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HEAVY METAL EVALUATION IN THE LOWER SECTOR OF DANUBE RIVER

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Abstract

Danube River is considered one of the most important European rivers and it flows for a total distance of 2,860 km. The river plays an important role in activities such as transport and commercial fishing, which makes it permanently subjected to anthropogenic pressures. Metals are the main pollutants in Danube River and most of the pollution sources in the basin are found in Romania. The aim of the study was to evaluate water quality of Danube River Lower Sector in terms of heavy metals concentration (Cd, Pb, Ni, Cu, Fe, Zn) and to evaluate the environmental risk assessment, by calculating the pollution index for each analysed metal. Water samples were collected from the lower sector of Danube River, at river kilometres 150 and 170. The main conclusion of this research is that Danube River water in the lower sector is classified as a class I in the national quality ranking of surface waters in case of Zn, Cu, Ni, Pb, Cd concentrations, except for Fe concentration that classified Danube River water as a class V in the ranking.

Key words*: Danube River, heavy metals, pollution, water quality.*

INTRODUCTION

Danube River is considered one of the most important European rivers, being the second largest river in Europe. Thus, it is subjected to anthropogenic pressures caused by the large quantities of waste water introduced into the water column (Ilie et al., 2014; Milanov et al., 2016; Subotic et al., 2013). Danube flows for a total distance of 2,860 km and it plays an important role in activities such as transport and commercial fishing, which makes it permanently subjected to natural and anthropogenic pressures (Milanov et al., 2016; Gasparotti, 2014). The pollution along the Danube is determined by the following: point sources (municipal, industrial and agricultural), diffuse sources (agricultural and agglomerations), effects of modifying the water flow regime through abstraction or regulation, morphological changes (Gasparotti, 2014). One of the most important factors affecting the water quality in the Danube river basin is the pollution with hazardous substances (Gasparotti, 2014). Most of the pollution sources in the Danube river basin are found in Romania (125), followed at a great distance by Bulgaria (41), Hungary (36) and Croatia (36) (Gasparotti 2014). Metals are considered to be among the main pollutants in Danube River in Serbia, especially in the area of Belgrade and Novi Sad. The Tisa River, the second tributary of the Danube River, is also contaminated by numerous industrial accidents in the Carpathian mountain region of Romania, which has a long tradition in mining, especially gold (Au), silver (Ag), lead (Pb), zinc (Zn), copper (Cu), cadmium (Cd) and manganese (Mn) (Miloskovic et al., 2016).

Metallic or metalloid ions pollution is a major environmental burden due to their flexibility, accumulation, non-biodegrability and endurance (Femina Carolin et al., 2017). In 2004, the amount of lead and zinc directly discharged in Danube River was 138 t/year, respectively 171 t/year (Dobrogea Waters Administration Administrative Basin, 2010). Transport activities are important sources of oil pollution and are the main source of lead in the Danube and its tributaries (Gasparotti, 2014). As well, intensive agricultural activities can act as a diffuse source of heavy metal pollution and can generate potentially toxic elements through the excessive use of agrochemicals substances

and fertilizers (Mico et al., 2006; Shan et al., 2013; Karishma et al., 2014; Ning et al., 2017; Shi et al., 2018).
Several studies have been conducted regarding heavy metal concentration in different components of Danube River (Visnjic-Jeftic et al., 2010; Ionita et al., 2014; Zrncic et al., 2013; Milanov et al., 2016; Subotic et al., 2013; Miloskovic et al., 2016; Jaric et al., 2011, Gati et al., 2013; Ionescu et al., 2014; Ilie et al., 2017; Ilie et al., 2014) but given the fact that the river is continuously subjected to anthropogenic pressures, constant monitoring is necessary. Therefore, the aim of the study was to evaluate water quality of Danube River Lower Sector in terms of heavy metals (Cd, Pb, Ni, Cu, Fe, Zn) in the water component.

MATERIALS AND METHODS

Sampling was conducted in the lower sector of Danube River, at river kilometer 150 (Galati city) - S1 and river kilometer 170 (Braila city) - S2 (Figure 1). In Galati city, water samples were collected from Danube River between coordinates 45.438301, 28.084317 - 45.418906, 28.044748. In Braila city water samples were collected between coordinates 45.270364, 27.983139 - 45.251696, 27.969320. Both cities carry out intensive riverine transport and dockyard activities along the water course. Gasparotti (2014) mentioned that the pollution point sources discharges are higher in the lower sector compared to the upper Danube region.

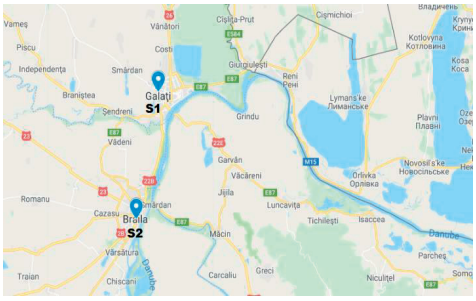

Figure 1. Sampling locations (source maps.google.com)

A total number of 50 water samples were collected, according to SR ISO 5667-6/1998, during spring season (April-May) 2018. Each station was divided into 25 collection points along the station and the water samples were collected from center of the river course, at a depth of 0.5 m.
The water samples were collected in 50 ml decontaminated polyethylene flasks and acidified in situ with 200 µl HNO_3 Suprapur 65% and analysed within the Ecotoxicology Laboratory, "Alexandru Ioan Cuza" University of Iasi, Faculty of Biology. Parameters such as temperature (T°C), dissolved oxygen (DO) and pH were measured in situ, using the WTW multiparameter portable set.
Water samples were filtered with ashes filter paper (70 mm diameter) for quantitative analysis and mineralized with HNO_3 Suprapur.
The method was described by Strungaru et al. (2015). The measurements of Zn and Fe were carried out with flame atomic absorption spectrometer GBC Avanta Australia and for the quantification of Cu, Cd, Pb, Ni the atomic absorption spectrometer, with continuum source of high-resolution, graphite furnace with platform (HR-CS-GF-AAS) ContrAA 600 model, Analytic Jena Germany, was used.
The results were compared with the present national legislation (Ord. 161/2006) in terms of quality classification of surface water (Table 1).

Table 1. Classification of surface waters, according to Ord. 161/2006 (µg L^{-1})

Quality class	Fe	Zn	Cu	Ni	Pb	Cd
I	0.3	100	29	10	5	0.5
II	0.5	200	30	25	10	1
III	1	500	50	50	25	2
IV	2	1000	100	100	50	5
V	higher values than class IV					

As well, in order to evaluate the environmental risk assessment, the pollution index (PI) was determined for each analysed element, following the formula:

$$PI = \frac{\sqrt{\left(\frac{C_i}{S_i}\right)^2_{max} + \left(\frac{C_i}{S_i}\right)^2_{min}}}{2}$$

where:

- PI = Pollution Index;
- C_i = Measured Value;
- S_i = Standard Value.

Evaluation of PI is as it follows: PI < 1: no effect, PI < 2: slightly affected, PI < 3:

moderately affected, PI < 5: strongly affected, PI > 5: seriously affected (Al-Hussaini et al., 2018).

Statistical analysis was performed by using Origin Pro Software. In order to evaluate the normality of data distribution, Kolmogorov-Smirnov normality was performed, followed by the variance test One-Way Anova and Tukey test.

RESULTS AND DISCUSSIONS

The variations of physio-chemical parameters between sampling stations are represented in Table 2 (mean values ± SD). The differences between the registered values in S1 and S2, in case of temperature and pH were not significant ($p > 0.05$).

Table 2. Registered values for water physio-chemical parameters

Location	pH	DO	T°C
S1	7.92 ± 0.19	7.11 ± 0.15	19.08 ± 1.67
S2	7.88 ± 0.14	7.32 ± 0.13	18.55 ± 1.56

In case of DO, the differences of the recorded values between S1 and S2 were significant ($p < 0.05$), with higher mean values in S2.

In case of Cd concentration (Figure 2) in water samples, the values had a normal distribution in both S1 and S2 ($p = 0.9780$, respectively $p = 0.7101$), with mean values of 0.243 ± 0.03 μgL^{-1}, respectively 0.158 ± 0.02 μgL^{-1}.

The variance test revealed significant differences ($p > 0.05$) in Cd concentration between S1 and S2, registering higher values in S1.

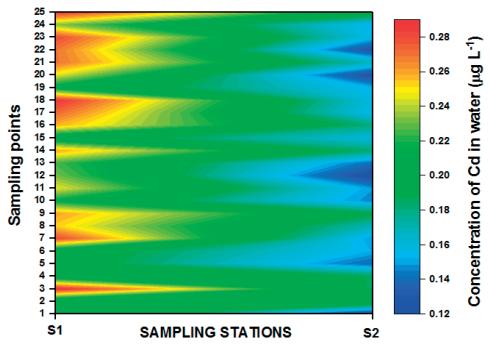

Figure 2. Concentration of Cd in sampling area

Nevertheless, the mean values for Cd concentration in S1 and S2 were lower compared to the maximum established concentration of Cd for quality class I waters by the present national legislation.

In case of Pb concentration (Figure 3) in water samples, the values had a normal distribution in both S1 and S2 ($p = 0.3727$, respectively $p = 1$), with mean values of 3.67 ± 0.11 μgL^{-1}, respectively 2.76 ± 0.14 μgL^{-1}.

The variance test revealed significant differences ($p > 0.05$) in Pb concentration between S1 and S2, registering higher values in S1. Nevertheless, the mean values for Pb concentration in S1 and S2 were lower compared to the maximum established concentration of Pb for quality class I waters by the present national legislation.

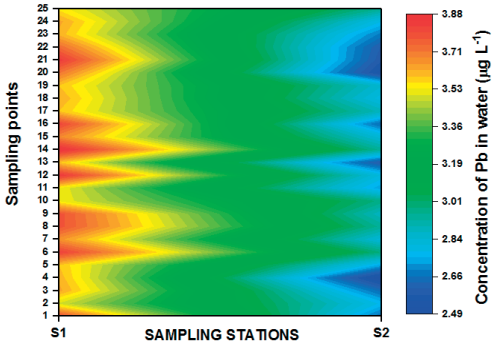

Figure 3. Concentration of Pb in sampling area

In case of Ni concentration (Figure 4) in water samples, the values had a normal distribution in both S1 and S2 ($p = 0.6687$, respectively $p = 1$), with mean values of 7.20 ± 0.57 μgL^{-1}, respectively 5.65 ± 0.83 μgL^{-1}. The variance test revealed significant differences ($p > 0.05$) in Ni concentration between S1 and S2, registering higher values in S1.

Nevertheless, the mean values for Ni concentration in S1 and S2 were lower compared to the maximum established concentration for Ni for quality class I waters by the present national legislation.

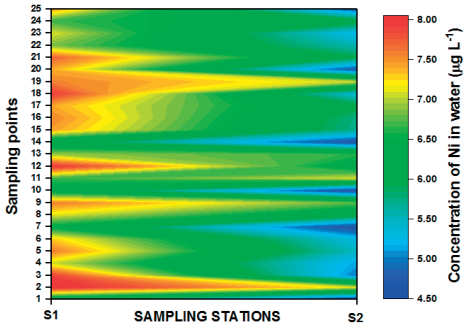

Figure 4. Concentration of Ni in sampling area

In case of Cu concentration (Figure 5) in water samples, the values had a normal distribution in both S1 and S2 ($p = 0.5959$, respectively $p = 1$), with mean values of 5.70 ± 0.65 μgL^{-1}, respectively 9.59 ± 1.05 μgL^{-1}. The variance test revealed significant differences ($p > 0.05$) in Cu concentration between S1 and S2, registering higher values in S2. Nevertheless, the mean values for Cu concentration in S1 and S2 were lower compared to the maximum established
concentration for Cu for class I waters by the present national legislation.

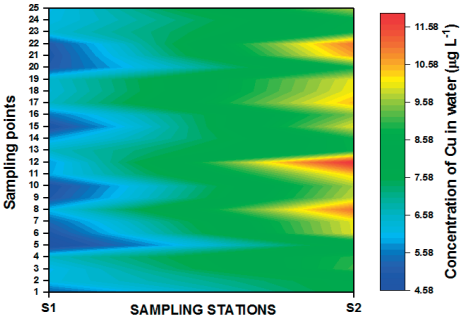

Figure 5. Concentration of Cu in sampling area

In case of Fe concentration (Figure 6) in water samples, the values had a normal distribution in both S1 and S2 ($p = 0.9100$, respectively $p = 1$), with mean values of 722.65 ± 149.39 μgL^{-1}, respectively 1244.68 ± 131.15 μgL^{-1}. The variance test revealed significant differences ($p > 0.05$) in Fe concentration between S1 and S2, registering higher values in S2. The mean registered values for Fe concentration in S1 and S2 assigned the water in the quality class number 5.

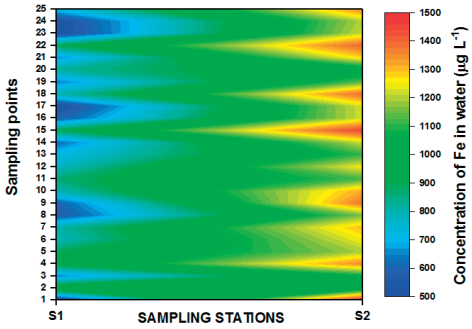

Figure 6. Concentration of Fe in sampling area

In case of Zn concentration (Figure 7) in the water samples, the values had a normal distribution in both S1 and S2 ($p = 1$, respectively $p = 0.5340$), with mean values of 16.27 ± 3.59 μgL^{-1}, respectively 38.90 ± 3.22 $\mu g L^{-1}$. The variance test revealed significant differences ($p > 0.05$) in Zn concentration between S1 and S2, registering higher values in S2. Nevertheless, the mean values for Zn concentration in S1 and S2 were lower compared to the maximum established concentration for Zn for class I waters by the present national legislation.

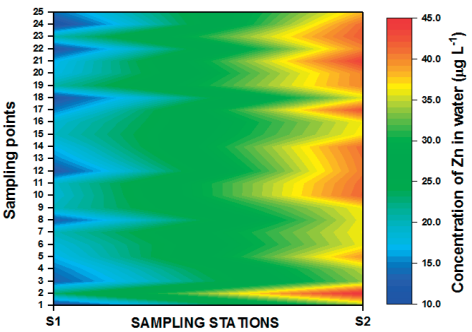

Figure 7. Concentration of Zn in sampling area

From the evaluation of PI (Table 3), it was observed that the values recorded for the concentration of all analysed metals had no effect ($PI < 1$) on both sampling sites, except for Fe concentration, which seriously affected ($PI > 5$) the water of Danube River in both sampling sites (S1 and S2). Similar results regarding the concerning values for Fe concentrations in Danube River water were reported by Enache et al. (2009) in Braila city.

Table 3. Pollution Index evaluation of each metal

Location	Pollution Index (PI)					
	Cd	Pb	Ni	Cu	Fe	Zn
S1	0.3	0.5	0.5	0.1	1863	0.1
S2	0.2	0.4	0.4	0.2	3004	0.3

The accumulation trend of metals in Danube River, lower sector, was as it follows: Fe>Zn>Ni>Cu>Pb>Cd.

Cd, Pb and Ni concentrations recorded the highest values in S1 (Galati city). This can be attributed by the anthropogenic pressure exercised by the dockyard situated on the river bank.

In case of Cu, Fe and Zn concentrations, the recorded values were highest in S2 (Braila city). This can be attributed to the intensive agricultural farming activities conducted in the Small Island of Braila located upstream the sampling area. According to Mico et al. (2006), Cu is released by the use of fungicidal substances, specific to agricultural activities, and also, by the use of copper sulphat, used as algaecide for the irrigation channels. Peng et al. (2019) mentioned that 75% of the Cu concentration in agricultural soils comes from the use of natural manure. As well, high amounts of Zn can be generated by the use of phosphate fertilizers (Mico et al., 2006).

CONCLUSIONS

The main conclusion of this research is that Danube River water in the lower sector is classified as a class I in the national quality ranking of surface waters in case of Zn, Cu, Ni, Pb, Cd concentrations, except for Fe concentration that classified Danube River water as a class V in the ranking.

Fe was the most abundant metallic element in both sampling sites of Danube River water and Cd was the least abundant.

This paper can contribute for the development of different sustainable management plans in water pollution.

Further research is needed in order to assess the possible impact of agriculture, in terms of heavy metals, on river systems.

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