3) are  $A = A_0$ ,  $N = N_0$  and  $P = P_0$ , where  $A_0$ ,  $N_0$  and  $P_0$  represents the values of state variables at discharge point. Usually, these initial concentrations are obtained as the means between the up-river values and those existing in the discharged pollutant flow. The growth algal rate  $k_c$  that appears in the equations (1) – (3) depends on the water temperature, solar radiation intensity and also on the concentration of nutrients (in the present case phosphorus and nitrogen) [10]. Moreover, in this model the nutrients that result by algae mortality are neglected. The value of growth algal rate  $k_c$  can be established using the formula  $\left(\frac{N}{N+K_{sN}}, \frac{P}{P+K_{sP}}\right)$ , where  $K_{sN}$  and  $K_{sP}$  are the halfsaturation constants of nitrogen and phosphorus. Because the algal growth rate  $k_c$  depends on the nutrients concentrations ( $N$  and  $P$ ), the solution of equations system (1) – (3) can be found using a numerical method. For that, a numerical computation program has been developed.

For relatively brief periods (for example, one season) the model can be simplified assuming that the variations of the growth algal rate  $k_c$  with temperature  $T$  and solar radiation intensity  $I$  are disregarded [11]. Moreover, in the case of simplified model it is possible to consider that the value of  $k_c$  is not influenced by  $P$  and  $N$  nutrients (the limiting effects of principal nutrients are neglected), and the equations (1) – (3) become:

$$\frac{dA}{dx} = \left(k_c - k_{ra} - \frac{v_a}{H}\right) \frac{A}{V} = kA, \quad (4)$$

$$\frac{dN}{dx} = -a_{na} k_c \frac{A}{V}, \quad (5)$$

$$\frac{dP}{dx} = -a_{pa} k_c \frac{A}{V}, \quad (6)$$

where  $k$  represents the phytoplankton accumulation rate ( $\text{day}^{-1}$ ). In this case the system (4) – (6) can be solved analytically and the concentrations of algal biomass and nutrients along of river have the following expressions:

$$A(x) = A_0 \cdot e^{kx}, \quad (7)$$

$$N(x) = N_0 + \frac{a_{na} k_c A_0}{k} \cdot (1 - e^{kx}) \quad (8)$$

$$P(x) = P_0 + \frac{a_{pa} k_c A_0}{k} \cdot (1 - e^{kx}). \quad (9)$$

The travel times  $t_N$  and  $t_P$  corresponding to the decrease of the concentration of  $N$  and  $P$  until the limiting values  $N_{lim}$  and  $P_{lim}$  are

$$t_N = \frac{1}{k} \ln \left[ \left( \frac{a_{na} k_c A_0}{k} + N_0 - N_{lim} \right) \frac{a_{na} k_c A_0}{k} \right], \quad (10)$$

$$t_P = \frac{1}{k} \ln \left[ \left( \frac{a_{pa} k_c A_0}{k} + P_0 - P_{lim} \right) \frac{a_{pa} k_c A_0}{k} \right] \quad (11)$$

and can be used to estimate the influence of pollutant flow level to the algal growth and also to choose the water treatment method [6, 12].

## Results and discussions

The numerical model was used to obtain the nutrients space distributions and algal biomass along a river with wastewater discharges from a punctual source. The river flow is  $Q = 5 \text{ m}^3/\text{s}$  and the phosphorus, nitrogen and biomass concentrations in water are  $P = 50 \text{ } \mu\text{gP/L}$ ,  $N = 1000 \text{ } \mu\text{gN/L}$  and  $A = 50 \text{ } \mu\text{gChla/L}$ . The flow of pollutant

discharge is  $Q_s = 0.075 \text{ m}^3/\text{s}$  and wastewater concentrations of nutrients and biomass are  $P_s = 5000 \text{ } \mu\text{gP/L}$ ,  $N_s = 5000 \text{ } \mu\text{gN/L}$  and  $A_s = 0 \text{ } \mu\text{gChla/L}$ . Based on the presented model, the computation of nutrients and algal biomass distributions is done for a river depth  $H = 1 \text{ m}$ , mean flow velocity  $v = 0.16 \text{ m/s}$  and assuming that the water temperature  $T$  is constant. The used values of numerical model parameters, which agree well with these reported in [13, 14], are given in table 1.

**Table 1**  
VALUES OF USED MODEL PARAMETERS

Parameter	Value	Parameter	Value
$k_c$ [ $\text{day}^{-1}$ ]	0,6	$K_{sp}$ [ $\mu\text{gP/L}$ ]	6
$k$ [ $\text{day}^{-1}$ ]	0,3	$K_{sn}$ [ $\mu\text{gN/L}$ ]	20
$k_{ra}$ [ $\text{day}^{-1}$ ]	0,285	$N:P:A$	7,2: 1: 1
$v_a$ [ $\text{m/day}$ ]	0,015	$T$ [ $^{\circ}\text{C}$ ]	20

Taking into account the literature results [14], the critical values of nutrient's concentration where these become limiting factors for algal growth are  $P_{lim} = 5 K_{ps} = 30 \text{ } \mu\text{gP/L}$  and  $N_{lim} = 5 K_{ns} = 100 \text{ } \mu\text{gN/L}$ . In this case, the travel times for that the concentration of nutrients in river becomes smaller than  $P_{lim}$  and  $N_{lim}$  are 2.9 days for nitrogen and 2.2 days for phosphorus. It results that from two investigated nutritive elements, the phosphorus is the first limiting factor for algal growth.

The system (1) – (3) was solved for two cases: a) for  $k_c = \text{const.}$  which allows using the analytical solution (7) – (9) and b) when  $k_c$  depends of  $P$  and  $N$  which impose a numerical solution. The resulting curves are presented in figures 2 – 4 and show the analytical and numerical variations of nutrient concentration and algal biomass content along the river. Using the simplistic model with  $k_c = \text{const.}$  (case a) it results that the concentration of nutrients at a certain downstream distance takes negative

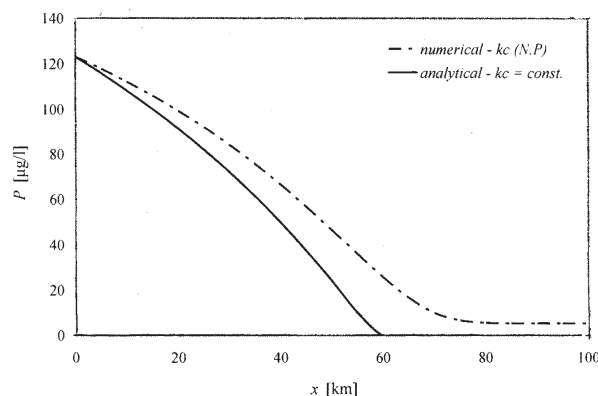


Fig. 2. Numerical and analytical variations of phosphorus concentration along the river

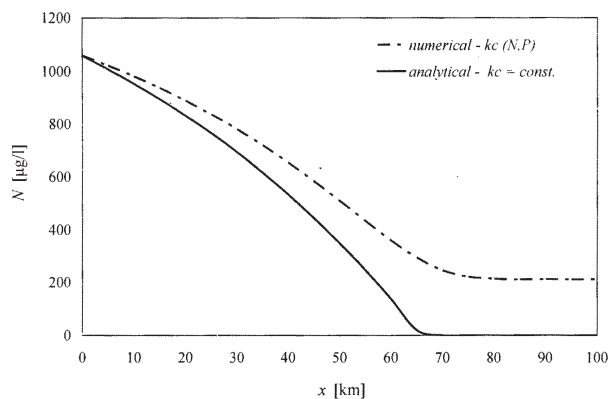


Fig. 3. Numerical and analytical variations of nitrogen concentration along the river

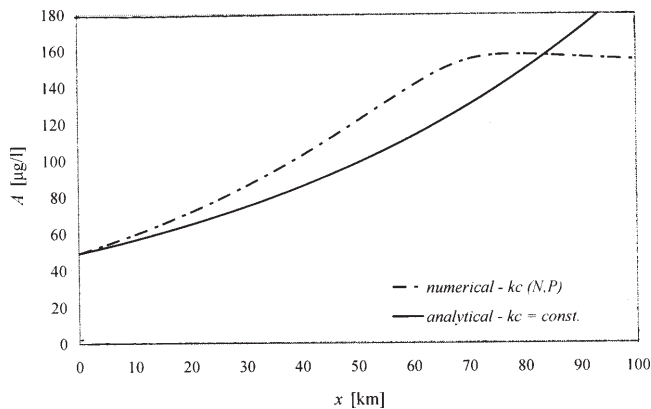


Fig. 4. Numerical and analytical variations of algal biomass concentration along the river

values (of course, physically that is not possible) and the algal biomass content increases. These are the limits of analytical solution which disregard the limitative effect of nutrients in the water. In fact, in case *a*) the computation must be stopped when the first nutrient concentration becomes zero (in our case at the moment when the soluble phosphorus is zero).

When the variation of the growth algal rate  $k_c$  with water nutrients is taken into account, the numerical solution (case *b*) all along of concerned river segment seems to be realistic. According to the principal mechanisms described in the second section of the paper, after the nutrients disparity, it results a diminution of the algal biomass content as the effect of the sedimentation phenomenon and algae death.

The usual method employed to limit the eutrophication process concerns the effluent treatment before his discharge. The proposed model also allows evaluating the effect of wastewater treatment on the river eutrophication process. Because the phosphorus becomes the first limiting factor for algal growth in our case, the wastewater treatment must reduce the phosphorus concentration in the polluted source. For example, when the effluent treatment reduces the phosphorus concentration  $P_s$  at 1000 and 2000  $\mu\text{gP/l}$ , it results significant decrease of algal biomass content along the river (fig. 5).

### Conclusion

The presented model allows illustrating the importance of the nutrients limitative effects on the river eutrophication process. This is visible when the variation of growth algal rate  $k_c$  with nutrients concentration is taking into account. The simplistic approach (where  $k_c$  is constant - case *a*), can be used only to obtain a rough estimation until the moment when the first nutrient disappears from the water. Using the presented model the first nutrient limiting factor of the algal growth can be obtained which allows choosing the parameters of wastewater source treatment. This approach can be improved by considering the variations in temperature and solar radiations intensity in water and also taking into account the hydrodynamic water flow.

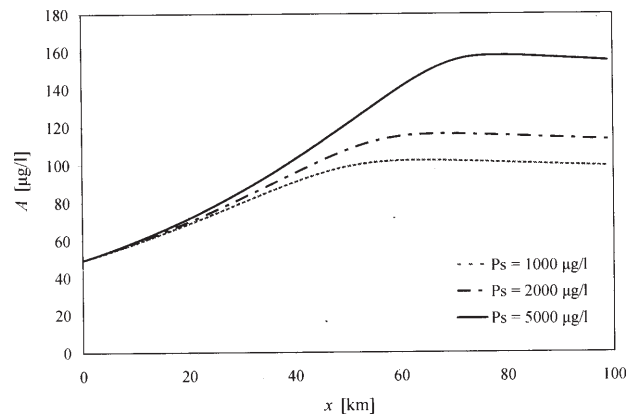


Fig. 5. Algal biomass variation along the river for different concentrations of phosphorus in wastewater pollution source

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