U.P.B. Sci. Bull., Series B, Vol. 76, Iss. 4, 2014 ISSN 1454 – 2331

CHARACTERIZATION OF THE EUTROPHICATION POTENTIAL FOR THE LOWER PART OF THE DANUBE RIVER

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An ecosystem is affected directly or indirectly by the physical status or chemical structure of pollutants, which are distributed differently on the biotic and abiotic level.

Specific functions and interdependencies between indicators monitored were established in order to characterize the pollutants share with impact of eutrophication. Interparametric correlations and primary statistical analysis (average, minimum, maximum) were characterized taking into account both the pressure and impact on the lower Danube section, at 10 monitoring locations between km 375 and km 175, over a period of 12 months.

The framing of monitored indicators in the quality classes according to Romanian legislation, M.O. 161/2006 and to European Water Framework Directive (WFD, Directive 2000/60/EC) was also accomplished. Good ecological status of the Danube was found, the negative impact on coastal marine water quality being reduced.

Keywords: eutrophication potential, nutrients, pollution, Danube River, water quality

1. Introduction

Rivers are dynamic ecosystems and problems like pollution, increased toxicity, eutrophication, acidification lead to decreased water quality [1, 2].

River water quality monitoring at international level has always been a complex task, the main problem being to improve the water quality of the ecosystem and implicitly to improve the capacity of water supply for household use, agriculture, industry, etc.

The hydrological cycle is a very important concept to maintain a healthy environment on earth, and to ensure adequate water resources. Therefore, the researches

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in hydrological domain have been expanded, by monitoring the pollutants transported by water and sediments in hydrographical basins [3].

The Danube, Europe's second as size river (2857 km), the only European river that flows from west to east, and flowing through nine countries, is one of the most important inland waterways in Europe [4, 5].

In Romania, the Danube stretch is 1075 km and has about 31 % of the total hydrographical basin of the Danube, amounting to about 250 000 km^2. This river represents also the largest source of pollution flowing into the Black Sea [6-8].

One of the main problems affecting the water quality of the Danube is loading with nutrients (N and P content), which leads to eutrophication and contamination by hazardous substances and oxygen depletion, being a significant problem for biodiversity on aquatic ecosystems [9].

European Commission has drafted the most substantial and complex legislative provision in water management, namely the Water Framework Directive (WFD 2000/60/EC), which is the most important legal instrument in the area of water and a prerequisite for the successful implementation of the concept of integrated environmental management [10, 11]. WFD purposes are to protect and to improve the status of all water bodies to the level of "good status", to ensure a good hydrochemical and ecological status of water [12, 13].

Under the coordination of the International Commission for the Protection of the Danube River (ICPDR), the states from Danube Basin, including Romania, cooperate for implementation WFD Danube Basin level in order to achieve a Unitary Management Plan of the Danube Basin [14], the river being a backing natural for many species of flora and fauna, some of them being endangered [15, 16].

The purpose of this paper was to investigate the share of the pollutants generators of eutrophication at the Danube River level, in 2011-2012 period, on the Calarasi-Braila stretch, km 375 - km 175. In this sector there are works to improve navigation conditions, which can lead to a high degree of eutrophication in the monitored locations. That is why it was important to establish the relationships between analyzed parameters and the land using degree.

2. Experimental

Monitoring plan established in this study, as well as the general features of the monitoring areas with the corresponding locations are shown in Table 1.

Table 1

Sampling site locations and their characteristics during 12 months

Watercourse	**Notation of sampling site**	**Lenght (km)**	**Average flow ($m^3 \cdot s^{-1}$)**
Bala Area	L1	347-343	4654
	L2		3087
	L3		1580
	L4		3514
Epurasu	L5	342+700	1361

Island	L6	341+800	219
	L7		1576
Lupu Island	L8	197-195	2713
	L9		1645
	L10		4367

2.1. Sampling

600 samples of water were collected from 10 locations (Table 1), on the Calarasi-Braila section between km 375 - km 175. The locations were monitorized monthly from September 2011 to September 2012 regarding the forms of nitrogen (total nitrogen - TN, ammonia nitrogen - NH_4-N, nitrites - NO_2-N, nitrates - NO_3-N) and phosphorus (orthophosphates - PO_4-P, total phosphorus - TP) and variation of water discharge. The total nitrogen (TN) and total phosphorus (TP) were analyzed both in the dissolved state and in the unfiltered samples. The obtained results were corroborated with the ones from the annual ICPDR reports.

Each water sample was taken directly from the river into a polyethylene container of 5 liters, and was transported directly to the laboratory of analysis, and stored at 4 ^{0}C. Water samples were collected from the 10 locations set in the monitoring plan of the left, and right banks, and from the center and preserved according to standard methods for surface water [17]. The average values of the indicators were used in this paper.

2.2. Reagents

The reagents used were of analytical purity, solutions were prepared with double distilled water, and the determinations were performed according to standards in force.

2.3. Analytical methods

Nutrients were analyzed in accordance with European standards, and water flow was calculated in base of the level measurements. Total phosphorus was analyzed by spectrophotometry after acidification with sulfuric acid and mineralization with potassium peroxodisulphate [18, 19]. The orthophosphates were also determined using spectrophotometry, after acidification with sulfuric acid and complex formation with a color reagent, (the blue colour was measured at a wavelength of 880 nm) [19, 20].

Nitrate ions form a yellow complex by reaction of sulfosalicylic acid in alkaline medium, which absorbance was measured at a wavelength of 415 nm [21]. The nitrite ions were analysed using their reaction with 4-amino benzene sulphonamide of at pH 1.9, in presence of ortho-phosphoric acid; they form a red complex, the absorbance being measured at 540 nm [20, 22]. The determination of ammonium is based on measuring the absorbance at the wavelength of 650 nm of the blue compound resulted from the reaction of the ammonium ion with salicylate ion and hypochlorite in the presence of nitroprusside sodium [23]. The total nitrogen was determined by titrimetry after acidification and distillation [18, 24]. All measurements were performed using a UV-Vis spectrometer Cary 300 Bio [25], and the values obtained were processed for setting the average values.

3. Results and Discussion

To characterize the nutrients share, specific functions were settled and interdependency between the monitoring analytes. The parametrical correlations were established. Analysis of the primary statistical values (average, minimum, maximum) was done, taking into account both the pressure and impact, because the impact assessment of Danube at the monitored section must be achieved on the basis of causal relationship with the pressures upstream, since the upstream sectors are subject of numerous and varied types of significant pressures (which modify the hydrological, physical-chemical and biological characteristics of the Danube after entering the country).

3.1. Correlations between parameters

To assess the parametrical correlations two specific functions have been considered, for phosphorus forms and for water discharge dependence, respectively (Qi).

Specific correlation for phosphorus forms

In accordance with the set of values reported, the predominance of orthophosphates was observed, and the other forms (hetero-polyphosphates) were preserved with concentrations in the same range (Fig. 1). On a relatively limited range by flow (1500 - 3500 $m^3 \cdot s^{-1}$), there is a tendency of decreasing TP/PO_4-P ratio as effect of the dilution (Fig. 2).

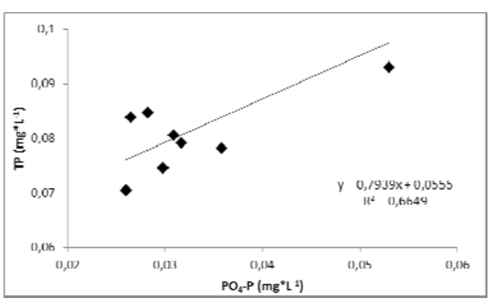


Fig. 1. Variation of total phosphorus upon the orthophosphate concentration

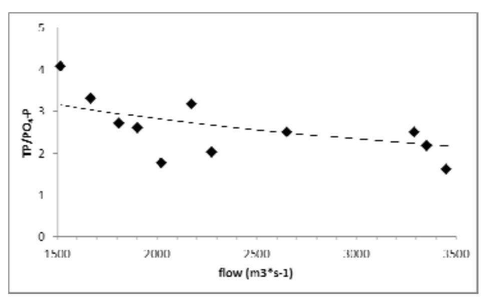


Fig. 2. Variation of TP/PO_4-P ratio upon the water discharge

Specific functions of water discharge dependence, respectively (Qi)

$$Ci = f(Qi) \tag{1}$$

where: Ci is the concentration in the major water course ($mg \cdot L^{-1}$), and Qi is the Danube river flow ($m^3 \cdot s^{-1}$).

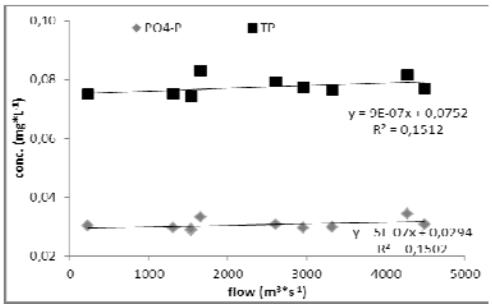


Fig. 3. Variation of PO_4-P and TP ratio upon the water discharge

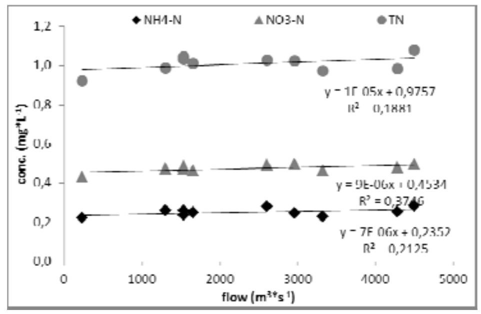


Fig. 4. Variation of NH_4-N, NO_3-N and TN ratio upon the water discharge

In figures 3 and 4, there is an increase in the content of nutrients with the water discharge, increase which arises from their entrainment as a result of erosion from the top layer of soil. Between nutrient concentrations and water flow was established a linear correlation with R^2 comprised in the range of 0.1502-0.2125, and the slope comprised in the range 0.0006-0.001. This low R^2 value illustrates that the dilution process of nutrients is dependent at high degree on the water discharge, when the diffuse pollution due to the top soil erosion is increased.

$$C_i = f(Li) \tag{2}$$

where:

$$Li = Ci \cdot Qi = 0,032 \cdot Ci(mg/L) \cdot Qi(m^3 \cdot s^{-1}) \ \ [KT/year] \tag{3}$$

in which 0,032 – constant for change from seconds to year, Ci – concentration ($mg \cdot L^{-1}$), Qi – water discharge (m^3/year), and Li is associated pollutant load (KT/year).

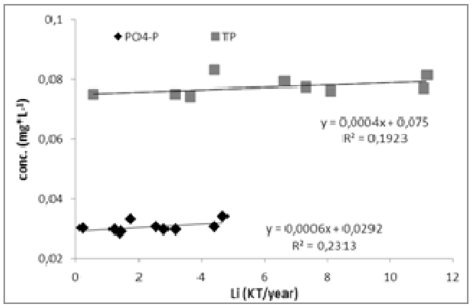


Fig. 5. Variation of PO_4-P and TP depending upon the pollutant load

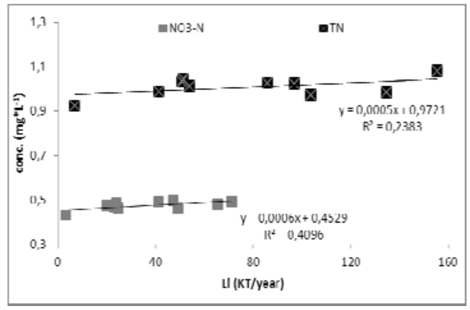


Fig. 6. Variation of NO_3-N and TN depending upon the pollutant load

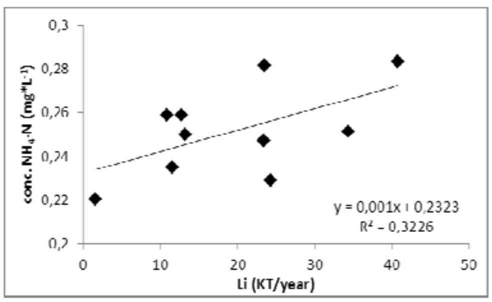


Fig. 7. Variation of NH_4-N depending upon the pollutant load

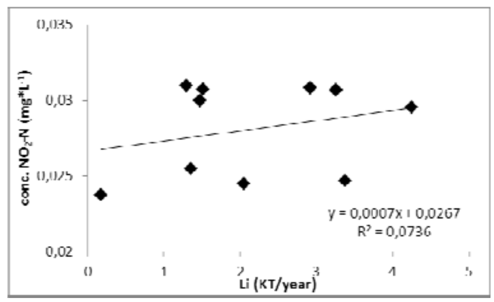
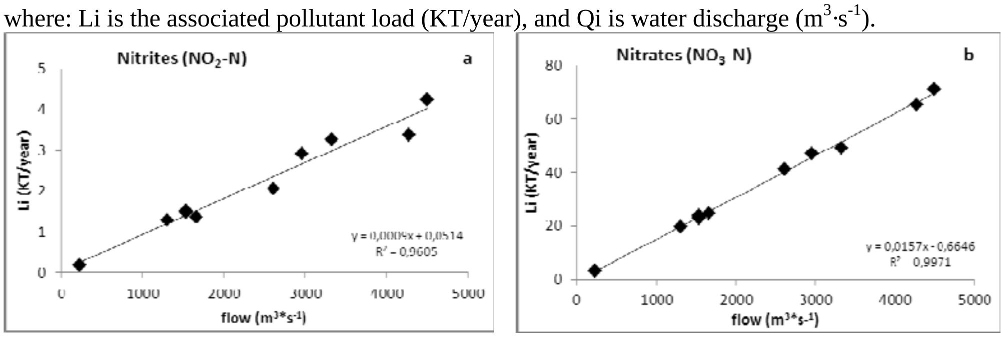


Fig. 8. Variation of NO_2-N depending upon the pollutant load

The function Ci = f (Li) is relevant in assessing the overall balance of nutrients at different sections level. Points dispersion arises from the uneven distribution of suspensions on cross section, respectively of the forms of N (organic) and P (TP) retained on them (Fig. 5-8).

$$Li = Ci \cdot Qi = f(Qi) \tag{4}$$

where: Li is the associated pollutant load (KT/year), and Qi is water discharge ($m^3 \cdot s^{-1}$).



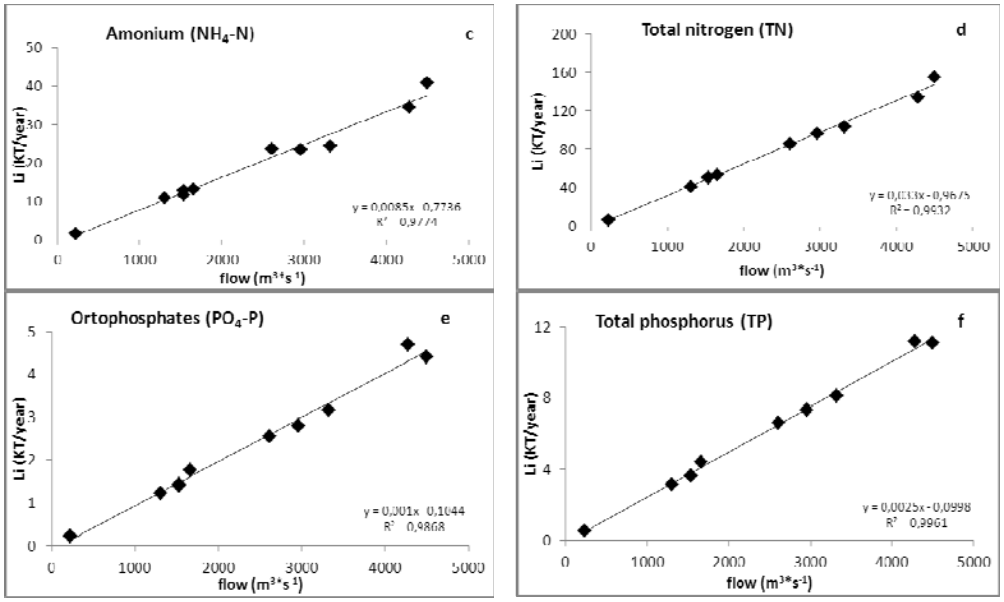


Fig. 9 a-f. Variation of mass loading of nutrients depending upon the water flow

Between the load of nutrients and Danube flow linear correlations were established (Fig. 9 a-f). The increase of the nutrients content (respecting concentration and massic loading associated) with the water flow leads to a cumulative effect of the share of diffuse pollution (increases with water flow) with dilution.

3.2. Primary statistical values

From the analysis of primary statistical values (average, minimum, maximum) (Fig. 10 a-f) for monitored quality indicators it results the following:

- NO_3-N varies in range of 0.213 (minimum) - 0.687(maximum), the average value being 0.314;
- NH_4-N varies in the range of 0.093-0.281, the average value being 0.187;
- NO_2-N is characterized by a variance between 0.023-0.029 with an average value of 0.025;
- TN varies in range 0.867- 1.543, the average value being 1,316;
- PO_4-P varies in the range of 0.034-0.040 and the average value is 0.036;
- TP is characterized by a variance between 0.053-0.145 with an average value of 0.084.

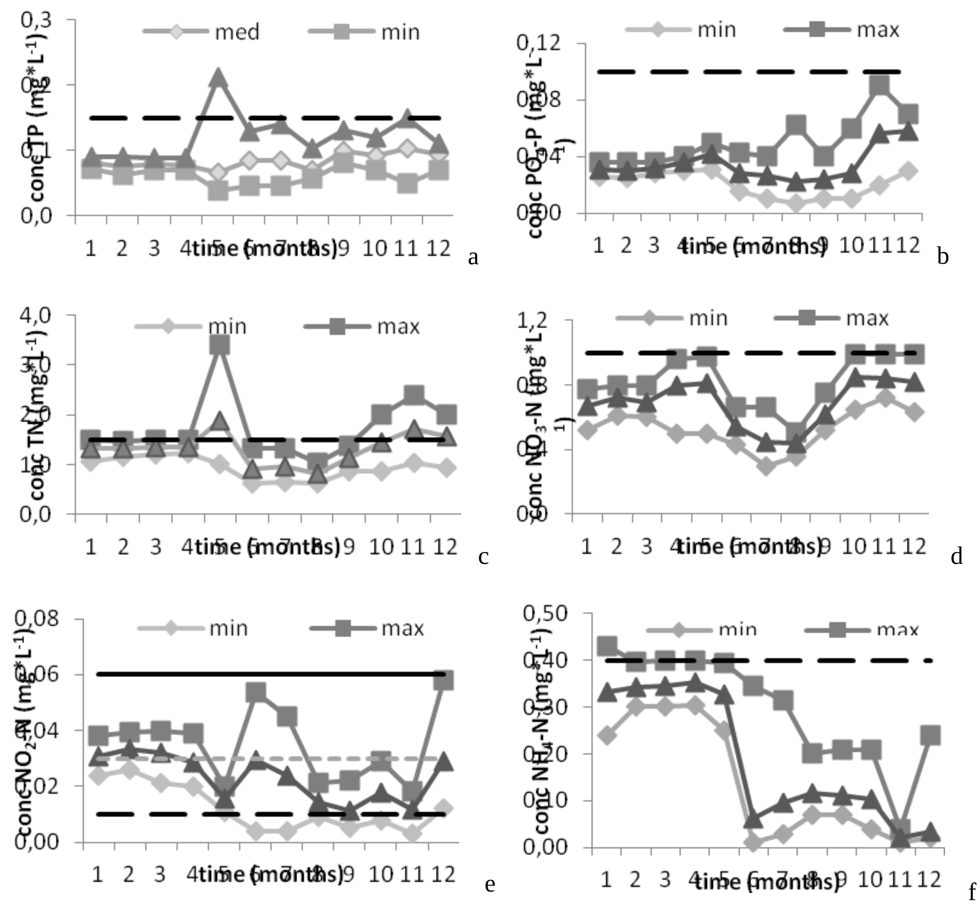


Fig. 10 a-f. Temporal variation of primary statistical values (min = minimum, max = maximum, med = average)

The loading with nutrients of Danube River is influenced mainly in spring and early summer due to high variations in flow, which are influenced by snow melt and rain conditions, respectively [3].

From the comparison of the average values with the limits prescribed in OM 161/2006 [26] (Fig. 10 a-f), the following quality items result: NO_3-N fall in class I, NO_2-N fall into classes I-III, NH_4-N fall into class I, TN, PO_4-P and TP also fall into I class.

4. Conclusions

Water analysis results since September 2011 till September 2012 show that the variation of indicators is due to the current environmental status of the Danube River as a result of environmental conditions, and not because of the works that took place during this period. In terms of nutrient content, the environmental quality of water falls into the category “good” to “moderate” appreciation which is consistent with historical data.

Based on the quality data corroboration with the water discharge the potential impact of hydraulic works can be estimated, that will reflect with priority the changing balance transfer of nutrients (N and P forms) as insoluble form (suspended solids and sediments). Whereas both PO_4-P and N soluble forms are not influenced, it can be estimated that hydraulic works mentioned above will not influence directly the potential for eutrophication.

The method used for parametric correlation of these studied indicators is accessible, easy and provides a global picture of surface water quality.

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