SOMEȘUL MIC RIVER (CLUJ COUNTY, ROMANIA) WATER QUALITY ASSESSMENT UNDER ANTHROPOGENIC IMPACT

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ABSTRACT. The quality of surface waters has an important role in the environmental context. Somesul Mic river quality, in the studied area, is influenced by the pollution resulted from Floresti locality and Cluj-Napoca city. Were collected and analyzed 28 water samples from the course of the river, on a distance of 20 km crossing Cluj-Napoca city. The studied physico-chemical parameters were: pH, redox potential (Eh), electrical conductivity (EC), total dissolved solids (TDS) and salinity, using a WTW 350i multiparameter. The anions (F, Cl, Br, NO₃, NO₂⁻, SO₄²⁻, PO₄³⁻) and cations content (Li⁺, Na⁺, K⁺, NH₄⁺, Ca²⁺, Mg²⁺) were analyzed using a IC 1500 Dionex Ion Cromatograph. The sampling was realized in two campaigns: Octomber 2018 and February 2019. According to the analyzed parameters, the quality of Somesul Mic River, in the investigated area, corresponds to a moderated water quality index (WQI = 64.94). In the investigated collection points, in three cases were identified high concentrations of nitrates (NO3-), above 5 mg/l. For most of the investigated parameters, the values measured in autumn 2018 were higher than those from spring 2019, one cause might be represented by the precipitations before October 2018, which brought a load of chemicals and contributed mainly to the higher nitrate values. The values of the analyzed parameters in spring 2019 tend to show an increasing trend from upstream to downstream.

Key words: surface water, pollution, water quality, water quality index, Someşul Mic

INTRODUCTION

The aim of the study is to follow the evolution over time of the water quality in correlation with the anthropogenic factor around the studied area. Through this study we propose an evaluation of the water quality in the Someșul Mic River under the action of anthropogenic impact. Thus we want to monitor water quality (depending on the analyzed parameters) in correlation with the development of human society along the river course. Şomeşul Mic River crosses Cluj-Napoca city, which extends in the Someşului Mic Corridor, at the contact of three large geographical units: the Transylvanian Plain, the Someşan Plateau and the Apuseni Mountains, at an average altitude of 360 m (Stoian, 2011), which leads to a great influence of anthropogenic impact on water quality.

Because the city of Cluj-Napoca developed along the Someșul Mic, this river strongly feels the influence of the anthropic factor. Due to the agriculture that is practiced on some lands upstream, the pesticides and fertilizers used (nitrites / nitrates) end up being discharged into the waters of Someșul Mic River after the washing of agricultural lands by rainfalls. Also another important role is played by industrial discharges, so that these anthropogenic actions lead to the degradation of surface water quality, an effect that will affect the well-being of the municipal population.

The Someșul Mic River is located in the Someș river basin, which has an area of 15,740 km². Somesul Mic is the most important tributary formed by the union of Someșul Cald and Someșul Rece. The surface occupied by the hydrographic basin of the studied river is 3773 km², having a length of 178 km and an average annual flow of 14.5 m³/s in Cluj-Napoca. Someșul Mic river has his origins in the Apuseni Mountains, mountains with many smooth peaks, only a few of them higher, of which the peak Vlădeasa (height 1836 m) located at the border of the basin, is the second highest in the Western Carpathians (lordan, 2014).

The upper basin of Someşul Mic includes 5 larger accumulation lakes (Fântânele, Tarniţa, Someşul Cald, Gilău, Someşul Rece I, the last with a catchment role) whose total volume represents 72.0% of the total volume of accumulations in the Someş basin (464.32 million m³) (Şerban et al., 2010).

In the municipality of Cluj-Napoca and the localities of Gilău, Floresti, Săvădisla and Baciu domestic and industrial wastewaters are collected in the sewerage network with a length of 516.5 km, and discharged into the river Someşul Mic after their treatment in the Someseni treatment plant. In general, the wastewater discharged into the Someşul Mic River falls within the maximum limits allowed by the regulatory acts except for the nitrogen indicator (R.S.M.C, 2011).

The number of the studies conducted in this area is limited, and only a few follow the parameters investigated in this paper, forwards are mentioned some of them: Luca et al. (2006) studied the aspects regarding the pollution and protection of surface waters in the Someş basin; Moldovan et al. (2009) studied the environmental exposure to perfumes and medicines from Somesul

Mic, before and after the modernization of the water treatment plant; Persoiu and Rădoane (2011) investigated the spatial and temporal responses of the Somesu Mic River to natural and anthropogenic controls over the past 150 years: lepure et al. (2014), make an ecological assessment of water quality in relation to hydrogeology in the asphalt urban aguifer: Somesul Mic; the study conducted by Ani et al. (2014) "Dynamic Simulation of Somes River Pollution Using MATLAB and COMSOL Models" implements a new approach to provide the possibility to use the parameter-dependent space of the river based on analytical models; the study conducted by Voicu and Bretcan (2014) aims to solve the problem related to the impact of fish migration on the Somesul Mic ("Solution for fish migration on the Somesul Mic river upstream - downstream of Mănăstur dam in Clui-Napoca"): Cîmpean (2018) conducted the "Taxonomic and ecological study on the communities of aquatic mites (Acari, Hydrachnidia) in the drainage basin of Somesul Mic river and their role as indicators of water quality, the parameters studied in this case were only those of a physico-chemical nature (pH, conductivity and dissolved oxygen); the study of Barhoumi et al. (2019), investigates the levels of trace metals and organic pollutants in the surface sediments of Somesul Mic River.

STUDY AREA

Cluj-Napoca is a metropolitan city in the northwest of Romania, located in the central part of Transylvania at a latitude and longitude of $46^{\circ}46'$ N, 23° 6' E, with an area of about 179.5 km² at about 410 m above sea level.

Along the Someșul Mic watercourse, 28 sampling points (see figure 1) have been established, taking into consideration the possible pressure points due to the impact of the urban wastewater discharge, the possible diffuse pressures generated by different plants located in the industrial area of the city and the use of chemical fertilizers in agriculture. The sampling was done along the course of Someșul Mic River, starting from the dam situated in Floresti locality (upstream) and ending with the bridge on Radu Tudoran Street (Cluj-Napoca). The first series of samples were taken at the end of October 2018, and the second series at the beginning of April 2019 (from the same sampling points, accordingly with the geographical coordinates). We chose these months of the year to be able to observe the changes in the quality of Someșul Mic river in 2 different periods, a cold period with low temperatures and in a warmer period.



Fig. 1. Water sampling points (Someșul Mic River)

MATERIALS AND METHODS

The water samples were collected and processed according to the standard procedure imposed by international protocols ISO 5567-2 and ISO 5667-3.

The samples were collected in 0.5 I clean polyethylene containers, and before sampling, the bottles were rinsed with sampled water, labelled. After introducing the water samples into the container, the air was completely removed from it and transported to the laboratory (during this time the samples were stored in the refrigerator at 4°C) within 12 hours and analysed in a timely manner, without the need for preservation. For ion analysis, the samples were filtered with a millipore filter (0.45 µm) and diluted according to the conductivity of the samples (to be below 100 μ S/cm²).

During the sampling period the meteorological conditions were as follows:

- First campaign (at the end of October 2018) there was heavy rainfall with a temperature of about 8-10 $^\circ C.$

- Second campaign - ambient temperatures of 21 °C, without precipitation.

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The following parameters were studied:

- pH, temperature, redox potential (Eh), electrical conductivity (EC), total dissolved solids (TDS), salinity (S), and the following ions: sodium, lithium, ammonium, potassium, magnesium, calcium, fluorides, chlorides, nitrites, bromides, nitrates, phosphates and sulphates).

The main physico-chemical parameters of the water were determined using a WTW 350i Multiparameter. The pH was determined according to SR ISO 10523: 2009. pH measurement is of great importance because a pH low or above 9 has toxic effects on aquatic organisms. This parameter is the most important to evaluate the corrosive properties of an aquatic environment.

For the determination of cations and anions, Ion Chromatograph DIONEX ICS 1500 was used, once the mechanical filtration phase of the samples was completed and the dilution (using ultrapure water, of 18 $M\Omega$.cm).

For the evaluation of the Someșul Mic river quality was calculated the Water Quality Index (WQI), the evaluation using integrated indices, can be a complex process, and includes a significant number of parameters. This contribute with different pressure on surface water quality (Bharti and Katyal, 2011; Teodorof et al., 2016).

In this study we used the Canadian method for calculating the water quality index for the Someșul Mic river, whose empirical equation and description is detailed in a previous study (Martonoș et al., 2018).

RESULTS AND DISCUSSIONS

In figure 2 are illustrated the differences in pH along the investigated points, in the first campaign the pH was influenced by the abundant rainfall of that period, as can be observed variations in the pH values. The electrical conductivity in the second campaign (2019) was much lower (average value: 92.25 μ S/cm), comparative to 2018 campaign (average value: 145.55 μ S/cm), observing major differences in certain collection points. The TDS values in 2019 were smaller than those registered in 2018 (see figure 3), these values and the variation registered in 2018 being influenced by the rainwater discharged into Somesul Mic river, this adding different contaminants in certain investigated points.

The obtained concentrations of Mg^{2+} (2018 average value (a.v.) = 3.50 mg/l, 2019 a.v. = 3.30 mg/l), Ca^{2+} (2018 a.v. = 27.06 mg/l, 2019 a.v. = 17.85 mg/l), K⁺ (2018 a.v. = 0.88 mg/l, 2019 a.v. = 0.88 mg/l), Na⁺ (2018 a.v. = 6.22 mg/l, 2019 a.v. = 5.12 mg/l), classifies this river, in the studied points, in class I of quality accordingly to Order 161/2006. The changes in the concentrations of cations are due to heavy rainfall in October 2018, comparative to April 2019, which changed the chemical composition of the water, and the

variations in concentrations recorded along the Someșul Mic River are due to occasional discharges of wastewater. The course of the river suffers modifications in its route through the city of Cluj-Napoca (as can be observed for example also in the case of Ca²⁺, in figure 4).



Fig. 2. pH variation on Someșul Mic River (through Cluj-Napoca)



Fig. 3. TDS variation on Someșul Mic River (through Cluj-Napoca)





Fig. 4. Ca²⁺ variation on Someșul Mic River (through Cluj-Napoca)

At the level of anions, we could observe the same variations as in the case of cations, with higher values recorded in the case of nitrates (see figure 5 a, b). The average values of SO_4^{2-} are the following: 12.98 mg/l (2018) and 12.6 mg/l (2019), classifying this part of the river in class I of quality accordingly this parameter. The concentrations of Cl⁻ varied between 3.02 mg/l – 27.21 mg/l, with an average value of 6.28 mg/l in 2018 and between 3.25-6.5 mg/l in 2019, with an average value of 4.9 mg/l. NO₂⁻ were identified only in 3 sampling points, with the following values: 1.34 mg/l (P7), 0.86 mg/l (P11), 0.90 mg/l (P20) in the 2018 campaign, in the 2019 campaign the concentration of nitrites was below the detection limit. The values recorded in the first campaign classify the river on those points in class V of quality (according Order 161/2006).

The algorithm for selecting the parameters taken into account to calculate WQI is based on the centralization of the results in each sampling point and the classification in classes according to Order 161/2006. The average value was calculated for the analyzed items and were selected the most significant parameters (those regulated by the national legislation). The average values were compared with the maximum allowed concentration (MAC) for class II (Order 161/2006). Applying the equation mentioned in methodology, we observed that for the analyzed parameters were identified 19 exceeding's of the MAC (according to class II – Order 161/2006); the nitrites and nitrates, recorded exceedances of MAC at the average values measured on Somesul Mic River.

The obtained value for WQI is 64.94, which shows that the degree of pollution of the Somesul Mic River is moderate.



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Fig. 5. Concentration of nitrates along Someşul Mic River, in the investigated points (A-2018, B-2019)

CONCLUSIONS

At the majority of the investigated parameters the obtained values were included in quality class I (for surface waters), in the case of pH only in two from the 28 sampling points the upper limit of 8.5 was insignificantly exceeded, in P12 with a value of 8.52 and in P22 with a value of 8.59.

In the collection point P7 was registered a value of 1.34 mg/l (4 times higher than the MAC for quality class V) for nitrites, and for chlorides a value of 27.21 mg, which includes this point in quality class II regarding the chlorides concentration.

Nitrates registered high values in 14 collection points out of 28, in these points the value exceeding the MAC for quality class II (according to order 161/2006), of 3 mg/l.

The significant variations of the investigated parameters along the river in autumn 2018, is possibly due to precipitation, which brought a load of chemicals, and contributed to higher levels of nitrates and nitrites.

For most parameters, the values measured in autumn 2018 were higher than those measured in spring 2019.

The values of the parameters analyzed in spring 2019 tend to show an increasing trend from upstream to downstream, this makes us conclude that Cluj-Napoca city influence the quality of Someşul Mic River, this being polluted on its route through the city, from different anthropic sources (agricultural lands near the water course on which chemicals are used, industrial waters, pluvial waters and other punctual sources).

The quality index shows us a moderate pollution of the Someşul Mic River (from the point of view of the analyzed parameters).

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