Biochemical Processes of Self-Purification Model in Small Rivers

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Abstract. The studying of water self-purification ability is a part of the regional limits developing problem that has the important role for the water quality management. This work shows that a simple model structure can be set up to describe the water quality in small river basins in terms of carbon, nitrogen and phosphorus compounds, when it is unfeasible to use complex models. In this article we used both mathematical modeling and natural sampling of surface water in small river of Central Siberia for the control parameters assessment. The obtained results have allowed analyzing the annual variations of the nitrification and denitrification rates, the mineralization rate of total phosphorus and organic nitrogen. The contribution of main biochemical processes in self-purification of the small river under conditions of Central Siberia climate is estimated numerically.

Keywords: self-purification processes, one-dimensional advective-diffusive equation, upwind approximation scheme.

1 Introduction

Water quality management is an essential problem for preserving water resources and facilitating sustainable socio-economic development in watershed systems. However, this task is usually affected by a variety of uncertainties raising from the stochasticity in hydrodynamic conditions, the variability in the pollutant transport, the physicochemical processes, the indeterminacy of available water and wastewater, etc. [1]. The studying of water self-purification ability is a part of the problem of the regional limits developing of water quality that has the important role for the water quality management. Mechanisms of self-purification processes are strongly influenced by local characteristics of stream. A model developed for a certain stream type and region is in many cases not applicable to other stream types or regions. Therefore, local stream characteristics should be included if the model should be more generally applicable [2].

Self-purification of natural water systems is a complex process that often involves physical, chemical, and biological processes working simultaneously. The water is purified in the sense that the concentration of waste material has been reduced mostly by means of biodegradation processes. Therefore, this process is very closely tied with the dissolved oxygen content and indeed with all the sources and sinks of oxygen in a river. So dissolved oxygen (DO) and biochemical oxygen demand (BOD) are critical water quality parameters. [3].

Research on the modeling of the BOD-DO interaction in the river has been dominated by the classical model of Streeter and Phelps, which first appeared in 1925, and has been improved by Dobbins and Camp, Peter Young and Bruce Beck, C.J.Harris, etc. [3]. These models have been widely used not only in to assess water quality, but also to predict damage resulting from the implementation of water resources management measures [4]. However, each water quality model has its own limiting conditions. Therefore, these models still need to be further studied to overcome these shortcomings.

Eutrophication of surface water is closely connected to the self-purification processes. Eutrophication is enrichment in nutrients, principally phosphorus and nitrogen, leading to an increase in algae and higher plant growth and a disturbance of the ecological balance of the aquatic ecosystem. In contrast to standing waters, the effects of eutrophication and enhanced organic load on running water ecosystems have not been given much attention [5] , [6]. Models that include all these factors are not yet available but there are many models which focus on only a part of these processes. Some of these parts can be used to fill in a complete stream eutrophication model. However, because of differences between stream types and regions these parts should first be tested for their applicability to the stream type and region of interest [2].

The present study is based on and continues the project aimed at the studying of self-purification processes under strong anthropogenic exposure in small rivers of Krasnoyarsk region that was started by authors in 2013. The principal equations of the developed self-purification model are specified in [7]. The developed model generally has shown a satisfactory capability in reproducing the measured values of nitrogen and phosphorus concentrations. The main goal of this paper is to study the contribution of biochemical transformation of biogens in self-purification processes of small rivers. For this goal it was developed mathematical approach for estimation of some biochemical parameters such as reaeretion and biodegradation rates, transformation rates of phosphorus and nitrogen compounds. Then it were calculated the amounts of these rates for small river of Central Siberia and finally, were described the regional features of ones varieties depends on hydrological conditions.

2 Object description

The Kacha river considering in this study is the river in the basin of Central Enisey. Hydraulically the river is subjected to spring flood, but water level reduces significantly during the summer months, when the water flow quality becomes critical and the self-purification processes are almost stopped. Sharp continental climate of Central Siberia, basin geology and vegetation define hydrological conditions of river flow. So, river flow rate and flow velocity differ significantly in various hydrological stages. For example, flow rate varies in the range 0.1 - 41 m3/s, maximum level reaches in spring flood. The maximal value of water temperature above 20 C is observed in June. All factors define regional features of the eutrophication processes.

To verify the developed model it was used the data from state monitoring network for the period since 1985 to 2014 in Kacha river. The hydrochemical parameters are measured one time in month (7-12 times in year). In this work we use the concentrations of oxygen, nitrogen, phosphorus and their compounds. The hydrological parameters such as river flow rate, temperature, stream velocity are measured every day. All measurements have carried out in three hydrological posts of Kacha river whose basin length is about 100 km.

Moreover, some complex parameters were measured in Kacha river during 2013 - 2016: pH, dissolved oxygen, BOD, redox potential and conductivity. An area of sampling lies near one of hydrological posts in estuary. These parameters measured two times in week during free ice cover period (since May to October).

3 Model structure

One of the difficult problems of self-purification studying - the variety of ecological structure from source to mouth of river [8]. The self-purification processes in the river are complex and can be described by a series of bio-chemical and hydrological parameters. Biochemical oxidation process through which organic wastes are consumed leaving behind end products such as carbons, phosphates and nitrates [3].

Inorganic carbon availability is determined by levels of dissolved carbon dioxide. Concentration of carbon dioxide is less significantly than dissolved oxygen concentration. So, carbon dioxide isn't key element in self-purification processes in the Siberian water ecosystems as this can be in equatorial and subequatorial ecosystems. In continental climate conditions carbon dioxide in water streams has influence mainly on redox processes. Organic carbon is included in the model indirectly via biochemical oxygen demand (BOD). The transformation processes of phosphates and nitrates are coupled in the model directly.

In general the one-dimensional advective-diffusive dynamic for reactive pollutant neglecting the diffusion term can be written as a differential equation [9], [10], [11]:

$$\frac{d(\omega \cdot C_j)}{dt} + \frac{d(Q(t) \cdot C_j)}{dx} = K_{C_j}(t) \cdot C_j \cdot \omega + G_j(t) \cdot \omega \tag{1}$$

where $K_{C_j}(t)$ is a function of decay of j pollutant concentration, that characterizes transformation velocity defined by the influence of chemical and biological processes, $Q(t)$ is a function of river flow rate, ω is cross-sectional area of river (m^2) and $G_j(t)$ is a runoff of j pollutant.

The equations system based on this (1) includes the equations for concentration of phosphate C_{PO_4}, total phosphorus C_{DOP}, ammonium nitrogen C_{NH_4}, nitrate nitrogen (including nitrite nitrogen) C_{NO_3}, total nitrogen C_{DON}, biochemical oxygen demand C_{org}, dissolved oxygen C_{O_2} [7]. This model is one-dimensional in the x-direction that can be appropriate only for small rivers that is characterizing by small fluctuations on vertical and horizontal coordinates. This assumption wouldn't be appropriate for large rivers. Two- and three-dimensional representations are also possible but they have considerable computational complexity.

This system is approximated by numerical equations with time-space grid $(t_n; x_i) : t_{n+1} = t_n + \tau(n = \overline{0, N})$, $x_{i+1} = x_i + \Delta(i = \overline{1, L})$, where $\tau = const$ is time step, $\Delta = const$ is space step. The upwind approximation scheme is used to solve these equations. It's explicit scheme based on three-point grid [7], [12]. To assure the convergence of numerical scheme here was used the assumption that space step must be greater than time step.

4 An intensity estimation of biochemical transformation processes

All model's rates vary with temperature, microbial metabolism, the composition and concentration of the biogens from the pollution source.

The estimation of K_{RO} and K_{BOD} parameters is important for selecting a solution curve that best represents a real system. However, there is no method available to determine values that fit precisely to the reality of a given water body. Reaeration coefficients vary widely due to their dependence on air-water interface turbulence making them complex and difficult to accurately measure. High nutrient levels result a high biomass of algae and plants and an increased biodegradation rate. If algae and plants produce oxygen during the day, they consume this during the night and an increased biomass means an increase uptake of oxygen at night. It also means an increase in organic matter when the organisms die. Decomposition of organic matter is increased in presence of high nutrient level, there is more organic matter to decompose and decomposition consumes oxygen. All these processes can lead to oxygen depletion [4], [13].

The highest K_{RO} values may be observed during summer due to the higher concentration of organic matter while maintaining a contribution of organic matter in the stream. A high temperature of water river promotes this process (greater 20^0C in July). The classical model of Streeter and Phelps defines the ratio of K_{RO}/K_{BOD} as the self-purification constant and it is equal 0.50–5.0. Several studies give methods to estimate K_{RO} and K_{BOD} that provide reasonable approximations within predefined limits. However, due to the non-linearity nature of these coefficients, there is no formula for generic cases.

The nitrification and denitrification velocity depends on temperature and pH value of surface water. For example, the denitrification process reaches maximal activity, when pH value is in the range 7.0–8.2. This process is stopping when the pH value is lower than 6.1 or higher than 9.6. Nitrogen mineralization is considered as transformation of organic nitrogen to inorganic.

Primarily, decay rates were included in the self-purification model as constants. However, the results of numerical calculations were differing from natural measurements considerably. This can was connected with significantly seasonal variability of these rates.

The algorithm of calculation of destruction rates includes next steps. Firstly, the equation (1) is written as the system including seven equations for next variables: concentrations of phosphorus compounds C_{DOP} and C_{PO_4}, ammonium compounds C_{NH_4}, C_{NO_3} and C_{NO_3}, biochemical oxygen demand C_{org}, and dissolved oxygen C_{O_2}. These equations were specified in [7]. Next the equations for biochemical destruction rates are obtained by algebraic manipulations with previous system. Finally, the rate's equations are written according numerical scheme. As a result of algorithm's applying it was obtained a system of six numerical equations:

1) Mineralization rate of total phosporus:

$$K(t)_{PO_4} = \frac{1}{C_{DOP}} \cdot \left(-\frac{d(C_{PO_4})}{dt} - \frac{1}{\omega} \cdot \frac{d(Q(t) \cdot C_{PO_4})}{dx} + G(t)_{PO_4} \right) \quad (2)$$

2) Nitrogen mineralization rate:

$$K_{NH_4}(t) = \frac{1}{C_{DON}} \cdot \left(\frac{d(C_{DON})}{dt} + \frac{1}{\omega} \cdot \frac{d(Q(t) \cdot C_{DON})}{dx} - G(t)_{DON} \right) \quad (3)$$

3) Nitrification rate:

$$\begin{aligned} K(t)_{12} = \frac{1}{C_{NH_4}} \cdot \Bigg(-\frac{d(C_{NH_4})}{dt} - \\ -\frac{1}{\omega} \cdot \frac{d(Q(t) \cdot C_{NH_4})}{dx} + G(t)_{NH_4} + K(t)_{NH_4} \cdot C_{DON} \Bigg) \end{aligned} \quad (4)$$

4) Denitrification rate:

$$\begin{aligned} K(t)_{NO_3} = \frac{1}{C_{NO_3}} \cdot \Bigg(-\frac{d(C_{N0_3})}{dt} - \\ -\frac{1}{\omega} \cdot \frac{d(Q(t) \cdot C_{NO_3})}{dx} + G(t)_{NO_3} + K(t)_{12} \cdot C_{NH_4} \Bigg) \end{aligned} \quad (5)$$

5) Biochemical degradation rate:

$$\begin{aligned} K(t)_{BOD} = \frac{1}{C_{org}} \cdot \Bigg(-\frac{d(C_{org})}{dt} - \\ -\frac{1}{\omega} \cdot \frac{d(Q(t) \cdot C_{org})}{dx} + K(t)_{NO_3} \cdot C_{N0_3} \cdot \beta_{O_2/DN} \Bigg) \end{aligned} \quad (6)$$

6) Reaeration rate:

$$\begin{aligned} K(t)_{RO} = \frac{1}{C_{O_2}} \cdot \Bigg(-\frac{d(C_{O_2})}{dt} - \frac{1}{\omega} \cdot \frac{d(Q(t) \cdot C_{O_2})}{dx} + \\ +K(t)_{12} \cdot C_{NH_4} \cdot \beta_{O_2/NT} + K(t)_{BOD} \cdot C_{org} \Bigg) \end{aligned} \quad (7)$$

where $\beta_{O_2/DN}$ is the yield factor describing the amount of oxygen used for denitrification (gO_2/gN), $\beta_{O_2/NT}$ is the yield factor describing the amount of oxygen used for nitrification (gO_2/gN).

Time-space grid for the equations (2)-(7) is the same as for equation (1).

Next step connects to defining run-off values. Low-water small rivers of Eastern Siberia are recharged mostly by groundwater in winter. This occurs because all precipitation falls in a solid phase and there is no their thawing. The water hardness value is the indicator of increase in a share of an underground water. In spring and summer this parameters is much lower because of influence of liquid precipitation. The volume of groundwater run-off is calculated with using the hydrochemical analysis of surface water quality of Kacha river. The greatest values characterize the groundwater run-off of nitrate nitrogen.

5 Results and discussion

The observation results received on three hydrological posts of the state monitoring network during 29 years were used as input data to calculate the biochemical parameters. The calculation results for whole time period were averaged monthly. In this study the length of computational domain was 100 km, space step was 0.5 km and time step was 1 day.

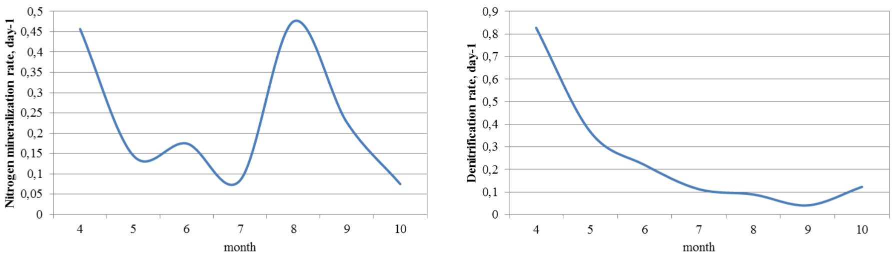

Fig. 1. Seasonal variations of nitrogen destruction rates for self-purification model

Some results of calculations by the system (2) - (7) are shown on Figure 1 - 2. Receiving numerical functions for describing the transformation rates allows considering an influence of all factors without construction of functional dependences. In general, the values of transformation rates demonstrate inhibition of self-purification processes in river.

Seasonal factor has influence on variations of all modeling parameters. The maximal values of reaeration rate are obtained for period from end of April to early in June. This can be explained by flood peak in Kacha river when flow rate and water level are highest. A decreasing of the nitrogen mineralization rate is induced by some reasons having regional features such as low flow rate, low concentration of dissolved oxygen and high level of chemical pollution. The

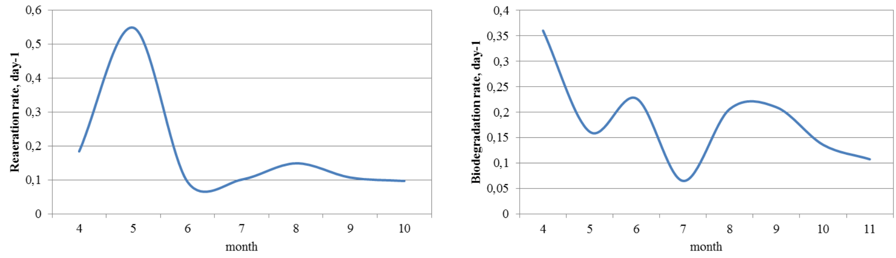

Fig. 2. Seasonal variations of oxigen transformation rates for self-purification model

biodegradation rate depends mostly on phytoplankton activity that is minimal in summer low water (during July). The value of this rate is increasing significantly in the period of spring and autumn high water seasons. The obtained dependencies of biochemical rates characterize both common seasonal variations features and regional specialty, for instance, high water level during flood, short vegetation period and low water temperature.

Variability ranges of the transformation rates and parameters of developing model are presented in Table 1. The variations of biochemical purification rates are studying not often, so ones have shown as variability ranges to compare with the data that were given for other rivers. These values agree in general with values obtained in other rivers and regions. However, exact comparison is incorrect because literature data were calculated for various water bodies differing both in climatic and hydrological conditions.

All factors influencing on the variability of biochemical parameters are generalized in Table 1. A water temperature is common factor for the most of calculated rates. Numerical estimations of temperature influencing on studied rates haven't obtained in this study. Overall on the base of water quality monitoring data it can conclude that the main processes of biogens transformation and water self-purification are observed in the period from April to October, when water temperature is higher than 0°C. Winter period is characterized the presence of ice cover on water surface, so the sampling in studied river aren't executed. And to estimate the values of biochemical parameters in this period it's impossible.

Table 1 presents a coefficient that was named in this study the contribution to the model accuracy. To define one the calculations with using equation (1) are executed for rates K_{RO}, K_{BOD}, K_{12}, K_{NO_3}, K_{PO_4}, K_{NH_4} as constant values and as functions of time (as shown in Fig. 1). The contribution to the model accuracy was obtained on the base of comparison of above mentioned calculations with monitoring data (Table 1). This coefficient characterizes numerically an influence of considering the biochemical rates like time functions in the developed model. This allows taking into account the influence of seasonal variability of all factors.

All processes in small rivers have different velocity, but the velocity of phosphorus transformation is a slowest. It can be explain that phosphorus concentra-

Table 1. The principle parameters of self-purification model

Rates and parameters	Variability range	Given in the literature data	Influencing factors	Contribution to the model accuracy, %
Reaeration rate K_{RO}, day^{-1}	$0.09 \ldots 0.55$	$0.1 \ldots 0.25$ [14] $0.05 \ldots 0.5$ [15]	temperature, BOD, dissolved oxygen	$7 \ldots 9$
Biodegradation K_{BOD}, day^{-1}	$0.05 \ldots 0.35$	0.06 [14] $0.4 \ldots 1.5$ [15]	temperature, nitrate nitrogen, BOD, dissolved oxygen	$9 \ldots 14$
Nitrification K_{12}, day^{-1}	$0.06 \ldots 0.6$	$0.027 \ldots 0.76$ [16] 0.04 [11]	temperature, pH value, nitrate and ammonium nitrogen concentration	$10 \ldots 15$
Denitrification K_{NO_3}, day^{-1}	$0.7 \ldots 1.1$	0.1 [11]	temperature, pH value, nitrate and ammonium nitrogen concentration	$12 \ldots 18$
Phosphorus mineralization rate K_{PO_4}, day^{-1}	$0.05 \ldots 0.2$	0.14 [11]	total phosphorus, phosphates	$2 \ldots 7$
Nitrogen mineralization rate K_{NH_4}, day^{-1}	$0.01 \ldots 0.45$	0.06 [11]	ammonium nitrogen, total nitrogen	$3 \ldots 9$

tion is lower significantly than nitrogen concentration in small rivers of Central Siberia. Also, nitrogen transformation processes demonstrate the greatest contribution to model accuracy.

6 Conclusions

This work presents numerical algorithm for estimation of biochemical coefficients of self-purification processes based on the developed mathematical model. The given algorithm was used to define the values of reaeretion and biodegradation rates, transformation rates of phosphorus and nitrogen compounds for small river in Central Siberia. It was analyzed the influence of regional hydrological and meteorological factors on temporal variations of biochemical coefficients of self-purification processes. It was estimated the contribution of developed approach to accuracy on numerical calculating of studying processes in comparison with experimental measurements.

To improve reproducing the measured values via model calculation the daily variations of the rates giving the greatest contribution to model accuracy will be studied further. The developed model can be useful to solve some problems, for instance an optimization of environmental monitoring, a forecasting of ecosystem productivity, a developing of regional water quality limitations and management of water quality.

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