ASSESSMENT OF SEASONAL VARIATIONS OF WATER QUALITY IN MOŞNA RIVER (SIBIU COUNTY)

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ABSTRACT. – Assessing of seasonal variations of water quality in Moşna River (Sibiu County). Evaluation of spatial and temporal variations of the river water chemistry represents a significant aspect of water quality assessment and future trends prediction. The aim of this work was to assess the spatial and temporal variation of Moşna River water quality using graphical and statistical methods. The pH, electrical conductivity, nitrate and nitrite contents of surface waters from 14 monitoring sites (10 sites along the river and 4 sites on the most important wastewater effluents) were monitored monthly from autumn 2013 to summer 2014. Box-and-whisker plots were used to evaluate the seasonal variations of water quality, while hierarchical cluster analysis was used to evaluate the spatial variation of water quality. Results indicated that the studied parameters varied mostly during spring and summer, while during the cold season the parameters variability was low. For the periods rich in precipitations (April - May) high values for pH and electrical conductivity were measured, as a consequence of meteoric water overflowing into the river body. High concentrations of nitrite and nitrate were observed during all year in all sampling sites.

Keywords: surface water, spatial and temporal variations, box-and-whisker plots.

1. INTRODUCTION

Worldwide the pollution of river waters with diverse chemical compounds represents a significant environmental apprehension. River waters quality is influenced by the basin lithology, climatic conditions and anthropogenic inputs (Noori et al., 2010; Bricker and Jones, 1995). The alteration of the river waters quality is determined by natural and anthropogenic inputs (industrial, urban and agriculture activities) (Zhao et al., 2014; Basu and Lokesh, 2013). The main natural contamination pathways (seasonal - dependent) are atmospheric deposition, vadose zone leaching or storm water runoff (Ouyang et al., 2006), while the main anthropogenic pathways are effluents and wastewaters discharge, emissions. Studies related to assessment of the spatial and temporal variations in surface water quality are made all over the world, because of the importance of fresh water (as a drinking resource and habitat for the aqueous life) and the imprinted variations by

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different factors (natural, anthropogenic) (Wilbers et al., 2014; Dimitrovska et al., 2012; Ouyang et al., 2006).

The objectives of the current study were to assess the quality of Moşna River and to evaluate the spatial and temporal variations of Moşna River water quality. The seasonal and spatial variations were assessed using graphical and statistical techniques.

2. MATERIALS AND METHODS

2.1. Study area description and sample collection

Moşna River is one of the Tîrnava Mare right side tributary. The junction occurs in Mediaş City. The city water treatment plant treats about less than a half of the produced wastewaters, while the rest is discharged untreated in the river system.

The studied sector of Moşna River crosses Şoalei Hills from Mediaş Plateau (Morariu et al., 1980). The climate is temperate continental with an average annual temperature of 8 °C and average annual precipitation of 600-800 mm (Reti and Roşian, 2007; Horhoi, 2001). Most of the annual precipitations fall during the spring and autumn months.

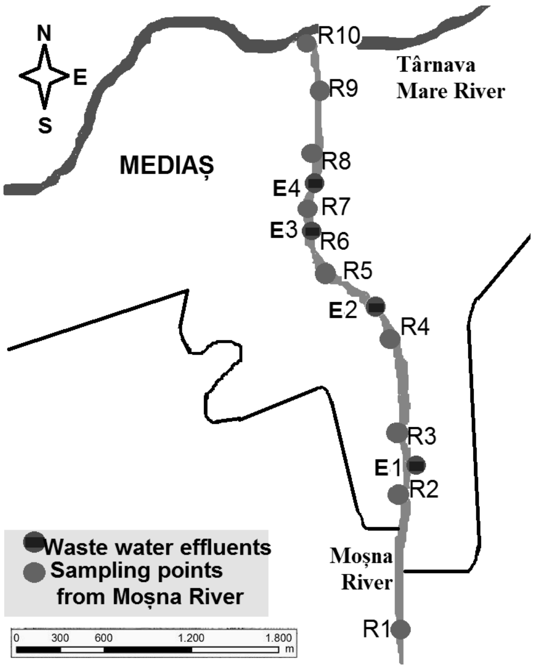

Fig. 1. ***Location of the sampling points, Mediaş City***

Moşna River crosses Mediaş City and collects household wastewaters from more than a half of the wastewaters produced in the eastern part of the city.

Sampling point R1 is located at 5 km distance upstream Mediaş City (in north of Sibiu County), while sampling points R2-R10 are located on the Moşna River across Mediaş City until the confluence with Tîrnava Mare River (Fig. 1). Sampling points E1-E4 are municipal wastewater effluents that are discharged untreated into the river.

Volumes of 250 ml of water samples were collected monthly from October 2013 to May 2014. The samples were collected in polyethylene bottles and stored at 4 ºC in the refrigerator until analysis.

2.2. Monitored parameters and analytical methods

In order to evaluate Moşna River quality and to assess the seasonal variation of the water quality, four chemical parameters were measured. For the determination of the physicochemical indicators (pH and electrical conductivity-EC), WTW 350 i Multiparameter was used. The nitrogen compounds (NO_2^- and NO_3^-) were measured using a mono-fascicle CECIL UV-VIS Spectrophotometer. The nitrite concentration was determined at 520 nm, based on the reaction of nitrites with sulphanilic acid and α-naphtylamine and formation of a red-violet compound, according to SR ISO 26777:2002. The nitrate concentration was determined at 410 nm, based on the reaction of sodium salicylate with nitrate in an acid medium (sulphuric) with formation of yellow coloured salts of nitrosalicylic acid according to the SR ISO 7890-3:2000.

The obtained data were represented using box-and-whisker plots and hierarchical cluster analysis (HCA). The statistical and graphical methods were obtained using XLSTAT software.

3. RESULTS AND DISCUSSION

Table 1 presents the summary statistics of pH, EC, nitrate and nitrite concentrations along the environmental quality standards according to Romanian legislation (M.O.161/2006). The results showed variable trends for the studied parameters and the contamination of Moșna River waters with nitrate and nitrite (Table 1).

Table 1. ***Summary statistics of EC, pH, NO_2^-, NO_3^-***

Variable			**EC** (μS/cm)	**pH** (pH units)	**NO_2^-** mgN-NO_2^-/l	**NO_3^-** mgN-NO_3^-/l
Surface water	Minimum		529	7.18	0.98	0.22
	Maximum		1356	9.44	3.7	10
	Mean		841	8.63	2.1	4.7
	Standard deviation		95	0.45	0.93	3.0
	Water quality standards*	I- Very good	-	6.5-8.5	0.01	1.0
		II- Good	-	6.5-8.5	0.03	3.0
		III- Moderate	-	6.5-8.5	0.06	5.6
		IV- Poor	-	6.5-8.5	0.30	11.2
		V- Very Poor	-	6.5-8.5	>0.30	>11.2
Wastewater	Minimum		637	6.67	1.4	2
	Maximum		2340	9.51	2.3	5.4
	Mean		1460	8.27	1.8	3.0
	Standard deviation		408	0.62	0.40	1.6
	Limit values for pollutants charging industrial and urban wastewater discharged into natural receivers**		-	6.5-8.5	1.0	25

* According to Romanian Legislation (M.O. 161/2004)

** According to Romanian Legislation (G.D. 352/2005)

Concentrations of NO_2^- exceed the EQS set by Romanian legislation (M.O.161/2006), having a very poor quality (class V).

For the identification of seasonal variations in water quality, box-and-whisker plots were used. The location and shape of the underlying distributions is provided by box-and-whisker (Razmkhah et al., 2010).

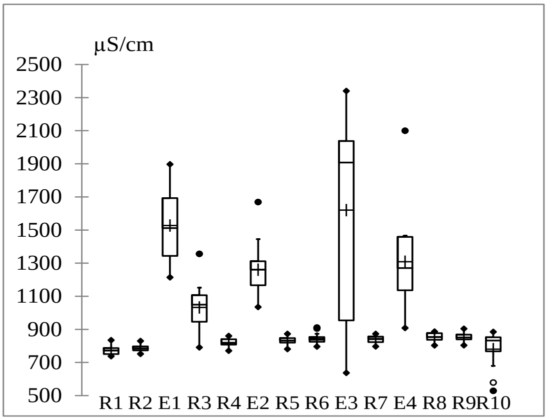

Fig. 2. ***Variation of EC***

Figure 2 indicates a higher variability of the EC for sewage waters (E1-E4) than for the river waters. The significant drop of the EC value in the river water downstream of the sewage waters discharge points is a consequence of the dilution of the wastewaters with less polluted river waters. Water of sampling point E3 presents the highest EC value in May (2340 μS/cm) while outliers were noticed in samples from R3, E2 and E4, reflecting the status of inorganic pollution. The most dispersed EC values were found in sample E3, also characterized with the highest average contamination.

The most important impact on the river waters EC is determined by the E1 that determines a significant increase of the river waters EC in sampling point R3.

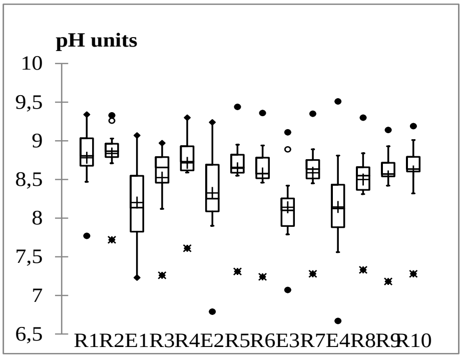

Fig.3. ***Variation of pH***

The periods characterized by high rainfall, such as April and May 2014 impress significant influences in the river chemical composition, respectively in the river quality.

Generally, the pH values were circum neutral or alkaline. Extreme values were noticed in all sampling points in October 2013, April and May 2014 (Fig. 3).

Nitrogen compounds (NO_2^- and NO_3^-) were the highest in sample R10 at the start of May 2014 (3.7 mgN-NO_2^-/l, 10mgN-NO_3^-/l), while sample R9 presents the lowest NO_2^- value for the same period (0.98 mgN-NO_2^-/l). The lowest NO_3^- concentration was measured for R5 at the beginning of May 2014 (0.22mg N-NO_3^-/l). With the help of the histograms, the distribution of data is represented for each measured parameter (Fig. 4).

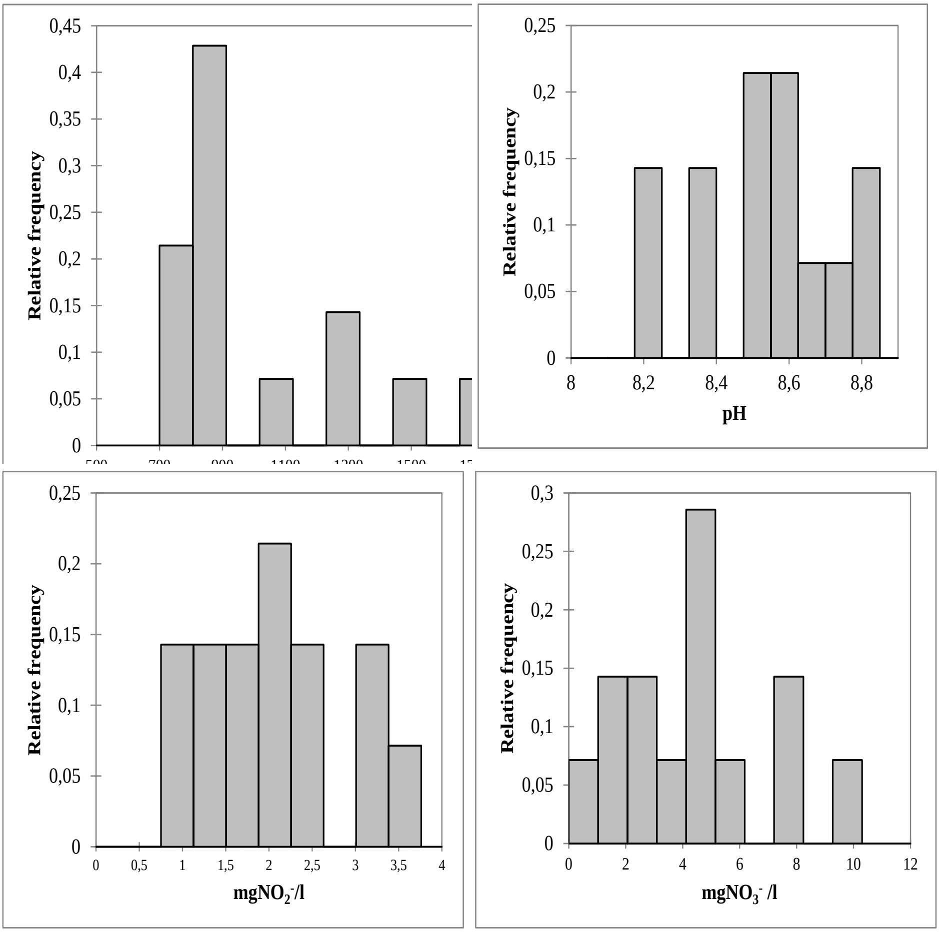

Fig. 4. ***Frequency of EC, pH, NO_2^-, NO_3^- in water samples***

The EC histogram is skewed right, indicating that the majority of the samples have EC values between 700 µS/cm and 900 µS/cm and fewer water samples have EC values higher as 1000 µS/cm. From the NO_2^- histogram, a symmetric data set can be observed (1-2.5, 3-3.5 mg N-NO_2^-/l), although the concentration of 2 mg NO_2^-/l has the higher relative frequency. On the other hand the histogram representation for the NO_3^- concentrations is a skewed right graph, with the exceeding of 0.25 relative frequency (concentrations between 4 mgN-NO_3^-/l - 5mgN-NO_3^-/l).

For the assessment of spatial variation of water quality, hierarchical cluster analysis was applied on the obtained data (Fig. 5).

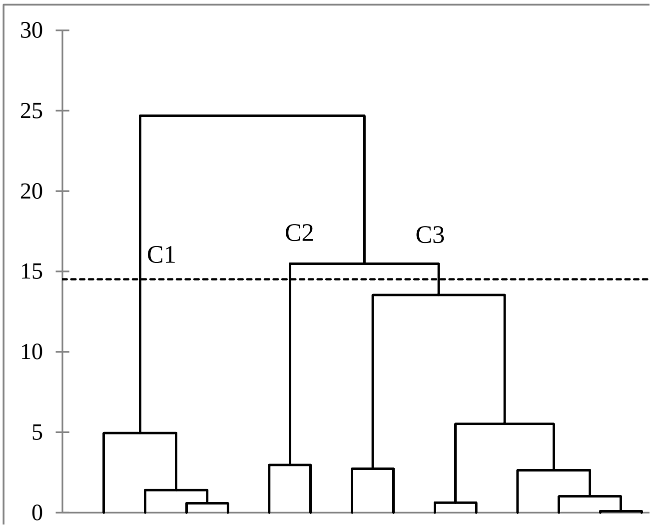

Fig. 5. ***Dendrogram of clustering water samples based on their pollution similarities***

The sampling sites were grouped into three clusters: cluster C1 groups the wastewater effluents with similar contamination level (E1, E2, E3, E4), the cluster C2, comprising the water samples with highest values for the nitrogen compounds (NO_2^- and NO_3^-) concentrations (R6 and R10) and the cluster C3, containing the largest number of sampling points (R1, R2, R3, R4, R5, R7, R8, R9) suggesting their similar chemical composition.

4. CONCLUSIONS

The studied sector of Moșna River presents seasonal variations, due to the small volume of water river (small scale riverbed), the intake of tributary water (household wastewater, as a wide variety of inorganic salts and organic matter) and meteoric water discharge. In the rainy months (April and May 2014) the chemistry and quality of river water are changed. The physicochemical parameters (pH, EC) are characterized by a constant trend during the first part of the sampling campaign, until the last two months (rich in precipitations) when the indicators present higher values. The river chemistry is rich in nitrogen compounds (2.1 mg NO_2^-/l, 4.2 mg NO_3^-/l - mean values) during the monitoring period, exceeding the EQS for NO_2^- sated by the Romanian legislation (0.3 mg N-NO_2^-/l).

In conclusion, the chemistry and quality of Moșna River present seasonal variations, due to the discharge of significant volume of wastewaters in the river, which impress high values of EC and pH in April and May 2014. In the rest of the sampling campaign (October-December 2013, January-February 2014), volume of river water did not decrease, hereby the chemical content is characterized with a constant trend.

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