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Surface Water Quality Assessment. Case Study: Târnava Mare River, Mediaş Town-Romania

KEYWORDS: Târnava Mare River, surface water quality, anthropogenic pollution

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ABSTRACT *In the present study, a hydrochemical investigation was conducted in an urban area (Mediaş town - Romania), in order to evaluate the ecological status of Târnava Mare River, an important river from Transylvania-Romania. 125 water samples were collected during February and May in 2011 and 2013 to analyze the temperature, pH, salinity, electrical conductivity, total dissolved solids, redox potential, F-, Cl-, Br-, NO2-, NO3-, PO43-, SO42-, Li+, Na+, K+, Mg2+, Ca2+ and NH4+. The study indicated the presence of some "hot spots" along Târnava Mare River, revealing the importance of water quality improvement, especially for sulphates, nitrite and ammonium content.*

INTRODUCTION

The surface water quality represents a very sensitive issue. Both anthropogenic processes (urban, industrial and agricultural activities, increasing consumption of water resources) and natural processes (changes in precipitations inputs, erosion) degrade the surface water quality and limits its use for drinking, industrial, agricultural, recreation or other purposes.

In the present study, a hydrochemical investigation was conducted in an urban area (Mediaş town - Romania), in order to: (1) determine the chemical composition of Târnava Mare River, an important river from Transylvania-Romania; (2) evaluate the ecological status of river water; (3) assess the anthropogenic influence on water quality and (4) establish if the river water can be used for agriculture purposes. Târnava Mare River springs from Gurghiu Mountains which represent a mountain unit of Moldavian-Transylvanian Carpathians. The river has a total length of 223 km and it flows through four counties. In Blaj town it joins the Târnava Mică River and together they form Târnava River. Târnava Mare River is submissive to a high degree of pollution due to the anthropogenic activities which take place along this river (Muntean et al, 2006; Vigh, 2008).

EXPERIMENTAL

The monitoring area, which has a length around 7 km, is representative for Mediaş town because a lot of wastewater is discharged in Târnava Mare River, especially in this monitoring area. To characterize the Târnava Mare River water quality, a monitoring was carried out during February and April 2011 and during February and April 2013. A total of 125 water samples were collected from nine points, which are representative for this area (Fig. 1). The screening from 2011 indicated that three sampling points (S3, S5 and S7) represented a high risk of pollution and in 2013 they have been intensively monitored.

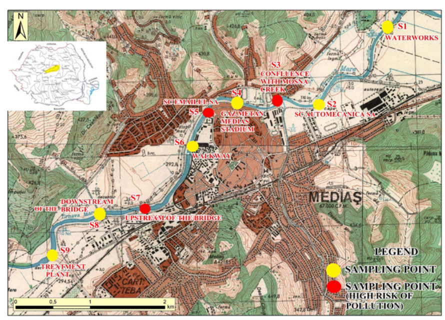

Figure 1: monitoring area of Târnava Mare River and the sampling points

Each water sample was analyzed for 19 physico-chemical and chemical parameters. The temperature, pH, salinity, electrical conductivity (EC), total dissolved solids (TDS) and redox potential (ORP) were measured in situ using a portable multiparameter (WTW 720i Germany). The analyzed dissolved ions were: F^-, Cl^-, Br^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+} and NH_4^+. The analyses were performed by ion chromatography (DIONEX ICS1500, USA).

RESULTS AND DISCUSSIONS

The laboratory results are synthetized in Fig. 2. The water samples proved to be generally slightly alkaline, having the pH between 7.06 and 9.38. As it is shown in Fig. 2, the pH permissible limit (6.5 - 8.5) set by the Romanian legislation for surface water classification (Law 161/2006) was exceeded during February (2013), April (2011) and May (2011 and 2013). The most basic waters proved to be those from sampling points S3 and S7 due to the fact that in the close vicinity of these two sampling points are discharged the wastewaters from an automobile service (S7) and from an electroplating shop (S3), where $Ca(OH)_2$ is used for metals precipitation. The high pH level registered in these two sampling points represents a risk for the aquatic life, because a pH over 8.5 inhibits the growth of the aquatic macrophytes by impairing iron and phosphorus uptake and it reduces fish production.

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All the analyzed water samples had a negative redox potential. The ORP decreased with the pH increasing, being highly negative (more than -100 mV) during April 2011 and May 2011 and 2013 (Fig. 2). The presence of such an oxidizing environment assure a stable environment for the oxides, hydroxides and certain metal salts (Fe, Mn, etc.) and an unstable environment for the organic matter which is decomposed.

The analyzed water samples proved to have relatively high levels of salinity (0.1–0.6‰) and electrical conductivity (522–1500 μS/cm), especially in April 2011 (Fig. 2). Generally, the EC of fresh waters ranges between 5 and 500 μS/cm. With the exception of the waters sampled in February 2011, during the other sampling campaigns there were registered exceeding of maximum permissible limit (1000 μS/cm) recommended by the international legislation (www.epa.gov). The highest EC were registered in sampling points S3, reflecting the pollutions caused by the discharge of the wastewater generated by the economic activities which take place in the close vicinity (electroplating shop). Such high levels of EC and salinity reflect the high amount of dissolved salts, that can reduce the light penetration into water and the dissolved oxygen level, or it can increase the water hardness, can affect the soil permeability and its aeration, indirectly affecting the plant growth. The major dissolved ions composition is dominated by the presence of calcium (44.88–167.83 mg/L), sodium (25.02–93.35 mg/L), sulphate (69.64–324.50 mg/L) and chloride (18.38–130.81 mg/L). Based on the level of these ions, most of the analyzed water samples can be classified as being 2nd water quality class (good ecological status) and 3rd water quality class (moderate ecological status) (Surface water classification Law 161/2006) (Fig. 2). High levels of sulphate or organic materials and deficient oxygen conditions can lead to high levels of hydrogen sulphide which is a threat for the aquatic life (Hannan et al., 2011). As such, the continuous monitoring of SO_4^{2-} is of great importance for Târnava Mare River. High Cl^- contents can destroy some microorganisms which are important in the food chains of aquatic life. Moreover, high Cl^- levels are harmful for metallic pipes as well as for agricultural crops if the river water is used for irrigation purposes (Nosheen et al., 2000). The analyzed water samples proved to have low concentrations of potassium (13.42–41.93 mg/L) and magnesium (1.52–12.29 mg/L). Considering the low level of magnesium, the analyzed water samples can be classified as 1st water quality class (very good ecological status) (Surface water classification Law 161/2006). For potassium there are no limits in the national surface water legislation.

The river waters had the N-NO_3^- levels between 0.31 and 0.61 mg/L, complying with the 1st quality class, while N-NO_2^- was detected only in points S3,S5 and S7 during February 2011 (0.09–0.30 mg/L), exceeding the limit for 3rd quality class (<0.06 mg/L). N-NH_4^+ was between 0.36–6.50 mg/L, exceeding the limits for 3rd (1.2 mg/L) and 4th (3.2 mg/L) quality class. During April 2013 the average

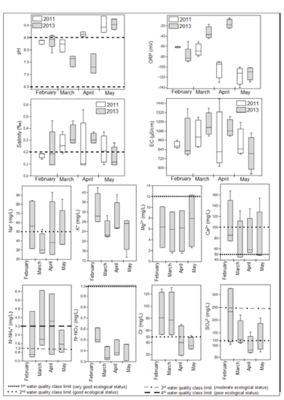

Figure 2: monthly variations of physico-chemical and chemical parameters

level of N-NH_4^+ (3.6 mg/L) corresponded to 5th quality class–very poor ecological status (N-NH_4^+>3.2 mg/L). The highest N-NH_4^+ levels were registered in point S3, due to discharging in the close vicinity of waste waters generated by the electroplating shop.

The monthly variation of physico-chemical and chemical parameters (Fig. 2) showed that the registered levels were generally lower during hot season than in cold season, due to the high dilution from rainy season and the manufacture production regime.

TABLE – 1 PEARSON CORELATION MATRIX

	pH	ORP	Sal	EC	TDS	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+	NO_3^-	Cl^-
ORP	-1.00											
Sal	-0.34	0.40										
EC	-0.39	0.45	1.00									
TDS	-0.56	0.62	0.97	0.98								
Na^+	-0.81	0.85	0.83	0.86	0.94							
K^+	-0.24	0.31	0.99	0.99	0.94	0.77						
Mg^{2+}	0.99	-1.00	-0.47	-0.51	-0.67	-0.88	-0.37					
Ca^{2+}	0.99	-1.00	-0.46	-0.51	-0.67	-0.88	-0.37	1.00				
NH_4^+	-0.77	0.81	0.86	0.89	0.96	1.00	0.81	-0.85	-0.85			
NO_3^-	0.39	-0.32	0.73	0.70	0.54	0.23	0.80	0.26	0.26	0.29		
Cl^-	-0.94	0.96	0.63	0.67	0.80	0.96	0.55	-0.98	-0.98	0.94	-0.06	
SO_4^{2-}	1.00	-1.00	-0.40	-0.44	-0.61	-0.84	-0.30	1.00	1.00	-0.81	0.33	-0.96

In order to identify the correlation between the analyzed parameter, the Pearson correlation matrix was calculated (Table 1). A very strong positive correlation (r>0.9) was observed between the following parameters: Mg^{2+}, Ca^{2+}, SO_4^{2-} and pH; ORP and Cl^-; EC, TDS, K^+ and Salinity; EC and K^+; Na^+, K^+, NH_4^+ and TDS; Na^+, NH_4^+ and Cl^-. Strong negative correlations were registered between: ORP, Cl^- and pH; Mg^{2+}, Ca^{2+}, SO_4^{2-} and ORP; Mg^{2+}, Ca^{2+}, SO_4^{2-} and Cl^-.

The possibility of using these waters for agricultural purposes has been assessed by calculating the sodium adsorption ratio (SAR).

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}$$

where, all ionic concentrations are expressed in milliequivalent/L. The SAR level ranged between 0.56 and 3.81. With the exception of sampling point

S3, the SAR level is lower than 3.0, value that indicate that the water can be used for agriculture purposes and there is no threat for vegetation. SAR level greater than 12.0 is considered a real threat for the survival of vegetation by increasing soil swelling (dispersion) and reducing soil permeability (Wang, 2013).

CONCLUSIONS

The data of the present study showed that the river water is slightly alkaline, having the pH between 7.06 and 9.38. In several samples the pH exceeded the permissible limit (6.5 -

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8.5) set by the national legislation for surface water.

The analyzed water samples had relatively high levels of salinity (0.1–0.6‰) and EC (522–1500 µS/cm), especially in April 2011, reflecting the high amount of dissolved salts.

The major dissolved ions composition was dominated by the presence of calcium (44.88–167.83 mg/L), sodium (25.02–93.35 mg/L), sulphate (69.64–324.50 mg/L) and chloride (18.38–130.81 mg/L).

The laboratory analysis revealed the presence of high levels of $N\text{-}NO_2^-$ (0.09–0.30 mg/L) and $N\text{-}NH_4^+$ (0.36 and 6.50 mg/L).

Considering the low level of Na^+, Ca^{2+}, Mg^{2+} and SAR (0.56–3.81), the investigated waters can be safely used in agricultural purposes as irrigation water (exception point S3).

The monthly variation of analyzed parameters showed generally lower levels in the hot season than in the cold season, due to high dilution during the rainy season and the manufacture production regime.

This study indicated the presence of some "hot spots" along Târnava Mare River, with a poor water quality (S3, S5 and S7). The discharges of the waste waters generated by the economic activities which took place along this river, especially in sampling points S3 (electroplating shop) and S7 (automobile service), may have an immediate or long-term harmful effect on the human health or the aquatic ecosystem. Moreover, they can produce anesthetic color, endanger water supplies and decrease recreational value of water ways.

This study reveals the importance of water quality improvement for the Târnava Mare River, especially for sulphates, nitrite and ammonium content.

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