Mathematical modelling of the distribution of non-conservative impurities

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Abstract. Currently, there is an increase in anthropogenic pressure on all ecological systems, including water bodies. It should be noted that the cost is high for experimental studies of the dynamics of the distribution of non-conservative impurities in the aquatic environment because they are associated with the use of expensive equipment (spectrophotometric, polarographic, spectrographic, etc.) and experimental facilities. In this regard, mathematical methods of modelling natural processes play an important role. In the work, a mathematical model is developed for studying the distribution of pollutants in rivers, taking into account chemical reactions, and the results of numerical experiments characterising the distribution of non-conservative nitrogen impurities in different periods of the year are presented.

1. Introduction
Currently, patterns of the effect of increased doses of substances dissolved in water on the flora and fauna of bodies of water and on human health have been established. To correctly assess the environmental consequences of real or possible situations in which a significant amount of harmful substances gets into the river, it is necessary to know the concentration of these substances and the dynamics of their change at different points of the river. Such studies are difficult due to the complexity of field measurements of the necessary parameters for modelling (diffusion, bottom roughness, etc.), the use of expensive equipment (spectrophotometric, polarographic, spectrographic, etc.), and experimental facilities.

Quite often, mathematical modelling and computational experiments are used as methods of exploratory analysis, which is preceded by experimental methods of studying the processes of mass transfer in an aqueous medium. The current state of computer technology and the degree of development of mathematical models of mass transfer allow creating effective computational algorithms and software packages to solve this problem [1-6].

The purpose of this scientific research is the development of a mathematical model for the propagation of non-conservative impurities in rivers, using models and methods for mathematical modelling of mass transfer in an aqueous medium; to assess the distribution of concentrations of nitrogen-containing impurities along the course of the river over time.

Nitrogen-containing impurities were chosen by us as objects of study because they are most widespread as toxicants directly related to environmental problems near large cities and agricultural enterprises standing on the banks of the river.
2. Materials and methods
Consider the theoretical provisions for constructing a mathematical model of the distribution of non-conservative impurities in rivers. It should be noted that the characteristics of the process of propagation of a multicomponent non-conservative admixture, averaged over a living river section, are considered. The position of each section is uniquely determined by the distance from the starting point. We will denote this value by $x$ and consider it as a spatial coordinate. The characteristics of the river itself are assumed to be stationary, but generally, depending on the $x$ coordinate. The quantitative characteristics of impurities are considered as functions depending on the $x$ coordinate and time $t$.

The composition of impurities will be described by the vector $A = (\alpha_1, ..., \alpha_p)$, where $\alpha_1, ..., \alpha_p$ – components of the impurity, $p$ – their number. The last component of the impurity is always (in winter) oxygen. The impurity concentration is described similarly: $C = (c_1, ..., c_p)$ where $c_1, ..., c_p$ – concentrations of the impurity components with the corresponding numbers.

2.1 Main balance sheet ratio
Let $v(x)$ – river speed, $S(x)$ – living area, $D$ – diffusion coefficient, $F(t, x) = (f_1(t, x), ..., f_p(t, x))$ – the density of impurity sources due to the influx of impurities through tributaries, $F_{chem}(t, x) = (f_1^{chem}(t, x), ..., f_p^{chem}(t, x))$ – the density of sources of generation (destruction) of impurities due to chemical reactions.

Consider the volume of water that is enclosed between living sections passing through points with coordinates $x_1$ and $x_2$. Let $m_i$ – mass of substance $a_i$ in this volume of water. The rate of change is due to the convective and diffusive transport of matter through the boundaries of the volume, its generation and destruction in chemical reactions occurring in this volume of water, and flow through inflows. We have a balanced ratio:

$$\frac{dm_i}{dt} = \int_{x_1}^{x_2} \left[ c_i(t, x_1) v(x_1) S(x_1) - c_i(t, x_2) v(x_2) S(x_2) + \int_{x_1}^{x_2} f_i^{chem}(t, x) S(x) dx + f_i(t, x) S(x) dx \right] d\xi, \quad i = 1, ..., p,$$

which can be written as follows:

$$\int_{x_1}^{x_2} \left\{ \frac{\partial C(t, \xi)}{\partial t} S(\xi) - \frac{\partial v(\xi) C(t, \xi)}{\partial \xi} S(\xi) - D \frac{\partial^2 C(t, \xi)}{\partial \xi^2} S(\xi) \right\} d\xi = 0.$$

Since $x_1$ and $x_2$ can take arbitrary values, the system of differential equations follows from the integral relation

$$\frac{\partial C(t, x)}{\partial t} = v(x) \frac{\partial C(t, x)}{\partial x} + D \frac{\partial^2 C(t, x)}{\partial x^2} + f_{chem}(t, x) + f_{chem}(t, x) + f_{cons}(t, x) + f_{sect}(t, x). \quad (1)$$

The term $F_{sect}$ takes into account the change in the area of the living section of the river:

$$F_{sect} = D \frac{\partial C}{\partial x} \frac{d \ln S}{dx},$$

and $F_{cons}$ – change in water flow in the river:

$$F_{cons} = -q C, \quad q = -\frac{1}{S} \frac{d(v S)}{dx}.$$

The amount of fluid flow through a certain cross-section of the river is determined by the sum of the costs of all tributaries located upstream. In this paper, for the sake of simplicity, we do not take into account evaporation, water flows through underground sources, the transition of water to solid form (ice) and other factors that usually have a negligible effect on the formation of the flow rate of water in the river. If necessary, these factors can easily be taken into account.

Let $K$ tributaries be located in the considered section of the river, the inflow zones of which correspond to the intervals $(x_{j1}, x_{j2})$, $j = 1, ..., K$. It is natural to assume that the confluence zones of various tributaries do not intersect, i.e.
\[(x_{j1}, x_{j2}) \cap (x_{i1}, x_{i2}) = \emptyset, \quad i \neq j, \quad i, j = 1, ..., K. \quad (2)\]

The flow rate changes only in the confluent areas. In other parts of the river, it does not change. Hence,

\[
\begin{cases}
q(x) \geq 0, & x \in \bigcup_{j=1}^{K} (x_{j1}, x_{j2}), \\
q(x) = 0, & x \notin \bigcup_{j=1}^{K} (x_{j1}, x_{j2}).
\end{cases}
\quad (3)
\]

2.2 Accounting for the flow of impurities through tributaries

Let \(C_{j}^{\text{imp}}(t) = (c_{i,1}^{\text{imp}}(t), ..., c_{i,p}^{\text{imp}}(t))\) − the impurity concentration in the \(j\)-th tributary. Assumption (2) allows us to introduce the function

\[
C^{\text{imp}}(t, x) = \begin{cases}
C_{j}^{\text{imp}}(t), & x \in (x_{j1}, x_{j2}), \quad j = 1, ..., K, \\
0, & x \notin \bigcup_{j=1}^{K} (x_{j1}, x_{j2}),
\end{cases}
\]

with the help of which the expression for the density of the sources of impurity production due to its intake through the tributaries is written in the following form:

\[F(t, x) = q(x)C^{\text{imp}}(t, x).\]

2.3 Accounting for chemical reactions

Let the first \(r\) components of the impurity be active, i.e. enter into oxidative reactions with oxygen dissolved in water. For the convenience of the presentation, we will assume that the numbering of reactions and active elements corresponds to the hierarchy of the reaction. In other words, the numbering of the elements is such that when the substance \(a_j\) interacts with oxygen, the substances \(a_{j+1}, ..., a_{p-1}\) are formed, and the substances \(a_1, ..., a_{j-1}\) are not formed. The quantities of formed substances and the amount of oxygen consumed in this reaction (calculated per unit mass of the substance \(a_j\)) will be denoted \(b_{j+1,j}, ..., b_{p-1,j}\) and \(a_j\). The numbers \(b_{j+1,j}, ..., b_{p-1,j}, j = 1, ..., r\) will be considered as some elements of the matrix \(B\) of dimension \(p \times r\). The remaining elements of this matrix are defined as follows:

\[b_{i,j} = -1; \quad b_{i,j} = 0 \text{ for } j > i; \quad b_{p,j} = -a_j. \quad (4)\]

The rate of oxidation of the substance is proportional to its concentration. The proportionality coefficient, which is usually called the coefficient of non-conservatism, depends on temperature, the speed of the river, and the level of oxygen saturation of the water. In further calculations, this formula is used:

\[k_j = \varepsilon \lambda_j, \quad \lambda_j = a_1 a_2 k_j^{s_0},\]

where \(k_j^{s_0}\) − a static coefficient of non-conservatism (its value is obtained in laboratory conditions at a temperature of 20 °C in a stationary solution at the maximum possible oxygen concentration at this temperature), \(\varepsilon\) − relative oxygen concentration:

\[
\varepsilon(t, x) = c_p(t, x)/c_p^{\text{sat}},
\]

where \(c_p^{\text{sat}}\) − maximum possible oxygen concentration at the considered water temperature. The coefficients \(a_1\) and \(a_2\) take into account the influence of temperature and river flow velocity.

Let \(\lambda_{i,j}\) − the rate of change in the concentration of the substance \(a_i\) in the \(j\)-th chemical reaction. Then, the following formula is valid:

\[\lambda_{i,j} = b_{i,j} k_j c_j.\]

Summing up the contributions of all reactions, we obtain

\[F^{\text{chem}} = \varepsilon B \cdot A \cdot C^a,\]
where \( C^a = (c_1, ..., c_p) \) – vector composed of concentrations of active impurity components, \( A - r \times r \) diagonal matrix with elements \( \lambda_{i,j} = \lambda_i \delta_{i,j}, \delta_{i,j} – \) Kronecker delta.

In cases where the cross-sectional area slowly changes along the river, you can neglect the term \( F^{sec} \). This assumption, and for large rivers it is quite justified, gives the right to consider its simplified version (5) in the future instead of equation (1):

\[
\frac{\partial C}{\partial t} = v \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} + \epsilon B \cdot A \cdot C^a - qC + F. \quad (5)
\]

It is assumed that at time \( t = 0 \), the concentrations of all impurity components are known, i.e. the initial state function vector is known

\[
C(0, x) = \Phi(x) = \left( \phi_1(x), ..., \phi_p(x) \right); \quad \phi_i(x) \geq 0, \quad i = 1, ..., p. \quad (6)
\]

We assume that in the upper section of the river, i.e. at \( x = 0 \), the concentration is known at all instants of time \( t \geq 0 \),

\[
C(t, 0) = \Psi(t) = \left( \psi_1(t), ..., \psi_p(t) \right); \quad \psi_i(t) \geq 0, \quad i = 1, ..., p. \quad (7)
\]

Also assume that

\[
\frac{\partial C}{\partial x} \bigg|_{x=0} = 0. \quad (8)
\]

This condition means that the water entering the upper section of the river is in a well-mixed state.

To simulate the distribution of non-conservative impurities in the aquatic environment, the processes of transfer of some non-conservative substances, for example, nitrogen in ammonium form and their oxidation products, are considered. The task includes the following set of components:

- \( NH_4 \) – ammonia form of nitrogen \( (M_1 = 18) \),
- \( NO_2 \) – nitrite form of nitrogen \( (M_2 = 46) \),
- \( H_2O \) – water \( (M_3 = 18) \),
- \( NO_3 \) – nitrate form of nitrogen \( (M_4 = 62) \),
- \( O_2 \) – oxygen \( (M_1 = 32) \),

where \( M_i \) – molecular weight of the corresponding chemical components. Two chemical reactions are considered:

\( NH_4 + 2O_2 = NO_2 + 2H_2O \),
\( 2NO_2 + O_2 = 2NO_3 \).

According to reference data [7]:

\( k_{1}^{st} = 0.069 \text{ 1/day}; \ k_{2}^{st} = 10.8 \text{ 1/day}. \)

The matrix of coefficients \( B = \{b_{ij}\} \) has the following form:

\[
B = \begin{pmatrix}
-1 & 0 \\
M_2/M_1 & -1 \\
0 & M_4/M_2 \\
-2M_2/M_1 & -M_5/M_2
\end{pmatrix} = \begin{pmatrix}
-1 & 0 \\
23/9 & -1 \\
2 & 0 \\
-32/9 & -8/23
\end{pmatrix}. \quad (9)
\]

The system of equations has the form:

\[
\begin{aligned}
\frac{\partial c_1}{\partial t} + U \frac{\partial c_1}{\partial x} &= D \frac{\partial^2 c_1}{\partial x^2} - \epsilon \alpha_1(c_1 - c_{1,b}) + q_1, \\
\frac{\partial c_2}{\partial t} + U \frac{\partial c_2}{\partial x} &= D \frac{\partial^2 c_2}{\partial x^2} + \epsilon \alpha_1 c_1 - \epsilon \alpha_2 c_2 + q_2, \\
\frac{\partial c_3}{\partial t} + U \frac{\partial c_3}{\partial x} &= D \frac{\partial^2 c_3}{\partial x^2} + \epsilon \alpha_2 c_2 + q_3, \\
\frac{\partial c_{oxygen}}{\partial t} + U \frac{\partial c_{oxygen}}{\partial x} &= D \frac{\partial^2 c_{oxygen}}{\partial x^2} - \epsilon \alpha_3 c_1 - \epsilon \alpha_4 c_2 c_2,
\end{aligned} \quad (10)
\]

where \( \alpha_1 = \frac{M_2}{M_1} = \frac{23}{9}, \alpha_2 = \frac{M_4}{M_2} = \frac{31}{23}, \alpha_3 = \frac{2M_2}{M_1} = \frac{32}{9}, \alpha_4 = \frac{M_5}{2M_2} = \frac{8}{23}, \epsilon(x,t) = \frac{c_{oxygen}}{c_{oxygen}^{sat}} \), \( c_1, c_2, c_3 \) – nitrogen concentration, respectively, in ammonium, nitrite and nitrate forms, \( c_{1,b} \) – background
nitrogen concentration in ammonium form, $\gamma_1$ and $\gamma_2$ – non-conservative coefficients, respectively, for nitrogen in ammonium and nitrite forms. In reference [7], it is recommended to use the formulas

$$\gamma_1 = ak_1, \gamma_2 = ak_2,$$

(11)

where coefficient $a$ – the flow velocity:

$$a = 1 \text{ when } u \to 0,$$

$$a = 5 \text{ when } u \geq 0.2 \text{ m/s}.$$

For the numerical values of the coefficients of non-conservatism for temperatures other than the reference, it is recommended to calculate them by the formula [1]:

$$a_1 = [1.12(T + 1)^{-0.022}]^{T-20^\circC},$$

The diffusion coefficient $D$ depends on flow velocity, roughness coefficient, average depth, and hydraulic radius. In the present work, since the flow velocity and other hydraulic parameters are considered known, we will assume that the function $D(x)$ is given.

For mathematical modelling of the distribution of non-conservative impurities in rivers in the summer, we describe several features. In the period of open water, which we will hereinafter call the summer period, there is good contact of water with air. It provides the maintenance of the highest possible concentration of oxygen. Chemical reactions are not able to change its concentration. For this reason, in summer there is no need to include oxygen in the composition of a multicomponent non-conservative impurity.

We obtain a system of equations for modelling the process of transport of nitrogen impurities in the summer:

$$\frac{\partial C}{\partial t} - v \frac{\partial C}{\partial x} = D \frac{\partial^2 C}{\partial x^2} + B \cdot A \cdot C^a - qC + F,$$

(12)

which must be solved together with the initial and boundary conditions (6) and (7), (8).

In the model under consideration, the concentrations of impurity components are small due to the strong mixing of the pollutant in large volumes of water. Therefore, the amount of water resulting from chemical reactions is not taken into account.

There are significant differences in mathematical modelling in the summer and winter periods. In the period of open water (summer), there is good contact of water with air, providing an excess of oxygen necessary for oxidation reactions. Therefore, in this case, there is no need to include oxygen in the set of variable components. Then, the matrix $B$ for the reactions of nitrogen compounds has the form:

$$B = \begin{pmatrix} -1 & 0 & 0 \\ M_2/M_1 & -1 & 0 \\ 0 & M_4/M_2 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 23/9 & -1 & 0 \\ 0 & 31/23 \end{pmatrix}.$$

Finally, we obtain a system of equations for modelling the transport of nitrogen compounds in the summer:

$$\begin{cases} \frac{\partial c_1}{\partial t} + U \frac{\partial c_1}{\partial x} = D \frac{\partial^2 c_1}{\partial x^2} & - \gamma_1(c_1 - c_{1,b}) + q_1, \\
\frac{\partial c_2}{\partial t} + U \frac{\partial c_2}{\partial x} = D \frac{\partial^2 c_2}{\partial x^2} & + \alpha_1 Y_1 c_1 - \alpha_2 Y_2 c_2 + q_2, \\
\frac{\partial c_3}{\partial t} + U \frac{\partial c_3}{\partial x} = D \frac{\partial^2 c_3}{\partial x^2} & + \alpha_2 Y_2 c_2 - q_3, \end{cases}$$

(13)

where $\alpha_1 = \frac{M_2}{M_1} = \frac{23}{9}, \alpha_2 = \frac{M_4}{M_2} = \frac{31}{23}.$

For numerical simulation of the process, an explicit difference scheme was developed and tested [8], [9]. The algorithm was tested by comparing the results of a numerical solution with a known analytical solution [10].
3. Results

3.1 Numerical experiment 1 (The content of non-conservative impurities with a constant discharge for 5 days in the summer).

When modelling, the following parameters were used:

\[ c_{1,b} = 0 \] – background concentrations of ammonium form of nitrogen, \( U = 4 \text{ km/h} \) – river speed, \( D = 0.72 \) – diffusion coefficient, \( T = 20 \text{ °C} \) – water temperature, \( k_1 = 0.002875 \text{ 1/hour} \), \( k = 0.45 \text{ 1/hour} \) – corresponding non-conservative coefficients, \( q_1 = 1 \), \( q_2 = 0 \), \( q_3 = 0 \) – concentration of ammonium, nitrite and nitrate forms of nitrogen, respectively, at the point of emergency discharge into the river (\( x = 0 \)).

The figures below show the results of numerical simulations of the distribution of non-conservative admixtures in the river in the summer, for different times.

![Figure 1](image1.png)

**Figure 1.** a - Impurity concentration 1 day after the onset of contamination (experiment 1), b - Impurity concentration 5 days after the onset of contamination (experiment 1).

As can be seen from the simulation results, the nitrogen content in the ammonium form gradually decreases until it reaches the level of background concentration. At the same time, due to chemical reactions, the level of nitrogen in nitrate form increases. The absence of nitrogen in nitrate form is explained by the rate of the chemical reaction; this form instantly turns into nitrate, due to which there is an increase in the concentration of nitrogen in the nitrate form.

3.2 Numerical experiment 2 (The content of non-conservative impurities with a constant discharge for 5 days in the winter).

Parameters: \( T = 3 \text{ °C} \) – water temperature, \( k_{1,\text{win}} = k_1 \cdot [1.12(T + 1)^{-0.022}]^{T-20\text{°C}} \), \( k_{2,\text{win}} = k_2 \cdot [1.12(T + 1)^{-0.022}]^{T-20\text{°C}} \). The remaining parameters are the same as in experiment 1.

The figures below show the results of numerical simulations of the distribution of non-conservative admixtures in the river at different times in winter.

![Figure 2](image2.png)

**Figure 2.** a - Impurity concentration 1 day after the onset of pollution (experiment 2), b - Impurity concentration 5 days after the start of contamination (experiment 2).
In winter, the limitation of the amount of oxygen necessary for oxidation reactions slows down the rate of chemical reactions. Ammonium nitrogen contamination remains almost constant over a long period of time.

3.3 Numerical experiment 3 (The content of non-conservative impurities in case of emergency discharge through the inflow during 5 days in summer).
In contrast to experiment 1, the discharge of nitrogen in ammonium form \( (q_1 = 100) \) occurs through the inflow at the point \( x = 300 \). The results of the numerical experiment are presented in figure 3.

The figure shows that the pollutant practically does not spread upstream, as is observed in practice. This fact suggests that the convective transfer process dominates the diffusion one. As you move away from the influx, the concentration of nitrogen in the ammonium form decreases due to the transition to the nitrite and nitrate forms.

3.4 Numerical experiment 4 (The content of non-conservative impurities in case of emergency discharge into the inflow during 5 days in winter).
In contrast to experiment 2, the discharge of nitrogen in the ammonium form \( (q_1 = 100) \) occurs through the inflow at the point \( x = 300 \). The results of the numerical experiment are presented in figure 4.

The experimental results correspond to the actual processes of the distribution of non-conservative impurities in the winter.

4. Conclusion
In the work, a mathematical model is developed for studying the concentrations of a pollutant (non-conservative impurity) that spreads in an aqueous medium. Sufficient attention is paid to accounting for chemical reactions to simulate the distribution of non-conservative nitrogen-containing impurities.
The numerical solution of the problem is performed by the finite difference method. The form of initial and boundary conditions for modelling is given.

The research presents the results of numerical modelling of the distribution of non-conservative impurities in the river. As a pollutant, nitrogen was taken in ammonium, nitrite, and nitrate forms. Numerical experiments were carried out at different times of the year, namely in the summer (unlimited amount of oxygen for chemical reactions) and winter (lack of oxygen for continuous chemical reactions) periods.

The developed mathematical model of the process of pollution of the aquatic environment (rivers) allows predicting the concentration of non-conservative impurities in different parts of the river. Numerical experiments allow us to optimise the work in determining the environmental load on the rivers.

Using the model will allow us to quickly assess the environmental situation during uncontrolled discharges of a pollutant, as well as reduce the cost of environmental protection measures that would reduce the negative impact of pollutants on water quality and the environment or properly respond to threats of this impact.

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