Quality Indicators for Suceava River

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Environmental factors, together with the anthropic activities carried out within the Suceava River catchment, are constantly influencing the physico-chemical parameters of the water. Suceava River has a mountainous flow, with fast and clean water, and a plateau flow, which is impacted by human activity. The physico-chemical parameters of the water of Sucheava River were analyzed between 2004-2014 at the Brodina (upper sector) and Mihoveni (lower sector) stations. The global analysis of water quality is the result of the interaction between two study models: the comparative one and the dynamic one. The comparative analysis of the chemical parameters was carried out through the correlation of the values obtained with the threshold values established through Order no. 161/2006. The results highlighted the fact that, within the upper sector, classes I and II are dominant. In the upstream sector, a slight degradation of certain parameters is noticeable due to the anthropic influence. The dynamic analysis was performed through the calculation of the water quality variance rate (r), revealing a tendency toward improvement of the parameters studied, with 78% of the values recorded at the station upstream (Brodina) and 64% of those registered at the station downstream (Mihoveni) exceeding 1. The present study focuses on the quality of the water of Suceava River because the latter is the main provider for the cities of Suceava and Radauti.

Keywords: physico-chemical parameters, water quality indicators, Suceava catchment

The ways in which water sources are used differ from one landform to another, based on the hydrological characteristics of the rivers and the needs of the inhabitants [1-2]. The assessment of the quality of surface water bodies through the monitoring of a large number of parameters constitutes a major water management objective, as well as a tool in the devising of efficient water management policies [3].

The spatiotemporal analysis of the water quality of Suceava River stems from both economic and social considerations. According to the stipulations of Directive 91/676/CEE on the protection of water bodies against nitrate pollution from agricultural sources, the entire Suceava catchment has been declared a "sensitive area" as far as nutrient-induced pollution is concerned. Furthermore, according to Directive 91/271/CEE on the treatment of urban wastewater, the groundwater and surface water of the Suceava catchment constitute the main source of drinking water for the city of Suceava and the settlements located along the valley.

The observance of the principles stipulated in the Water Framework Directive has led to a sustainable management of water bodies through the employment of monitoring and assessment tools meant to ensure both good water quality and the progressive reduction of pollution [4-5]. Analyses on the parameters which determine the quality of surface water bodies have been carried out both nationally and internationally [6-19]. The main indicators assessed as part of these analyses are the following: dissolved oxygen, biochemical oxygen demand ($CCBO_5$), chemical oxygen demand, nutrients (nitrates, nitrites, total ammonium and total phosphorus), as well as salinity indicators such as fixed residue, chlorides, calcium, sulphates, total magnesium and total iron [20]. The quality of the water of Suceava River is constantly being monitored, as the former represents the main water supply for the urban and rural settlements located within its catchment.

Study area

The Suceava catchment is situated in north-eastern Romania, at the border with Ukraine. It has an elongated shape and it follows the NV-SE direction. Suceava River is the first significant tributary that discharges into the Siret after the latter enters Romania (fig. 1). The Suceava catchment occupies the northern extremity of Obcina Feredeului, the northern and eastern portions of Obcina Mare, Obcinele Brodinei, the Radauti Depression and, partially, the Suceava Plateau (the Piedmont Plateau and the Dragomirnei Plateau).

The catchment is delineated by the 25°26'20'' E long. and 26°33'10'' E long. meridians, and by the 47°31'10'' N lat. and 48°00'00'' N lat. parallels, respectively. It covers an area of 2.625 km^2 (2298 km^2, which account for 87%, on the territory of Romania, and 13%, namely 327 km^2, on the territory of Ukraine). The area of the catchment includes two important urban centers: Suceava and Rãdãui.

Method

The analysis of the chemical properties of the water of Suceava River was based on data collected from measurements carried out within the National System of Water Quality Monitoring between January 2004 and December 2014 at two monitoring points: Brodina (142 km from the mouth) and Mihoveni (45 km from the mouth). Through the devising of management plans for each

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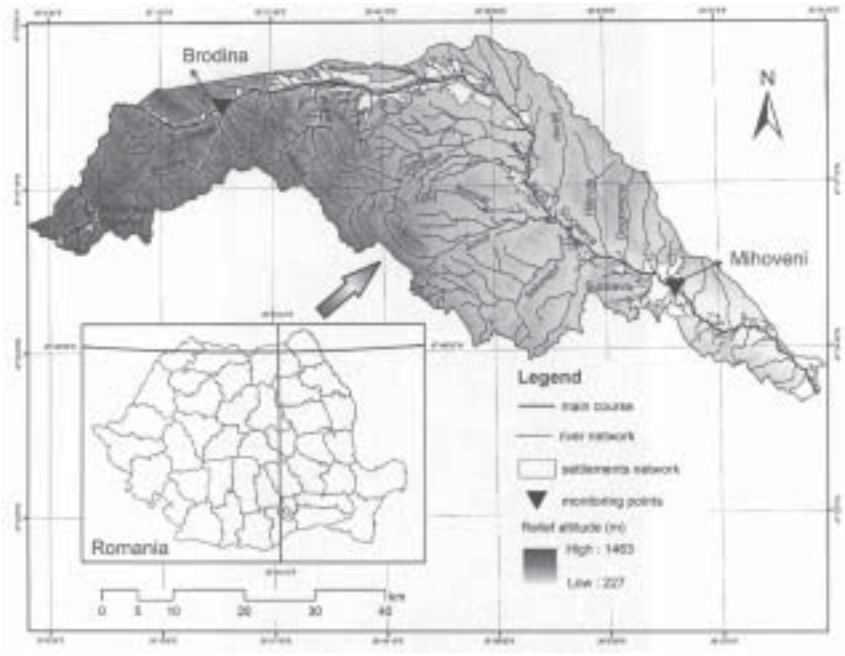

Fig. 1. Location of the Suceava catchment on the Romanian territory

catchment, in agreement with the EC Water Framework Directive 2000/60, an abiotic tipoloy of rivers, based on natural conditions (altitude, mean depth, geology, retention time), was established.

For each river, the pollution-related pressures (punctiform, diffuse and hydromrphological) are identified. An assessment of the anthropic impact is carried out through the analysis of the groups of chemical indicators based on which the quality classes in which each sector of the river is included, along with the ecological state of the water, are established [21-24]. The global analysis of water chemistry and water quality may be the result of the interaction between two study models:

- according to the Normative on the establishment of quality classes for suface water bodies so as to determine their ecological state (Ord. MMGA no. 161/2006), which states that a river is a static ecosystem, therefore it operates with the absolute values of the results of the analysis, five water quality classes are carefully delineated based on the stipulated limits;

- the river is regarded as a dynamic ecosystem, therefore it operates with values that are average, maximum or minimum, compared with the quality indicators of the current period (2014) and those of 2004 [25].

For the river as a dynamic ecosystem, the increase, decrease or stagnation (preservation) tendency of water quality was calculated for each indicator, according to the formula:

$$r = \frac{\sum_{i=1}^{k} n_i^{(+)} / n}{\sum_{j=1}^{m} n_j^{(-)} / n} = \frac{\sum_{i=1}^{k} f_i^{(+)}}{\sum_{j=1}^{m} f_j^{(-)}} \quad (1)$$

where:

r – the quality variance rate;

k – the number of positive values;

m – the number of negative values;

$n_i^{(+)}$ – the number of values of the absolute frequency of the increases

$n_j^{(-)}$ – the number of values of the absolute frequency of the decreases

n – the total number of absolute frequency values

$f_i^{(+)}$ and $f_j^{(-)}$ – relative frequencies

If *r* displays values over 1, there is a tendency toward the improvement of water quality. If the values are below 1, there is a tendency toward decrease in water quality. If r=1, the parameter analyzed remains stable throughout the time span studied. By summing up the tendencies that trigger the same change in water quality (with or without a change in quality class), the tendency frequency graph was obtained for each river sector studied. With its help, based on the dynamics of the tendencies, the evolution of surface water quality (in the form of increase, decrease or preservation) within the Suceava catchment was analyzed.

Results and discussions

From a physico-chemical point of view, streams suffer a series of transformations as they flows from their source to their mouth (table 1). In the case of Suceava River, significant modifications are noticeable in the quantity of dissolved oxygen, with values between 2.68 mg O_2/L at Brodina and 1.68 mg O_2/L at Mihoveni. The lowest oxygen content is registered during the summer months, when high temperatures favour the thriving of bacteria that consume large amounts of oxygen. Values <4 mg O_2/L are also due to the unmonitored discharge of untreated or improperly treated wastewater, which leads to lower quality classes. The lower oxygen content of the upper, mountainous sector, is due to the descreased flow and the discharge of wastewater from settlements without septic tanks. Moreover, certain nutrients ($N\text{-}NO_3^-$) undergo changes in all values (minimum, maximum and average) as the river travels downstream, under the influence of an increased contribution of water used in agriculture or from lands treated with chemical fertilizers. A very large proportion originates in the untreated wastewater of Suceava city. Significant changes also occur in the case of indicators such as as fixed residue, chlorides, calcium and magnesium, particularly as far as maximum values are concerned.

In the case of total Fe, the same increase tendency is noticeable for the maximum and average values as the river travels downstream. The presence of iron in surface water bodies is due to both natural factors (high concentrations in the bedrock) and anthropic factors (the unmonitored discharge of wastewater by economic agents). The most signficant pollution sources are found in the area of the urban centers of Suceava and Radauti.

Monitoring sector	Brodina			Mihoveni		
Values	min.	max.	med.	min.	max.	med.
Dissolved oxygen (mgO_2/L)	2.68	14.29	10.56	1.68	14.23	10.30
Dissolved oxygen (%)	9.87	134.60	90.47	71.95	120.80	93.30
CBO_5 (mgO_2/L)	0.10	5.50	1.58	0.50	7.90	8.77
CCO-Mn (mgO_2/L	0.80	45.00	3.42	0.90	25.60	3,68
CCO-Cr (mgO_2/L)	1.32	17.13	5.64	2.60	40.56	8.17
$N\text{-}NH_4$ (mg/L N)	0.01	0.94	0,05	0.10	0.43	0.12
$N\text{-}NO_2$ (mg/L N)	0.00	0.09	0.07	0.00	0.12	0.02
$N\text{-}NO_3$ (mg/L N)	0.01	1.38	0.45	0.25	10.31	2.15
Total P (mg/L P)	0.01	32.40	0.26	0.02	1.41	0.04
Fixed residue (mg/L)	121.00	325.00	204.90	4.10	616.00	353.54
Chlorides (mg/L)	2.10	12.80	6.13	6.40	110.40	28.97
Sulphates (mg/L)	8.90	62.50	25.09	15.30	63.18	40.79
Calcium (mg/L)	28.80	73.70	48.26	22.44	133.00	61.81
Magnesium (mg/L)	1.90	48	10.28	4.80	37.40	15.10
Total Fe ($Fe2^+ + Fe3^+$)(mg/L)	0.01	3.6	0.09	0.01	14.00	0.21

Table 1
MAIN CHEMICAL PARAMETERS FOR THE BRODINA AND MIHOVENI SECTORS (2004-2014)

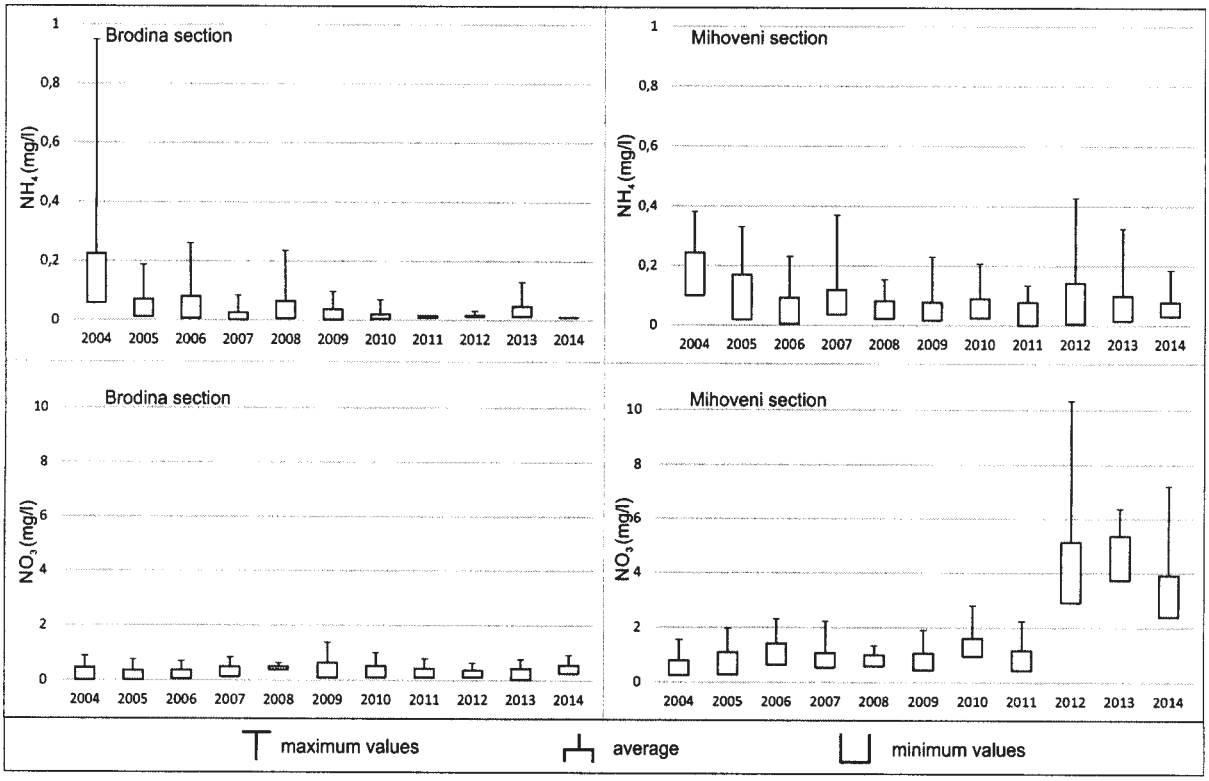

Fig. 2 Variation of minimum, average and maximum values of ammonium ($N\text{-}NH_4$) and nitrates ($N\text{-}NO_2$) at the Brodina and Mihoveni stations between 2004-2014

The multiannual regime of each parameter is conditioned by the hydrological regime of Suceava River and by the anthropic activities carried out within the catchment. During periods of high flow, concentrations are reduced. The highest values are recorded for average and minimal flow, when the speed of the water is low, and its dissolution capacity increases. In the upper sector, the natural factor is dominant, therefore the hydrochemical parameters are nearly within the normal range. The contribution of wastewater increases in the lower sector, especially after the river crosses Suceava City, when a significant increase in nutrients (ammonium and nitrates), chlorides, sulphates etc. occurs (ACET S.A., AMBRO S.A. etc.) (fig. 2).

In order to assess the quality of the water of Suceava River, two methodologies were applied: the comparative one and the dynamic one. In the first case, the values measured for various chemical parameters were compared with the threshold values stipulated in the Normative on the establishment of quality classes for surface water bodies so as to determine their ecological state (Ord. MMGA no. 161/2006) (table 2). For oxygen, the following quality indicators were taken into account: dissolved oxygen, biochemical oxygen demand and chemical oxygen demand. The values of dissolved oxygen (O_2/L) place the water in quality classes I and II (over 80% of cases). In certain cases, however, the values drop, corresponding to quality class V (highly degraded). Such values are due to climatic factors (reduced precipitation, high temperatures, high water evaporation capacity), and they are registered during the summer months, as a result of anthropic activities.

Quality classes	I		II		III		IV		V	
Monitoring points	*U	**D	*U	**D	*U	**D	*U	**D	*U	**D
Dissolved oxygen (mgO_2/L)	27.3	9.1	54.5	81.8	-	-	-		18.2	9.1
Dissolved oxygen (%)	81.8	100	-	-	9.2	-	-		9.0	-
CBO_5 (mgO_2/L)	72.7	27.3	27.3	63.6	-	-	-	9.1	-	-
CCO-Mn (mgO_2/L	63.4	45.4	18.6	36.4	9.0	-	9.0	9.1	-	9.1
CCO-Cr (mgO_2/L)	63.6	18.1	36.4	63.6	-	18.3	-		-	-
N-NH_4 (mg/L)	90.9	90.8	-	9.2	9.1	-	-		-	-
N-NO_2 (mg/L)	45.4	-	36.4	18.1	9.1	36.3	9.1	45.6	-	-
N-NO_3 (mg/L)	90.9	-	9.1	72.7	-	-	-	27.3	-	-
Total P (mg/L P)	18.5	-	27.2	-	27.2	36.4	18.0	63.6	9.1	-
Fixed residue (mg/L)	100	63.6	-	36.4	-	-	-		-	-
Chlorides (mg/L)	100	-	-	63.6	-	36.4	-		-	-
Sulphates (mg/L)	81.8	54.5	9.1	45.5	-	-	-		9.1	-
Calcium (mg/L)	27.3	9.0	72.7	63.6	-	27.4	-		-	-
Magnesium (mg/L)	36.5	18.1	54.5	72.7	9.0	-	-	9.2	-	-
Total Fe (Fe2+ + Fe3+)(mg/L)	90.5	72.7	-	-	-	18.3	-		9.5	9.0

*U=upstream; **D= downstream

Table 2
WATER QUALITY CLASSES FOR SUCEAVA RIVER AT THE BRODINA (UPSTREAM) AND MIHOVENI (DOWNSTREAM) STATIONS BETWEEN 2004-2014

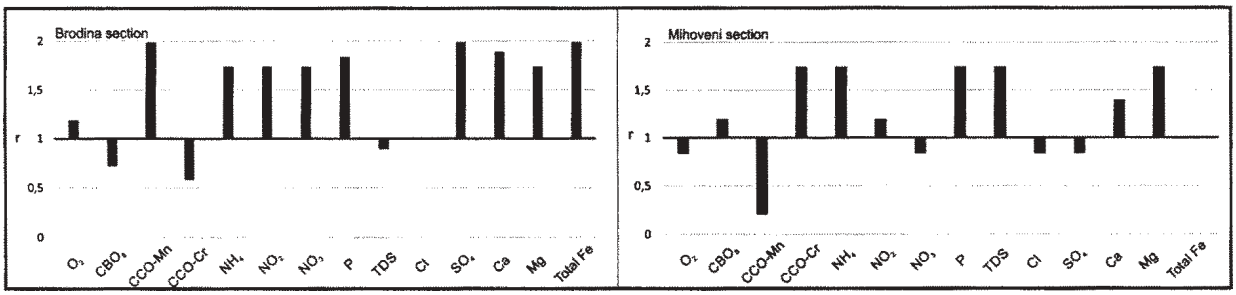

Fig. 3 Dynamics of parameter *r* at the Brodina and Mihoveni stations between 2004-2014

The anthropic influence intensifies as the surface of the catchment grows, both through the contribution of water drained from agricultural lands onto which nitrogen- and phosphorus-based fertilizers are applied, and through that of untreated wastewater. In this case, there is a significant difference between the Brodina station, with higher quality classes (I or II), and the Mihoveni station, with lower quality classes (III or IV). The difference is visible for nutrients and nitrites (N-NO_2): at Mihoveni, 81% of the maximum annual values (2004-2014) correspond to lower quality classes. Total phosphorus (P) at Mihoveni is 100% within classes III and IV (with quantities that often exceed 1.2 mg/L as a reult of anthropic contamination with detergents). Under normal conditions, the concentration of total phosphorus does not exceed 0.1 – 0.5 mg/L.

80.3% of the course of Suceava River belongs to quality classes I (very good) and II (good), and only 19.7% (34 km) to classes II and III (good and moderate, respectively). In order to highlight the qualitative changes that the water undergoes, the quality variance rate (*r*) was calculated for each of the hydrochemical parameters analyzed (fig. 3). For both monitoring stations (Brodina and Mihoveni), a rather pronounced dynamics of this rate is noticeable. At Brodina, most of the values of *r* are positive, which suggests an improvement in water quality. In the case of biochemical oxygen demand (CBO_5), of chemical oxygen demand through the oxidation of potassium dichromate in an acidic environment (CCO-Cr), as well as in that of the fixed residue, the quality variance rate exhibits values over 1, which prove that, between 2004 and 2014, a slight degradation tendency was recorded.

The high values of the quality variance rate (*r*) recorded within the Brodina sector are determined by natural conditions typical for mountainous areas, as well as by traditional agricultural practices, which do not involve the use of chemical fertilizers or microelements such as calcium (Ca) or sulphates (SO_4). The oxygen indicators at the Mihoveni station maintain the improvement tendency, while nutrients (N-NO_3), Cl and SO_4 display a slight degradation tendency. Even if the values of *r* are slightly negative, the anthropic impact upon water quality is noticeable.

Certain parameters display constant values ($r = 1$) at both stations, namely chlorides at Brodina, and total Fe at Mihoveni. The average values of *r* for the 2004-2014 time span indicate a constant improvement of water quality at both Brodina ($r = 1.5$) and Mihoveni ($r = 1.28$). The increase in quality is due to the rehabilitation and modernization of wastewater treatment plants, the closure of landfills that did not meet the required standards, and the establishment of ecological areas. The implementation of European environmental programs has led to the improvement of the quality of wastewater from various sources. Unfortunately, many such programs have not been completed, and the consequences are visible in the values of the hydrochemical parameters.

From a qualitative point of view, the surface water bodies of the Suceava catchment are up to standards, although often exposed to pollution. This is particulary true for the lower sector, where the anthropic influence is felt as a result of the discharge of wastewater, the draining of water from agricultural lands, the improper storage of waste, the reduced wastewater treatment capacity (70% of what is, in fact, necessary, according to the Strategy for the socio-economic development of Suceava County between 2008-2013) etc. During Communism, Suceava City was acknowledged as a significant industrial center, therefore a generator of great air, water and soil pollution. The industry of Suceava City is now considerably diminished, yet pollution-related issues remain.

Conclusions

The surface water bodies of the Suceava catchement are, qualitatively speaking, within legal limits. However, they are often subjected to pollution from anthropic sources. The measurements carried out at the Brodina and Mihoveni monitoring stations, located on Suceava River, have revealed the degradation of certain chemical indicators, particularly that of nutrients, in the lower sector. The upper course of the river is characterized by quality classes I and II, while the lower one falls into classes II and III. The changes in water quality are due to anthropic activities, which generate pollutants through the industry of Suceava and Rãdãui, agricultural practices, including the use of chemical fertilizers based on nitrogen and phosphorus, wastewater from households or treatment plants etc.

The dynamic analysis, which relies on the calculation of the water quality variance rate between 2004-2014, highlights the fact that, at both monitoring stations, an improvement in water quality is recorded (1.5 at Brodina and 1.28 at Mihoveni). The decrease in pollution levels is due to the disapperance of certain pollution sources (factories, slaughter houses etc.) from the Suceava catchment.

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