

## SPREADING AND TRANSFORMATION OF NUTRIENTS IN THE REACH OF THE BECEJ-BOGOJEVO CANAL, SERBIA

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**Abstract:** One of the major waterways in Serbia is the hydro-system Danube-Tisa-Danube (HS DTD) in the Province of Vojvodina. Since its water quality has been significantly deteriorated, especially on some reaches, the aim of the paper is to test a combined approach based upon leading European and United States concepts for assessment and better management within the hydrosystem. Transport and transformation of nutrients, including nitrogen compounds,  $\text{NH}_4\text{-N}$  and  $\text{NH}_3\text{-N}$ , and total phosphorous, have been modeled for one of the most polluted reaches of the canal Becej-Bogojevo. Modeling of the watercourse applied QUAL2K water quality modeling tool. Calibration of the model and subsequent validation required series of field measurements, including hydrometric measurements, quality parameters of the water samples and meteorological data. The developed model of the system was applied for analyzing different possible scenarios where water quality and hydrometric historical data were used as inputs. Obtained results gave an insight in the behavior of these pollutants in the investigated aquatic surrounding. Application of the methodology could form a basis for integral management of the pollution in the whole canal network of the HS DTD. By producing a pattern of source allocation, i.e. sharing of the pollution loading among the sources, it would contribute in the process of attaining the compliance with standards.

**Key words:** water quality, modeling, nutrients, QUAL2K, Fish directive, TMDL, environmental protection

### 1. INTRODUCTION

The most important legal framework within the European Union (EU), which regulates water policies, is the Water Framework Directive (WFD) (Directive, 2000/60/EC). The main goal of the WFD is reaching good water quality for all water bodies in the EU member states by the year 2015. Concerning this fact, efforts have been intensified on research and assessment of water quality related issues across the EU. These issues cover a variety of water related topics eg. preservation of human health, environment and biodiversity (Ferencz & Balog, 2010, Gurzau, et al. 2010, Dragičević, et al. 2010, Pârvulescu & Hamchevici, 2010, Gurzau, et al. 2011). That stands especially for the South-East Europe region in countries which relatively recently joined the EU, as well as for ones that are at its threshold.

The Republic of Serbia is striving towards the membership within the EU and reaching good water

quality poses an important challenge. For the northern province of Vojvodina, Hydrosystem Danube-Tisa-Danube (HS DTD) represents important canal network. It intersects the province from north-west end to the south west part. Total length of the HS DTD is 960 km including canals, and partly reconstructed natural watercourses. It is navigable on about 600 km. Level of the water in the HS DTD has been regulated by sluices, and pump stations. It connects 80 settlements with above one million of inhabitants of Vojvodina gravitating towards it. The main purpose of the HS DTD is drainage, irrigation, flood protection, navigation and water supply of industry. Therefore, it faces serious water quality deterioration problems, especially on some reaches. Water quality of the HS DTD has been affected by different influences originating from point and non point sources. The paper examines water quality, spreading and transformation of nutrients along the most polluted reaches of two canals - canal Vrbas-Bezdan and Becej-Bogojevo.

Corresponding legislative policies, e.g. EU WFD and US Clean Water Act (USEPA, 1999), impose the limit values for the total amount of pollutants allowed to be released in the watercourse by all sources. They differ in that EU standards impose limit values of total pollutants expressed as concentration, while US standards impose limit values to be expressed as loading capacity, i.e. Total maximum Daily Load (TMDL) (USEPA, 1999). In this paper a novel approach has been applied that combines elements of both the EU WFD's and the United States Environmental Protection Agency's (US EPA) TMDL.

Finally, modeling and simulations are performed, using QUAL2K water quality simulation tool, to analyze possible scenarios. Based on the obtained results TMDL values has been determined in order to satisfy limit values set by the Fish directive (Directive, 2006/44/EC) for Cyprinid fishes. This procedure could be the basis for the integral management of pollution in the canal.

## 2. MATERIALS AND METHODS

### 2.1. Site description

The canals of the HS DTD are lowland watercourses and are characterized by low mean stream velocity, and mild slope. The canal Vrbas - Bezdán is 80,9 km long and starts near the town of Vrbas at the point called Triangle, since it represents point of confluence between that canal and the Becej - Bogojevo canal. It finishes in the Danube river at Bezdán lock. The Becej-Bogojevo canal is 90 km long and it starts from the Tisa river at Becej lock (Fig. 1). The regime of both canals has been regulated by locks Vrbas and Kucura. Significant polluters of the Vrbas - Bezdán canal waters are food processing industries, farms and municipal wastewater discharge, etc. All these point sources either do not have at all waste water treatment plants, or they do, but not fully functioning. The reach between Vrbas and the Triangle is at the present is almost fully filled with industrial sludge, while canal Becej-Bogojevo has been designated as a fishing area. Still, due to the inflow of the polluted water occasional fish kills occur and the local inhabitants have repeatedly complained about unpleasant odor, and poor aesthetic outlook.

After the year 2000 a few efforts have been made in order to assess pollution level in the reach passing through Vrbas town. The project Revitalization of the DTD Grand Canal thought Vrbas was focused upon monitoring water quality, polluting effluents, planning of central wastewater treatment plant and mentioned coverage with sludge

(NIVA, 2006). Both studies confirmed that pollution of the canal is not only local problem, but it also reaches the Tisa river, and represents also significant pollution source for the Danube river. Based on estimated nutrient pollution 70% of pollution comes from industrial sources, while 20% and 10% are coming from municipal and agricultural sources, respectively (NIVA, 2006).

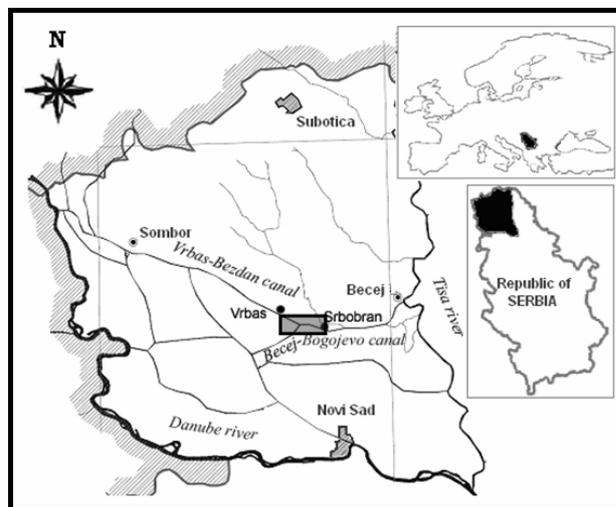


Figure 1. Map of the HS DTD in Backa district with investigated reaches of the Vrbas-Bezdán and the Becej-Bogojevo canals

### 2.2. Input data

Sampling for calibration of water quality was conducted in autumn in 2009, while validation was performed with measurements taken in spring, and summer in 2010. Samples were taken directly from canal current, from 1 m depth. Water quality analyses have included measurement of the following parameters: temperature, dissolved oxygen (DO), pH, conductivity, suspended solids, ammonium nitrogen ( $\text{NH}_4\text{-N}$ ), nitrate nitrogen ( $\text{NO}_3\text{-N}$ ), inorganic phosphorus (inorganic P) and total phosphorus (total P). Concerning hydrometric data two hydrometric measurements were taken on 14.58 km, and 4.47 km of the Becej-Bogojevo canal (Fig. 2) resulting in precise determination of its mean velocity and flow rate. Polluted canal reach Vrbas-Triangle was considered as a point source pollutant for the main Becej-Bogojevo canal. Its flow rate has been estimated by subtracting of two measured flow rates.

Both hydrometric measurement and water sampling were performed on the same day, within a few hours. Since water quality modeling requires input of certain meteorological parameters, following data were obtained simultaneously with other measurements: air temperature, due point temperature, wind speed and cloudiness.

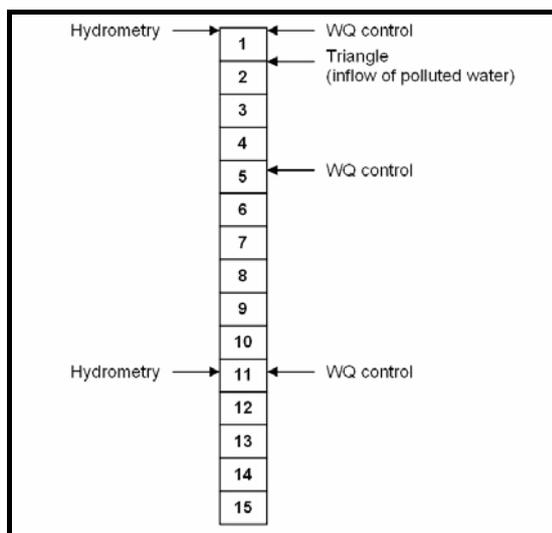


Figure 2. Modeling segments, point of pollution inflow, water quality (WQ) and hydrometric measurements

Water quality analyses showed significant concentrations of  $\text{NH}_4\text{-N}$ , inorganic P, and total P in polluted water and for this reason water quality modeling was focused upon these parameters. These measurements were applied to develop the model of this watercourse and perform its calibration and validation. Then the model has been used for simulating of the possible case scenarios. It was fed by the input data, including flow rates of both canals and major sources of pollutions, obtained from the database of Public Water Management Company (PWMC) Vode Vojvodine, and its cadastre of polluters.

### 2.3. Selection of modeling tool

QUAL2K is a river and stream water quality model, i.e. water quality modeling tool, which is intended to represent a modernized version of the QUAL2E (Chapra et al. 2006). The former version QUAL2E model has been enlisted among the major models currently in use (Cox, 2003, Horn et al. 2004).

The model simulates water flow as a one-dimensional, steady-state process that considers water quality parameters (DO, biological oxygen demand, sediment oxygen demand, algae, etc.), hydrometric and meteorological parameters and conventional pollutants such as nitrogen and phosphorus compounds. Because of its wide applicability and ease of use, Fan et al (2009) selected QUAL2K model for assessing water quality subject to contaminant loading. The tool was previously used for conditions characterizing canals in Vojvodina (Salvai & Bezdan, 2007, 2008; Piperski & Salvai, 2007, 2008).

QUAL2K simulates concentration changes of nitrogen and phosphorus compounds. For example study performed by Boyacioglu & Alpaslan (2007) modeled influence of  $\text{NO}_3\text{-N}$ , while Ennet et al. (2008) modeled  $\text{NO}_3\text{-N}$ ,  $\text{NH}_4\text{-N}$ , total nitrogen, inorganic P, and total P. Besides, the tool also models concentrations of  $\text{NH}_3\text{-N}$ , since it has been proven to be toxic for water organisms. However, in previous work no attention has been given to analyzing spreading of this compound. One of the main contributions of the paper is modeling of this water quality parameter.

#### 2.3.1. Unionized Ammonia

The tool simulates total ammonia. In water, the total ammonia consists of two forms: ammonium ion ( $\text{NH}_4^+$ ) and unionized ammonia ( $\text{NH}_3$ ). At normal pH (6 to 8), most of the total ammonia will be in the ionic form. However, at high pH,  $\text{NH}_3$  predominates. The amount of  $\text{NH}_3$  can be computed as (Chapra, et al. 2006):

$$n_{au} = F_u n_a \quad (1)$$

where  $n_{au}$  is the concentration of  $\text{NH}_3$  [ $\mu\text{gN/l}$ ],  $n_a$  is the total ammonia nitrogen [ $\mu\text{gN/l}$ ] and  $F_u$  is the fraction of the total ammonia that is in  $\text{NH}_3$  form,

$$F_u = \frac{1}{1 + 10^{-\text{pH}}/K_a} \quad (2)$$

where  $K_a$  is the equilibrium coefficient for the ammonia dissociation reaction, which is related to temperature by

$$\text{p}K_a = 0.09018 + \frac{2729.92}{T_a} \quad (3)$$

where  $T_a$  is absolute temperature [K], and  $\text{p}K_a = -\log_{10}(K_a)$ .

#### 2.3.2. Phosphorus compounds

Total P represents sum of organic and inorganic P compounds. Inorganic P increases due to organic phosphorus hydrolysis (DOPHydr) and phytoplankton respiration ( $r_{pa}\text{PhytoResp}$ ). It is lost via plant photosynthesis ( $r_{pa}\text{PhytoPhoto}$ ) and bottom algae uptake (BotAlgUptakeP). In addition, a settling loss (IPSettl) is included for cases in which inorganic P is lost due to sorption onto settleable particulate matter such as iron oxyhydroxides (Chapra, et al. 2006):

$$S_{pi} = \text{DOPHydr} + r_{pa}\text{PhytoResp} - r_{pa}\text{PhytoPhoto} -$$

$$\text{BotAlgUptakeP} - \text{IPSettl} \quad (4)$$

Where  $S_{pi}$  represents sources and sinks of inorganic P

$$\text{IPSettl} = \frac{v_{ip}}{H} p_i \quad (5)$$

where  $v_{ip}$  is inorganic P settling velocity [m/d],  $H$  is water dept and  $p_i$  is inorganic P concentration.

### 2.3.3. Canal segmentation

Qual2K requires dividing reach into segments, where it is considered that water is well mixed in each segment both laterally and vertically. Modeling segments are presented in Fig. 2. Each segment is 1km long except of the last one, of 0.58km. The program is employing hydraulics based on non-uniform, steady flow.

### 2.4. TMDL development

A concept of TMDL is established by Section 303(d) of the Clean Water Act [40 CFR 130.7 (c)(1)] and EPA's Water Quality Planning and Management Regulations (40 CFR Part 130). In the 1999 Protocol for Developing Nutrient TMDLs, EPA suggested several methods for the development of numeric criteria for nutrients (USEPA, 1999). TMDL represents the maximal amount of any pollutant that a waterbody can receive without impairing the water quality recommended by standards. Advantage of application of TMDL values lies in possibility of controlling inflow of pollutant load, and therefore represents the basis on which strategies for improvement and preservation of water quality could be developed.

A TMDL is the sum of the individual wasteload allocations for point sources and load allocations for nonpoint sources, including natural background, with a margin of safety. The TMDL can be described by the following equation 6:

$$\text{TMDL} = \text{LC} = \sum \text{WLA} + \sum \text{LA} + \text{MOS} \quad (6)$$

where:

**LC** is loading capacity, or the greatest loading a waterbody can receive without violating water quality standards;

**WLA** is wasteload allocation, or the portion of the TMDL allocated to existing or future point sources;

**LA** is load allocation, or the portion of the TMDL allocated to existing or future nonpoint sources and natural background; and

**MOS** is margin of safety accounting for uncertainty about the relationship between pollutant loads and receiving water quality.

A TMDL can be expressed in terms of mass

per time, toxicity, or other appropriate measures (USEPA, 1999). According to Borah et al. (2006) QUAL2K model can be used for calculating nutrient TMDLs for watercourses.

Integral approach requested by the TMDL concept has many similarities to the EU Water Framework Directive, and therefore its application within the Framework was elaborated by a number of authors (Lawson, 2005, Irvine, et al., 2005).

## 3. RESULTS AND DISCUSSION

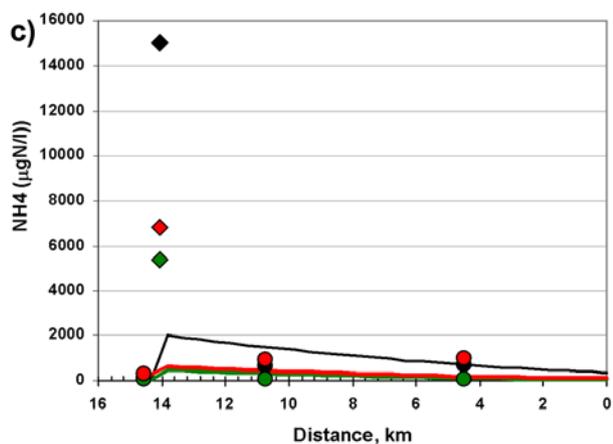
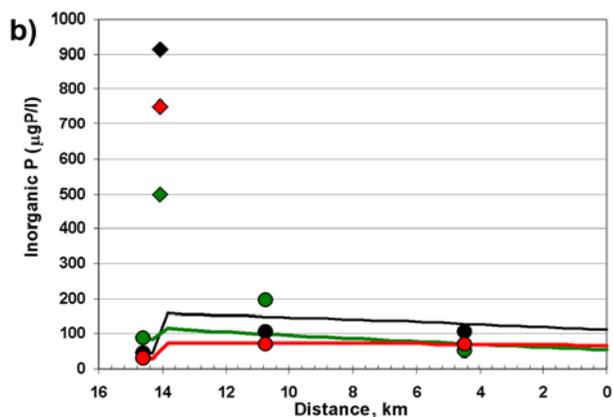
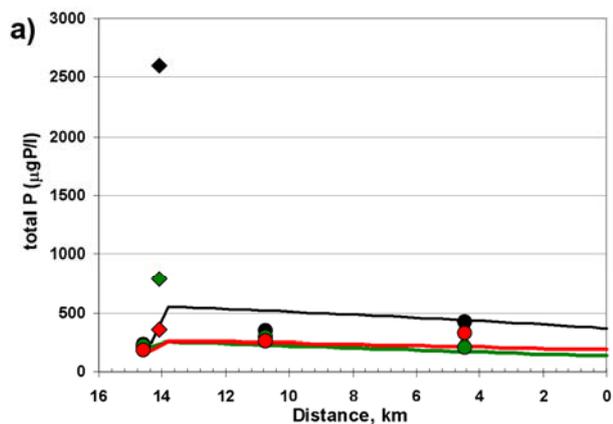
### 3.1. Model calibration and validation

The model was developed and then calibrated with data of water quality and hydrometric measurements obtained in the reach of the Becej - Bogojevo canal on September 23<sup>rd</sup>, 2009. Validation was performed using data measured on May 4<sup>th</sup>, and August 13<sup>th</sup>, 2010. Calibration and validation were performed for parameters which indicate pollution by following nutrients: inorganic P, total P, and NH<sub>4</sub>-N (Fig. 3). Since Fish directive (Directive, 2006/44/EC) concerns limit values for total P this parameter has been analyzed in detail. In addition, input values for inorganic P were used for better calibration of total P concentration. In order to obtain more precise modeling results, parameters indicating general conditions of water quality were also included: DO, conductivity, and pH, as well as above mentioned hydrometric measurements. Meteorological data were used in order to calculate heat budget.

Values shown in the figure 3 cover the distance of 14.58 km along the Becej-Bogojevo canal. At its 14.08 km is point of confluence with the Vrbas-Bezdan canal which is regarded as point source of pollution. These point source pollution values are marked with squares in Fig. 3. They also represent the inputs for developed simulation model. Measured values along the Becej-Bogojevo canal are marked with the circles, while simulation results are shown with lines for each of data sets. It can be seen that they correspond to each other in a satisfactory manner.

### 3.2. Analyses of possible scenarios

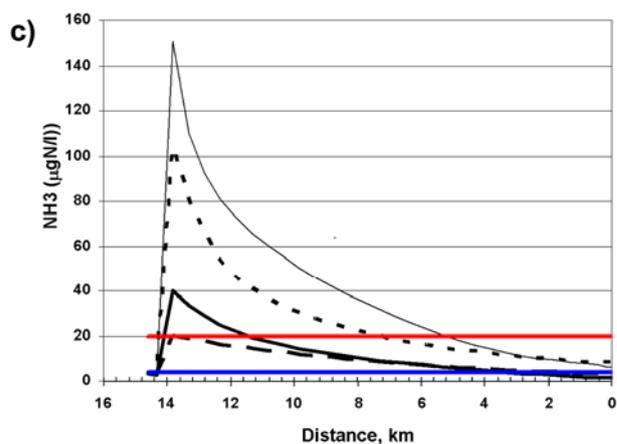
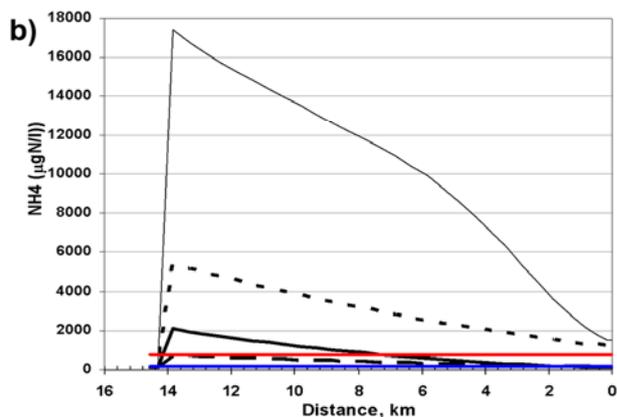
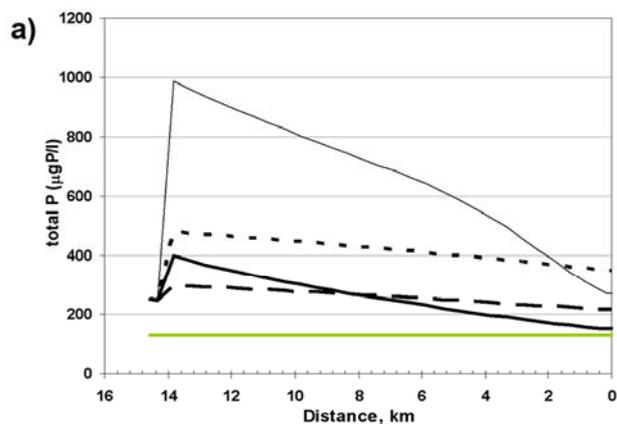
The model of the system was used for analyzing different possible scenarios where water quality and hydrometric historical data were used as inputs. Data of major polluters were obtained from the Cadastre of Polluters of the PWMC Vode Vojvodine for the period of 2006-2009, and supplemented with data from the study conducted by NIVA (2006).



modeled    measured    polluted water  
 Calibration, Sept, '09: —●—    ●    ◆  
 Validation, May, '10: —●—    ●    ◆  
 Validation, Aug, '10: —●—    ●    ◆

Figure 3. Calibration and validation of inorganic P, total P, and NH<sub>4</sub>-N, along the reach of the Becej-Bogojevo canal.

Coming from the municipality of Vrbas there are six point source polluters: meat factory, pig farm, sugar factory, edible oil factory, confectionary company and bakery, out of which only meat factory and pig farm were identified as significant contributors to overall nutrient loading.



Simulation 1    —    Total P for Cyprinid waters    —  
 Simulation 2    - - -    Guide    —  
 Simulation 3    ·····    Mandatory    —  
 Simulation 4    —    —

Figure 4. QUAL2K simulations of total P, NH<sub>4</sub>-N, and NH<sub>3</sub>-N along the Becej -Bogojevo canal with limit values recommended by the Fish Directive.

Flow rates of both canals the Vrbas - Bezdan and the Becej-Bogojevo were obtained from corresponding locks at Vrbas and Kucura. Flow rates were taken for the last decade (2000-2009). The maximum and average values are 17.24 and 5.21 m<sup>3</sup>/s. Simulations were run using following

combinations as input values:

- Simulation 1 - Average canal flow rate, minimal pollutants concentrations and its minimal discharge;
- Simulation 2 - Average canal flow rate, average pollutants concentrations and its average discharge;
- Simulation 3 - Maximal canal flow rate, minimal pollutants concentrations and its minimal discharge; and
- Simulation 4 - Maximal canal flow rate, average pollutants concentrations and its average discharge.

Corresponding input data are listed in Table 1, while Figure 4 presents simulation results for four selected scenarios (Simulation 1 ÷ Simulation 4).

Concentration of total P was higher than recommended already at 14.58 km of canal Becej-Bogojevo, i.e. before joining with polluted Vrba - (Fig. 4a). This issue requires further investigation. The situation gets worse at the point of source confluence at 14.08 km. However, responses show decrease in total P concentrations till the end of the investigated canal reach. The decrease of inorganic P downstream is caused by sorption onto settleable particulate matter, thus decreasing concentration of total P. Besides, concentrations of  $\text{NH}_4\text{-N}$ , shown in figure 4b, change in a similar manner. Reduction in concentration of  $\text{NH}_4\text{-N}$  downstream arises due to process of nitrification. According to the Fish directive concerning Cyprinid waters, guide value for  $\text{NH}_4\text{-N}$  is  $\leq 0.2 \text{ mgNH}_4/\text{l}$  ( $\leq 0.15 \text{ mgN/l}$ ), while mandatory concentration is  $\leq 1 \text{ mgNH}_4/\text{l}$  ( $0.78 \text{ mgN/l}$ ). Also, the  $\text{NH}_3\text{-N}$  is especially recognized as dangerous for fishes, and thus it sets  $\text{NH}_3\text{-N}$  guide and mandatory

values at  $\leq 0.005 \text{ mgNH}_3/\text{l}$  ( $\leq 0.004 \text{ mgN/l}$ ), and  $\leq 0.025 \text{ mgNH}_3/\text{l}$  ( $\leq 0.020 \text{ mgN/l}$ ), respectively. Figure 4c gives simulation results for concentration changes of  $\text{NH}_3\text{-N}$  for different scenarios with respect to limit values set by the directive.

Simulation 1 indicates the worst results for all parameters, but their concentrations are rapidly decreasing until the end of the reach. Generally, simulation 1 and 2 where average flow rate was applied show at first rapid concentration increase for all parameters, then also significant decrease until the end of the reach. This is due to relatively lower flow rate which leaves the system more time for biochemical processes. Simulation 3 and 4, where maximal flow rate was applied, show better assimilation of pollutants' concentrations, but the decrease is not so rapid as in cases 1 and 2. The best results for  $\text{NH}_4\text{-N}$  and  $\text{NH}_3\text{-N}$  are obtained in simulation 3, where the parameters stay within mandatory limit values.

### 3.3. TMDL development and discussion

The following part shows the approach in determining of TMDL by use of an example. According to the methodology described in chapter 2.4, TMDL values have been calculated for total P,  $\text{NH}_4\text{-N}$ , and  $\text{NH}_3\text{-N}$ , in case of average flow rate (Simulation 2). The calculated TMDL values are shown in the Table 2. The study assumed mandatory values for  $\text{NH}_4\text{-N}$  and  $\text{NH}_3\text{-N}$ , and recommended values for total P from the Fish directive. MOS values are already incorporated in the directive.

Table 1. Input values for polluting substance, their flow rates and canal flow rates used in different simulations

Variants of simulations	Canal flow rate (m <sup>3</sup> /s)	Point source flow rate (m <sup>3</sup> /s)	Total P (mg/l)	Inorganic P (mg/l)	$\text{NH}_4\text{-N}$ (mg/l)
Simulation 1:	5.21	0.05	17.64	12.30	222.07
Simulation 2:	5.21	0.08	50.89	15.38	1197.65
Simulation 3:	17.24	0.05	17.64	12.30	222.07
Simulation 4:	17.24	0.08	50.89	15.38	1197.65

Table 2. The TMDL values for total P,  $\text{NH}_4\text{-N}$  and  $\text{NH}_3\text{-N}$  for the Becej-Bogojevo canal, according to data for the simulation 2

Parameter	TMDL*	Comparison with simulation results			
		Background pollution (clear water)	Point source pollution	Peak load	TMDL values exceeded by
	kg/day	kg/day	kg/day	kg/day	kg/day
Total P	58.5	114.3	333.9	448.2	389.7
$\text{NH}_4\text{-N}$	351.1	45.7	7824.3	7870.0	7518.9
$\text{NH}_3\text{-N}$	9.0	1.5	66.9	68.4	59.4

\*According to the Fish directive 2006/44/EC

Obtained TMDL values were put into comparison with Simulation 2 results. In this example, the background load and point source pollution represent historical data, while the pick loads are result of system simulations. It should be noticed that the peak load actually equals the sum of the background load and point source pollution. This is in accordance with the nature of considered pollutants showing the tendency to decrease in concentration with the distance. Yet, some other parameters, like dissolved oxygen, would express different behavior (Cox, 2003).

The results from table 2 finally indicate that peak loadings by great amounts exceed required TDML limits. Application of the developed model and TMDL limit values can produce such a pattern of source allocation, i.e. sharing of pollution loading among the sources that would lead to the compliance with the standards.

#### 4. CONCLUSION

This paper analyzes the application of water quality modeling methodology for accessing dynamical properties of the particular watercourse, considered as one-dimensional, steady-state process. Bio-chemical aspect of the modeling focuses on the concentration changes of nutrients, including nitrogen compounds,  $\text{NH}_4\text{-N}$  and  $\text{NH}_3\text{-N}$ , and total P, as they have harmful impact on aquatic organisms. Increased concentrations of these pollutants endanger the reaches of canals Vrbas-Bezdan and Becej-Bogojevo, which was the main reason for selecting them as the object for this study.

Application of the developed model and limit values can produce such a pattern of source allocation, i.e. sharing of pollution loading among the sources that would lead to the compliance with the standards. The novelty of the approach is that it combines policy of both acts, namely, limit values were taken from Fish directive, while the load sharing is expressed as TMDL. This way each polluter has more clear insight in the bounds it has to stay within.

Finally, application of the methodology could form a basis for integral management of the pollution in the whole canal network of the HS DTD in Vojvodina.

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