sciendo Ovidius University Annals Series: Civil Engineering, Year 25, 2023
DOI: 10.2478/ouacsce-2023-0004

Mathematical modelling and simulation of the river waters nitrification process

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***Abstract* – This paper presents the mathematical model of the nitrification process starting from the kinetic equations describing this process. The mathematical model was developed using Scilab-Xcos program and allows the visualization in time of the water concentration evolution of the following parameters: organic nitrogen (N_{org}), ammonia nitrogen (NH_3-N), nitrite nitrogen (NO_2-N), nitrate nitrogen (NO_3-N), oxygen (C) and biochemical oxygen consumption for the oxidation of organic substances containing carbon (L_C). Also in this work is presented an example of simulation of the above mentioned parameters.**

Keywords: dissolved oxygen in water, modelling, nitrification, Scilab-Xcos, simulation

Nomenclature

N_{org} – concentration of organic nitrogen in water [mg/l];
NH_3-N – concentration of ammonia nitrogen in water [mg/l];
NO_2-N – nitrite nitrogen concentration in water [mg/l];
NO_3-N – nitrate nitrogen concentration of water [mg/l];
L_C – biochemical oxygen consumption for the oxidation of organic substances containing carbon [mg/l];
T – water temperature [^{0}C];
t – time [days];
C – oxygen concentration in water [mg/l];
C_s – saturation concentration of oxygen in water [mg/l];
v – average river water velocity [m/day];
H – average river channel depth [m];
L – average river channel width [m];
K_{01} – oxidation constant of organic nitrogen [day^{-1}];
K_{12} – oxidation constant of ammonia nitrogen [day^{-1}];
K_{23} – oxidation constant of nitrate nitrogen [day^{-1}];
K_{LC} – constant consumption of organic substances containing carbon [day^{-1}];
K_a – constant reaeration [day^{-1}];
K_{01}(20) – constant oxidation of organic nitrogen at temperature of 20 ^{0}C [day^{-1}];
K_{12}(20) – constant oxidation of ammonia nitrogen at temperature of 20 ^{0}C [day^{-1}];
K_{23}(20) – constant oxidation of nitrate nitrogen at temperature of 20 ^{0}C [day^{-1}];
K_{LC}(20) – constant consumption of organic substances containing carbon at temperature of 20 ^{0}C [day^{-1}];
K_a(20) – constant reaeration at temperature of 20 ^{0}C [day^{-1}];

f_{12}, f_{23} – correction factors to decrease the oxygen concentration in water;
r_{12}, r_{23} – the amount of oxygen consumed to convert one gram of nitrogen from ammonia to nitrites and from nitrites into nitrates respectively;
θ_{01}, θ_{12}, θ_{23}, θ_{LC}, θ_a, – empirical correction factors;
Q – total flow;
q_i – source discharges that pollute;
C_i – concentrations of polluting sources.

1. INTRODUCTION

In wastewater discharged from domestic or livestock farms, there can be organic substances and inorganic combinations of nitrogen, mainly ammonium salts. Some industrial wastewaters, such as those released by coke-chemical plants, can contain large amounts of organic matter with nitrogen or inorganic nitrogen combinations such as: NH_4^+, NO_2^-, NO_3^2 [1].

Human activity is one of the most encountered sources of nitrogen emission, especially in the hydrosphere. The main effects (disadvantages) of nitrogen accumulation in water are: dissolved oxygen depletion in receiving waters, the stimulation of eutrophication, the increase of the toxicity of the aquatic life, the risk of endangering public health and a reduced probability that water could be reused [2].

This paper presents the forms in which the nitrogen can exist in wastewater, the necessity of its removal from wastewater, the description and the mathematical modelling of the nitrification process using Scilab-Xcos program.

2. NITRIFICATION PROCESS

2.1. Forms in which nitrogen is found in natural waters

Nitrogen is one of the chemical elements present in all four main components that make up the biosphere: the atmosphere, hydrosphere, the earth's crust and tissues of living or dead organisms. Each element contains nitrogen in various forms.

In the environment, nitrogen can be found in several forms, depending on its nature and on the given oxidation. Thus, by its nature, it can be organic or inorganic nitrogen. Inorganic nitrogen, depending on the oxidation state in which it can be found, can exist in one of the forms mentioned in table 1 below.

Table 1

Nitrogen compound	Symbol
Ammonia	NH_3
Ammonium ion	NH_4^+
Nitrogen gas	N_2
Nitrite ion	NO_2^-
Nitrate ion	NO_3^-

The total nitrogen that can be found in wastewater is composed of organic nitrogen, ammonia (or ammonium), nitrites and nitrates.

Ammonia exists in aqueous solution or as a gas called ammonia (NH_3) or the ammonium ion (NH_4^+), depending on the solution pH, according to the following equilibrium reaction: $NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$.

Thus, at pH levels > 9.25 ammonia can predominantly be found, while at pH levels <9.25 is predominantly ammonium.

Nitrites (NO_2^-) are relatively unstable and easily to be oxidized to the nitrate form. They indicate a previous pollution in the stabilization process and rarely exceed 1.0 mg/l in wastewater or 0.1 mg/l in surface waters. Nitrites present in effluent wastewater plants can be oxidized by chlorine, but this process involves an increase in the dose of chlorine or in the disinfection cost respectively.

Nitrates (NO_3^-) are the most oxidized form of nitrogen that can be found in wastewater. They can vary within 0÷20 mg/l in the treated wastewater.

Ammonia (NH_3) is found in very small amounts, either in free form (gas), near decomposing substances or in the soil as ammonium salts.

Ammonia toxicity compared to that of the ionic form, is much higher.

Ammoniacal nitrogen is expressed in the ammonium ion NH_4^+ (mg/l), in total nitrogen N-NH_4^+ (mg/l) or NH_3 (mg/l). 1.0 mg of nitrogen N corresponds to 1.286 mg and 1.216 mg NH_4^+ and NH_3.

Nitrites NO_2^- is the first step of ammonia oxidation. At 1.0 mg of total nitrogen correspond 3.285 mg NO_2-N.

Nitrates NO3-, represent an advanced stage of ammonium oxidation, their presence suggesting an older contamination process.

Nitrates can be of animal origin, from the protein mineralization processes, or they can be of mineral origin resulted from water flows over the surfaces where fertilizers were used. At 1.0 mg of total nitrogen correspond 4.427 mg NO_3-N.

Organic nitrogen consists of several families of compounds: amines, amino acids, herbicides, nitroso derivatives, macromolecular combinations (proteins, peptides, chlorophylls, humic acids).

The usual concentrations of nitrogen compounds found in untreated domestic wastewater vary in the range of 8÷35 mg/l for organic nitrogen, 12÷50 mg/l for free ammonia and 20÷85 mg/l for total nitrogen.

The content of nitrates and nitrites in domestic wastewater is generally small.

Nitrification (figure 1) is the process by which the biological oxidation of ammonium is carried out. This is done in two stages, first in the form of nitrites and second in the nitrates form [1].

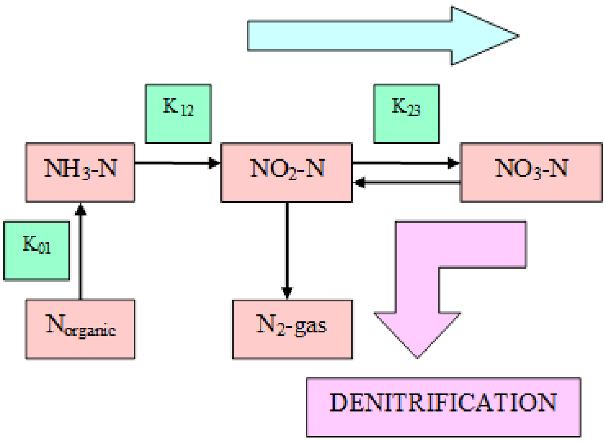

Fig. 1 Nitrification processes (where there is enough oxygen in the water) and denitrification (where there is no oxygen in the water)

Responsible for these two stages are mainly two aerobic chemoautotrophic bacteria (they obtain energy from chemical reactions, by oxidizing inorganic compounds such as ammonia and nitrogen oxides in an aerobic environment, using the inorganic carbon from carbon dioxide for synthesis) known as nitrosomonas and nitrobacter. Overall nitrification stages are represented by the formula:

$$NH_4^+(ammonium) + O_2 \xrightarrow{Nitrosomonas} NO_2^-(nitrite) + O_2 \xrightarrow{Nitrobacter} NO_3^-(nitrate)$$

The transformation reactions are generally coupled and they rapidly occur to the form of nitrate, the level of nitrates at a certain time, being relatively low. The nitrogens formed can be used in synthesis to support plants growth or can be substantially reduced by denitrification [1].

2.2. Necessity of removing nitrogen from wastewater

The excessive accumulation of different forms of nitrogen in the surface and underground waters can lead to both adverse ecological effects and harmful effects on human health.

From the study of the potential sources of production of substances with a high degree of pollution, it is found that, nowadays, nitrogen is a constant presence both in the wastewater from the population and from the industries.

The discharge of waste water, treated or untreated, regardless of its nature, containing nitrogen compounds, have harmful effects on the emissaries, especially if they are lakes or rivers with low flow rates, where the process of water self-purification becomes insufficient, the water quality being severely damaged and also difficult to recover over time.

An indirect effect of the discharge of these types of water is the eutrophication process.

Due to the nitrogen compounds present in the water taken from rivers, water treatment costs increase when the water capture is located downstream of the discharge points of the insufficiently treated wastewater [1].

3. THE MATHEMATICAL MODEL OF THE PROCESS OF NITRIFICATION IN RIVER WATER

Nitrification is a process by which the biological oxidation of nitrogen - found in water in the form of ammonium ions (NH_4^+), or in the form of gas (NH_3) - is carried out in a first stage to the nitrite phase (NO_2^-) and then to the nitrate phase (NO_3^-). This takes place in an aerobic environment, mainly due to two aerobic autotrophic bacteria, respectively *nitrosomonas and nitrobacter*, commonly called nitrifiers or nitrifying bacteria [1]. Figure *2* presents schematically such a process.

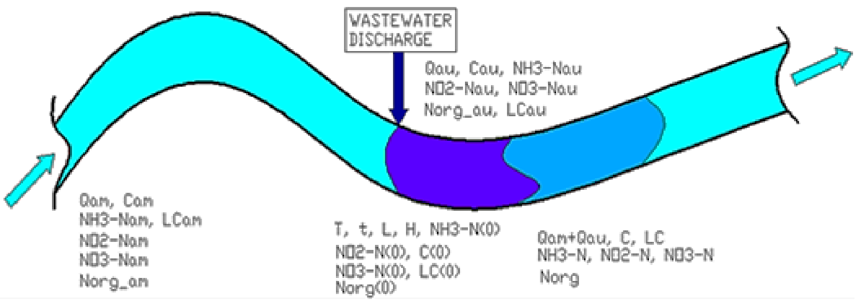

Fig. 2 River scheme for which the mathematical model was developed

The mathematical equations that describe the nitrification process and oxygen consumption in the nitrogen and carbon phase are [3-8]:

$$\frac{d\left[N_{org}\right]}{dt} = -K_{01} \cdot \left[N_{org}\right] \tag{1}$$

$$\frac{d\left[NH_3 - N\right]}{dt} = K_{01} \cdot N_{org} - K_{12} \cdot f_{12} \cdot \left[NH_3 - N\right] \tag{2}$$

$$\frac{d\left[NO_2 - N\right]}{dt} = K_{12} \cdot f_{12} \cdot \left[NH_3 - N\right] - K_{23} \cdot f_{23} \cdot \left[NO_2 - N\right] \tag{3}$$

$$\frac{d\left[NO_3 - N\right]}{dt} = K_{23} \cdot f_{23} \cdot \left[NO_2 - N\right] \tag{4}$$

$$\frac{dL_C}{dt} = -K_{L_C} \cdot L_C \tag{5}$$

$$\frac{dC}{dt} = -K_{L_C} \cdot L_C - r_{12} \cdot K_{12} \cdot f_{12} \cdot [NH_3 - N] - \\ - r_{23} \cdot K_{23} \cdot f_{23} \cdot [NO_2 - N] + K_a \cdot (C_s - C) \tag{6}$$

where:

$$K_{01} = K_{01}(20) \cdot \theta_{01}{}^{(T-20)} \tag{7}$$

$$K_{12} = K_{12}(20) \cdot \theta_{12}{}^{(T-20)} \tag{8}$$

$$K_{23} = K_{23}(20) \cdot \theta_{23}{}^{(T-20)} \tag{9}$$

$$K_{L_C} = K_{L_C}(20) \cdot \theta_{L_C}{}^{(T-20)} \tag{10}$$

$$K_a = K_a(20) \cdot \theta_a{}^{(T-20)} \tag{11}$$

$$\theta_{01} = 1.085, \theta_{12} = \theta_{23} = 1.05, \theta_{L_C} = 1.047, \theta_a = 1.024 \tag{12}$$

$$f_{12} = 1 - e^{-K_{12}*C} \quad (13)$$

$$f_{23} = 1 - e^{-K_{23}*C} \quad (14)$$

$$r_{12} = 3.43 gO/gN, r_{23} = 1.14 gO/gN \quad (15)$$

$$K_a(20) = \frac{a \cdot v^b}{H^c} \quad (16)$$

Table 2 Coefficient (*Ka)* values equation (16) determined by various authors

Nr. Crt.	a	b	c	Limits of application	Authors
1	3.93	0.5	1.5	H = 0.3÷9.14 m v = 0.15÷0.49 m/s	O'Connor-Dobbins (1956)
2	5.026	1	1.67	H = 0.61÷3.35 m v = 0.55÷1.52 m/s	Churchill et al. (1962)
3	5.3	0.67	1.85	H = 0.12÷0.73 m v = 0.3÷0.55 m/s	Owens & Gibbs 1964
4	5.5773	0.607	1.689	H = 0.12÷3.48 m v = 0.04÷1.52 m/s	Bennett and Rathburn (1972)

$$C_s = 14.652 - 0.41022 \cdot T + 0.007991 \cdot T^2 - 0.000077774 \cdot T^3 \quad (17)$$

$$v = \frac{Q}{L \cdot H} \quad (18)$$

If there are several impurity sources with variable flows and loads, the total concentration (C) is determined with the relation:

$$C = \frac{\sum (C_i \cdot q_i)}{Q} \quad (19)$$

Starting from the above equations [3-8], I developed in Scilab-Xcos [9] the schemes from figures 3, 4 and 5, with the help of which, different scenarios can be simulated. Thus, for different temperatures, flow rates of river water and wastewater flows, it is possible to see how the concentrations of: organic nitrogen (N_{org}), ammonia nitrogen (NH_3-N), nitrite nitrogen (NO_2-N), nitrate nitrogen (NO_3-N), oxygen (C) evolve over time and biochemical oxygen consumption for the oxidation of carbon containing organic substances (LC) in water.

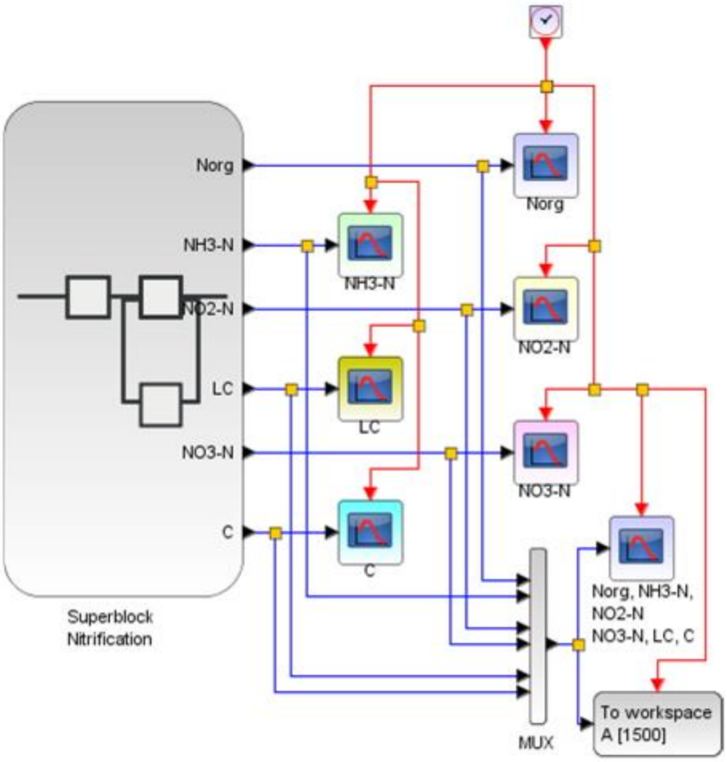

Fig. 3 Xcos simulation scheme of the nitrification process and the evolution of dissolved oxygen concentration in water

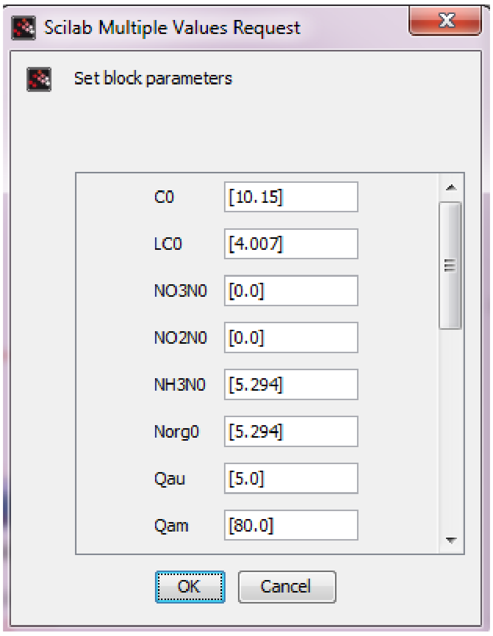

Fig. 4 Parameters box Superblock Nitrification in figure 3

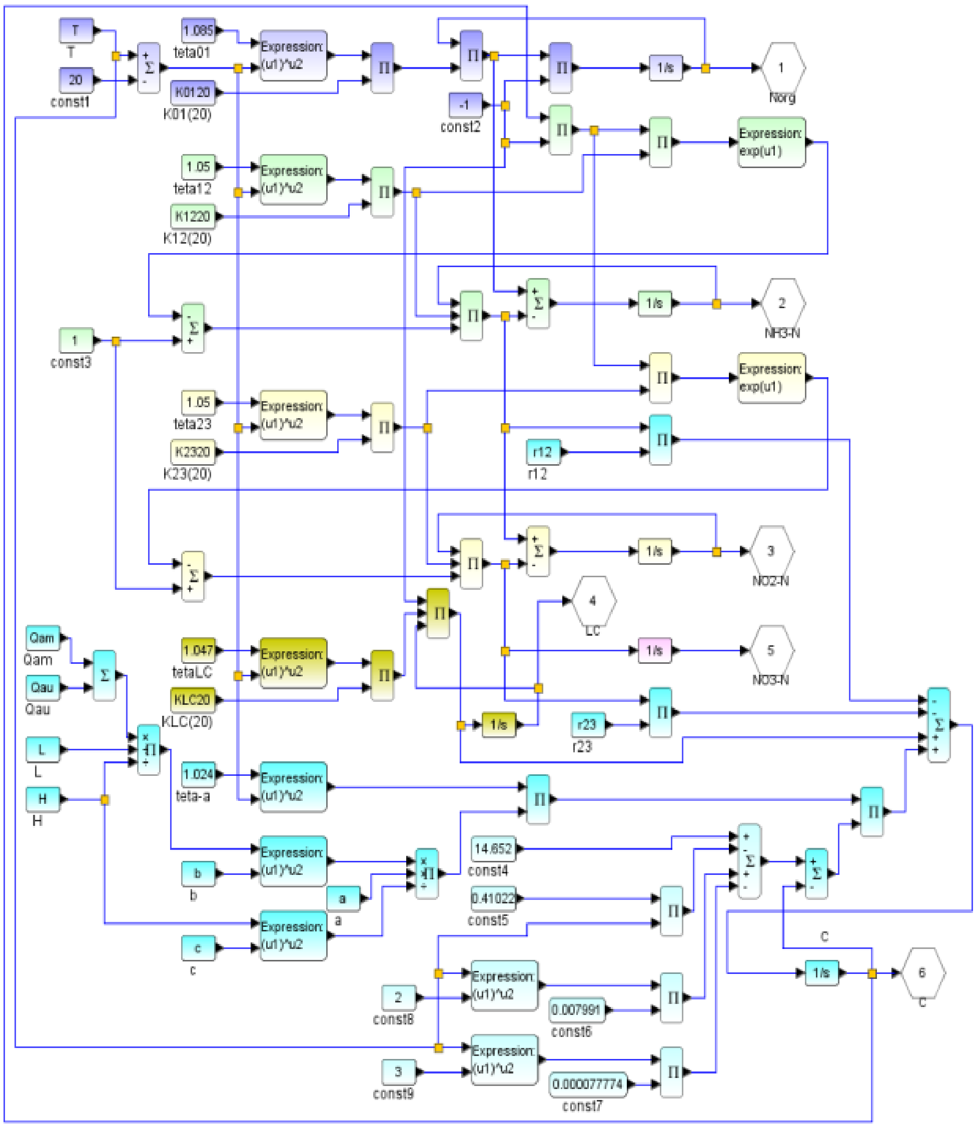

Fig. 5 Superblock Nitrification Xcos diagram in figure 3

4. EXAMPLE OF SIMULATION

Initial data:

- River flow upstream of the wastewater discharge $Q_{am}=80\ m^3/s$;
- Wastewater flow $Q_{au}=5\ m^3/s$;
- Concentration of dissolved oxygen in river water upstream of the wastewater discharge $C_{am}=0.94\cdot C_s$;

- Concentration of dissolved oxygen in wastewater $C_{au}=3\ mg/l$;
- Consumption constant of organic substances containing carbon at temperature of 20 ^{0}C $K_{LC}(20)=1.1\ day^{-1}$;
- The oxidation constant of organic nitrogen at temperature of 20^{0}C $K_{01}(20)$ =0.25 day^{-1};
- The oxidation constant of ammonia nitrogen at temperature of 20 ^{0}C $K_{12}(20)$=0.25 day^{-1};
- The oxidation constant of nitrate nitrogen at temperature 20 ^{0}C $K_{23}(20)$ =0.75 day^{-1};
- Average river channel width $L=90\ m$;
- Average river channel depth $H=2.5\ m$;
- The coefficients of equation (16) a = 3.93, b = 0.5, c = 1.5 (O'Connor-Dobbins 1956);
- Water temperature $T=10^0\ C$;
- The time for which the simulation is done $t=20\ days$;
- $L_{Cau}=35mg/l$; $L_{Cam}=2.07mg/l$;
- $N_{org.am}=5mg/l; N_{org.au}=10mg/l; (NO_2\text{-}N)_{am}=(NO_2\text{-}N)_{au}=(NO_3\text{-}N)_{am}=(NO_3\text{-}N)_{au}=0mg/l;$ $(NH_3\text{-}N)_{am}=5mg/l; (NH_3\text{-}N)_{au}=10mg/l;$
- Biochemical oxygen consumption for the oxidation of carbon-containing substances from water at the wastewater discharge point is:

$$LC(0)=\frac{Q_{am}\cdot L_{C\,am}+Q_{au}\cdot L_{C\,au}}{Q_{am}+Q_{au}}=4.007mg/l$$

- Concentration of dissolved oxygen in the water at the point of discharge of wastewater is:

$$C(0)=\frac{Q_{am}\cdot C_{am}+Q_{au}\cdot C_{au}}{Q_{am}+Q_{au}}=10.15mg/l$$

- Concentration of organic nitrogen in water at the discharge point of the wastewater is:

$$N_{org}(0)=\frac{Q_{am}\cdot N_{org\,am}+Q_{au}\cdot N_{org\,au}}{Q_{am}+Q_{au}}=5.294mg/l$$

- Concentration of ammonia nitrogen in water at the discharge point of the wastewater is:

$$(NH_3-N)(0)=\frac{Q_{am}\cdot(NH_3-N)_{am}+Q_{au}\cdot(NH_3-N)_{au}}{Q_{am}+Q_{au}}=5.294mg/l$$

- Concentration of nitrite nitrogen in water at the discharge point of the wastewater is:

$$(NO_2 - N)(0) = \frac{Q_{am} \cdot (NO_2 - N)_{am} + Q_{au} \cdot (NO_2 - N)_{au}}{Q_{am} + Q_{au}} = 0mg/l$$

- Concentration of nitrate nitrogen in water at the discharge point of the wastewater is:

$$(NO_3 - N)(0) = \frac{Q_{am} \cdot (NO_3 - N)_{am} + Q_{au} \cdot (NO_3 - N)_{au}}{Q_{am} + Q_{au}} = 0mg/l$$

Following the simulation above, you can graphically see the evolution (in time and for a certain temperature) of the following parameters: biochemical oxygen consumption for the oxidation of organic substances containing carbon in water (L_C), organic nitrogen concentrations in water (N_{org}), nitrogen ammonia (NH_3-N), nitrite nitrogen (NO_2-N), nitrate nitrogen (NO_3-N) and dissolved oxygen concentration in water (C) (figure 6).

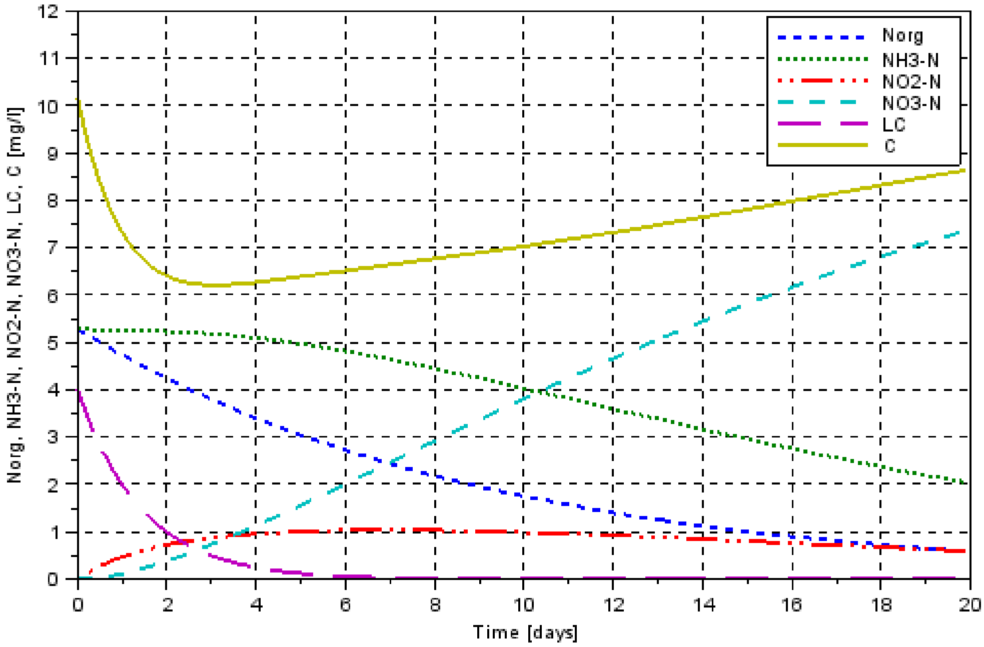

Fig. 6 Evolution of the biochemical consumption of oxygen in the river water for the oxidation of organic substances containing carbon (L_C), of the concentrations in water of organic nitrogen (N_{org}), ammonia nitrogen (NH_3-N), nitrite nitrogen (NO_2-N), nitrate nitrogen (NO_3-N) and dissolved oxygen concentration (C) in water for a period of 20 days for water temperature of 10 ^{0}C

5. CONCLUSIONS

The calculation programme (Figures 3÷5) developed by the author of this article in Scilab-Xcos, solves the mathematical equations (1÷6) that describe the evolution of oxygen concentration in the water of a river C, biochemical oxygen consumption for the oxidation of the organic substances containing (L_C) carbon in water and organic nitrogen concentrations in water (N_{org}) ammonia nitrogen (NH_{3}-N), nitrite nitrogen (NO_{2}-N), nitrate nitrogen (NO_{3}-N). Thus, this program is useful at designing and operating the wastewater treatment plants, simulations can be made and thus it is possible to see how the above-mentioned parameters evolved during the simulated time period and for the specific conditions of each individual case, under the conditions to vary the determening parameters in the case of these these processes (temperature, river water flow, wastewater flow, wastewater loads, etc.).

Moreover, this calculation program is also useful for the exploitation of the watercourses, as the pollution sources have a high organic load and if there is a supply in the reservoirs associated to the stream, the stream flow can be supplemented in order to reduce the the impact of pollution. This program can be used for simultating different scenarios in order to see for which flow rates of watercourse, respectively, the impact of pollution is minimal [8].

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Note:

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