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ASSESSING THE DANUBE WATER QUALITY INDEX IN THE CITY OF GALATI, ROMANIA

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Abstract: The present paper mainly aims at assessing the Danube water quality as regards its physicochemical parameters, as well as at monitoring the effect of the wastewater treatment plant activation in the city of Galati in 2012. The Principal Component Analyses (PCA) were made to mark out the correlations between the different parameters obtained in different seasons and in various sampling points, as well as the correlations between the physicochemical parameters and the WQI. In order to assess the Danube water quality, the following physicochemical parameters were taken into account: pH, BOD, COD, DO, P-PO_4^{3-}, N-total, N-NO_3^-, N-NO_2^-, N-NH_4^+, SO_4^{2-}, Cl^-, Cr-total, Pb^{2+}, Cd^{2+}, Ni^{2+}, Fe-total, Mn-total, Zn^{2+}, As^{2+}. The water samples were collected from 5 sampling points situated upstream, along and downstream the city of Galati for a period of 12 seasons, starting from the autumn of 2010 and continuing up to the summer of 2013. The water quality assessment was made according to the water quality index (WQI). The conclusions regarding the influence of the anthropogenic activity on water quality could be drawn by observing the water quality variations as conditioned by the sampling points and the nearby industrial or municipal sites. Given the fact that there were more monitoring points in the envisaged area, the water quality assessment was made by taken into consideration the data resulting from all the sampling points.

Keywords: Danube River; PCA; physicochemical parameters; water quality assessment, water quality index (WQI)

1. INTRODUCTION

The main reason for water quality monitoring was traditionally represented by the need to find out the extent to which the water in the monitored watercourse was suitable for different purposes (Malviya et al., 2011). The aims of water quality monitoring have changed at present. They mainly envisage analysing/ assessing the evolution in the aquatic environment quality and the ways in which the environment is affected by various releases of contaminants resulting from human activities. This type of monitoring is generally known as the monitoring of the impact of anthropogenic activities on the environment (Bayoumi Hamuda & Patkó, 2011, Karavadut et al., 2011, Rubio-Arias et al., 2012, Popa et al., 2012).

Water quality monitoring and assessment is based on the identification of the fundamental physical, chemical and biological water properties. It is a process which implies analysing, interpreting and mentioning these properties in the larger context of human activity, human usage and of natural environment conservation (Guidelines for Drinking-water Quality, 2011). The continuous deterioration of the surface water quality is easily noticeable in the urban areas as a result of the industrialization process and of the sewage discharged directly in the water streams (Gharibi et al., 2012; Gurzau et al., 2010).

The permanent/continuous monitoring of the surface water quality in the Lower Danube- Galati area is important both for assessing the quality of the Danube water as a source of drinking water for over 600000 people (the Galati - Braila urban area) and for quantifying the anthropogenic effects on the surface waters in one of the most important European hydrographic basin, namely the Danube - Siret - Prut rivers basin (Fig. 1). The field observations were meant to quantify the influence of activating the first municipal wastewater treatment plant in Galati, which represents an important investment for limiting the environmental impact, despite its being used only for the settling and separation of the resulting sludge (the chemical and biological treatment will be active after 2013).

The surface waters in our country have undergone a significant pressure which may result in the deterioration of the aquatic ecosystems and in a series of dramatic changes in areas such as the Danube Delta (situated close to the area monitored in the present paper).

Assessing the Water Quality Index (WQI)

The concept of water indexing by means of a numerical value which expresses its quality based on physical, chemical and biological measurements was developed in 1965 in the USA. This concept was more widely analysed at the beginning of the 1970's when specialists in the field aimed at finding a way to compare the water quality in all the areas of a given country (Lumb et al., 2011). This proved to be a useful tool in comparing water quality over a given period of time. As regards Europe, the specialists introduced a concept based on normalising the water quality parameters (concentration) and their combination in a model which includes all the parameters analysed, each having a certain weight in the final calculation.

The WQI differences in European and US and Canada calculation, respectively, lie in the statistic method used and in the means of interpreting the parameters and their weight.

The water quality index (WQI) is an adimensional number which combines more water quality factors in a unique number by normalising the values of the subjective evaluation curves (Ramakrishnaiah et al., Akkaraboyina & Raju, 2012; Miller et al., 1986). The factors which have to be included in the WQI model may vary depending on the uses of the water from the water stream analysed and on the local interests. Some of these factors include DO (dissolved oxygen), pH level, BOD (biochemical oxygen demand), COD (chemical oxygen demand), total coliform bacteria, temperature, nutrients (nitrogen and phosphorus) etc. These parameters appear at different intervals of time and are expressed by means of different measurement units. In the present paper we considered it useful to analyse the quantifiable parameters of some heavy metals concentration in the surface waters as influenced , on the one hand, by the economic activities in the area, (the ore port which supplies one of the largest steel and iron works in Eastern Europe and other economic activities which use the same evacuation systems as the population of the city throwing the waste water into the Danube, Prut and Siret rivers before 2013), and by the contribution of the two important rivers that flow into the Danube, namely the Prut and the Siret, on the other.

WQI provides complex scientific information and specifies by means of a single number whether the analysed water corresponds to the quality standards required for its use in various human activities. It also indicates any relative change in water quality. The results obtained are used to decide whether the water can be used by the population (in our case, if there are any problems regarding its use as drinking water) to monitor its quality in time and to compare it with other bodies of water on the planet. In order to determine whether a body of water can be used for one purpose or another, relevant pieces of information should be combined, such as the usage of some biological indicators referring to different species that live in the area. The quality of the water used as potable water or in industrial activities such as food production, as well as of the water used for recreational purposes, has a great impact on people's health.

WQI is an important indicator which may be relatively easily determined, its importance resulting from the crucial role of water resources. This indicator is accepted as one of the 25 indicators by means of which the quality of the environment is assessed, more precisely, the so called Environmental Quality Indices (Environmental Performance Index – EPI) (Lumb et al., 2011). In Europe is used, the same, and WPI (water pollution index) that refer to the quality and pollution of watercourses (Milanovic et al., 2011).

Specialists have suggested various methods for determining/ assessing the WQI. The present paper uses an algorithm which will take into consideration the 19 parameters monitored, calculating the influence of each parameter (***Wi***) in calculating the indicator (Chowdhury et al., 2012). The Danube waters are included in the second quality category (this fact is accepted in the majority of the scientific studies on the Danube), so all the calculations started from this categorization Jakovljevic, 2012; Kolarevic et al., 2011; Taki et al., 2012; Takic et al., 2012, Georgescu et al., 2011, Bayoumi Hamuda et al., 2011).

The studies in the field have accepted various methods of determining the WQI. The present paper focuses on the ***Weighted Arithmetic Water Quality Index Method*** (Brown et al., 1972; Tripaty & Sahu, 2005; Tyagi et al., 2013). For determining the water quality index, the following empiric equation is used:

$$WQI = \frac{\sum W_i q_i}{\sum W_i} \quad (1)$$

where WQI represents the water quality index and it is a number between 0 and 100 (it can exceed 100 if the area is heavily polluted); q_i represents a relative value of the water quality for each parameter, i represents the number of the parameters taken into consideration; W_i represents a factor which measures the importance of a given parameter in calculating the WQI (relative weight). Q_i is calculated by using the following mathematical formula:

$$q_i = 100\frac{V_i - V_0}{S_i - V_0} \quad (2)$$

where V_i represents the measured value (determined experimentally) of the i parameter; V_o represents the ideal value of that parameter (it is 0 for all the parameters excepting the pH for which the value is 7 and the DO for whose value is 14.6 mg L^{-1}); S_i represents the standard value legally accepted for the water category in which the analysed water sample was included.

The W_i factor is calculated by using the following formula:

$$W_i = \frac{K}{S_i} \quad (3)$$

where K is a constant value calculated by the formula below:

$$K = \frac{1}{\sum \left(\frac{1}{S_i} \right)} \quad (4)$$

WQI will be calculated by taking into consideration the Romanian standards for the surface waters (Law 311 of 28 June 2004).

Depending on the water quality index, the water can included in one of the following quality classes/ categories (Table 1).

Table 1. Water quality classification based on WQI value (Chowdhury et al., 2012)

Water quality	Exce-llent	Good water	Poor water	Very poor water	Water unsuita-ble for drinking
WQI value	0-25	26-50	51-75	75-100	>100

2. STUDY AREA

The area in which the study was conducted had the following GIS coordinates:

S1- situated upstream Galati city (45° 20' 93 N 28° 00' 88 E),

S2 – the Siret- Danube confluence (45° 24' 3945° 24' 39 N 0.28° 01' 53 E),

S3 – Deversor Bac (45° 24' 96 N 0.28° 01' 97 E),

S4 – the Prut – Danube confluence (45° 27' 66 N 0, 28° 14' 0.39 E),

S5- Reni (45° 18' 13.03 N 28° 23' 29.80E).

The sampling points are shown on the map represented in figure 1.

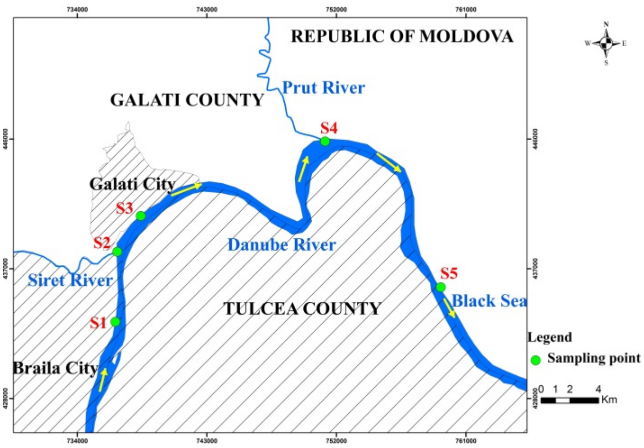

Figure1. The geographic distribution of the sampling points

3. MATERIALS AND METHODS

The samples were taken by using the standard procedure. Polyethylene recipients were used and the samples were analysed on the spot, whenever possible, or they were sent in the shortest time possible to the accredited water testing laboratory (The Regional Center of Research and Monitoring the Environment Quality belonging to the “Dunarea de Jos” University of Galati, Romania).

Sampling and sample analyses for physicochemical parameters were realized according the following Standard methods: SR EN 1899-2:2002 for BOD determination, SR EN ISO 6878:2005 for P-PO_4 determination, SR EN ISO 11732:2005 for ammonium determination, ISO 15705:2002 for COD determination, SR EN 26777:2006 for nitrogen from nitrite determination, SR EN ISO 11905-1:2003 for nitrogen from nitrate determination (Romanian Standards for Water Quality). pH and OD measurement were executed with a HANNA HI 9828 multiparameter analyser. Heavy metals were spectrophotometrically determined by using a Spectroquant NOVA 60 spectrophotometer and Merck kits.

The WQI in all the sampling points and in the monitoring seasons were calculated by means of the measured parameters. Statistical research was made for the results interpretation by using the Principal Component Analyses (PCA) (Garizi et al., 2011). This method highlighted the distribution points where water quality is good, as opposed to those in which water quality is affected by the sewage and industrial water coming from Galati City and by the quality of the water in the Prut and Siret rivers. The correlations between the values of the physico-chemical parameters and the WQI were also made by means of the PCA.

4. RESULTS AND DISCUSSION

The *K* si *Wi* values were calculated taking into consideration the classification of the water in the Danube as a second-quality-category water and the standard values stipulated by the normative documents in force. The results obtained are presented in table 2.

19 physicochemical parameters were monitored in order to calculate the WQI, aspect which led to the gathering of a large amount of experimental data and to numerous calculations made according to the suggested algorithm. As a consequence, the present paper provides only 3 examples illustrative for the calculation of the WQI values, (Table 3).

Analysing the data in table 2 and table 3, the conclusion could be drawn that the highly toxic elements for which the acceptable limits are really low (see heavy metals such as Cd, Pb, Cr and Ni, and the nitrogen in nitrites - nitrite nitrogen, $N\text{-}NO_2$) represent the most significant parameters in assessing the WQI values.

The WQI values presented in Table 4 and illustrated by figure 2 were obtained by using the above mentioned parameters and the values experimentally measured in the 5 sampling points over a three-year period of time.

The fact can be noticed that the introduction of a series of less frequently used parameters, such as the heavy metals, in calculating the WQI favours a more comprehensive assessment of the anthropogenic impact of specific industrial activities on water quality. Moreover, it favours a clearer differentiation regarding the impact of the various chemical species, in our case the nitrites and heavy metals. As a result, the disadvantages of strictly taking into consideration the nitrites (with the legally accepted limit of 0.03 mg/L in our country) are eliminated, this more minute analysis greatly influencing the assessment of the WQI and the quality of the data obtained.

The calculations made pointed out the fact that the WQI reached its minimum of 39.01 in the winter of 2012 and its maximum of 65.21 in the autumn of 2012 (Fig. 2).

The values recorded in the S1 and S5 sampling points were below 50, which led to the inclusion of the water in these points in the “good water” category. The S1 sampling point is situated downstream the ore port at the Siret and Danube rivers confluence. The water intakes from which 80% of the necessary water, the drinking water included, is intaken are situated in the same area. The S5 sampling point is situated farther from the Prut and Danube rivers confluence, and the water quality is significantly improved in this point, aspect which illustrates the Danube self-treatment capacity.

Table 2. Values of constant *K* and relative weight, W_i

Nr. crt.	Parameters	S_i	$1/S_i$	k	W_i
1.	pH	8.2	0.121951	$7.89\cdot10^{-4}$	9.62E-05
2.	DO	7	0.142857		0.000113
3.	BOD	5	0.2		0.000158
4.	COD	25	0.04		3.16E-05
5.	NH_4^+	0.8	1.25		0.000986
6.	$N\text{-}NO_2^-$	0.03	33.33333		0.0263
7.	$N\text{-}NO_3^-$	3	0.333333		0.000263
8.	N_{total}	7	0.142857		0.000113
9.	$P\text{-}PO_4^{3-}$	0.2	5		0.003945
10.	SO_4^{2-}	120	0.008333		6.58E-06
11.	Cl^-	50	0.02		1.58E-05
12.	Cr -total	0.05	20		0.01578
13.	Pb^{2+}	0.01	100		0.0789
14.	Cd^{2+}	0.001	1000		0.789
15.	Ni^{2+}	0.025	40		0.03156
16.	Fe - total	0.5	2		0.001578
17.	Mn - total	0.1	10		0.00789
18.	Zn^{2+}	0.2	5		0.003945
19.	As^{2+}	0.02	50		0.03945

DO (dissolved oxygen), BOD (biochemical oxygen demand), COD (chemical oxygen demand).

Table 3. Examples of WQI calculation for three different sampling points in the summer of 2012

Parameter		S1		S3		S5	
	W_i	q_i	$q_i x W_i$	q_i	$q_i x W_i$	q_i	$q_i x W_i$
pH	9.62E-05	100.8333	0.009701	105	0.010102	106.6667	0.010262
DO	0.000113	128.9474	0.014534	117.8947	0.013288	112.1053	0.012636
BOD	0.000158	74	0.011677	54	0.008521	64	0.010099
COD	3.16E-05	50.8	0.001603	74	0.002335	67.6	0.002133
NH_4^+	0.000986	35.75	0.035258	18.5	0.018246	67.375	0.066449
$N-NO_2$	0.0263	203.3333	5.347667	196.6667	5.172333	203.3333	5.347667
$N-NO_3$	0.000263	170.3333	0.044798	124.6667	0.032787	264.6667	0.069607
Ntotal	0.000113	89.14286	0.010048	87.28571	0.009838	133.5714	0.015055
$P-PO_4^{3-}$	0.003945	48	0.18936	5.3	0.020909	57.5	0.226838
SO_4^{2-}	6.58E-06	97.5	0.000641	115	0.000756	81.66667	0.000537
Cl-	1.58E-05	90	0.00142	114	0.001799	86	0.001357
Cr -total	0.01578	68	1.07304	84	1.32552	76	1.19928
Pb^{2+}	0.0789	79	6.2331	88	6.9432	72	5.6808
Cd^{2+}	0.789	31	24.459	48	37.872	37	29.193
Ni^{2+}	0.03156	48	1.51488	64	2.01984	36	1.13616
Fe - total	0.001578	108	0.170424	108	0.170424	76	0.119928
Mn-total	0.00789	100	0.789	87	0.68643	41	0.32349
Zn^{2+}	0.003945	85	0.335325	93.5	0.368858	45	0.177525
As^{2+}	0.03945	21	0.82845	18	0.7101	4	0.1578
WQI		41.07		55.39		43.75	

Table 4. WQI values for all the sampling points during the 3 years envisaged

Nr. crt.	Season	Sampling points				
		S1	S2	S3	S4	S5
1.	AUTUMN 2010	47.07	56.87	64.6	61.11	45.24
2.	WINTER 2011	41.83	50.09	53.89	50.17	40
3.	SPRING 2011	40.75	51.67	55.76	50.07	42.49
4.	SUMMER 2011	44.02	53.06	62.08	58.7	44.09
5.	AUTUMN 2011	48.33	56.56	65.21	61.65	45.8
6.	WINTER 2012	39.01	56.15	53.81	56.63	44.96
7.	SPRING 2012	40.73	52.95	53.04	54.86	41.12
8.	SUMMER 2012	41.07	54.02	53.39	53.63	43.75
9.	AUTUMN 2012	44.66	56.12	55.64	56.72	40.83
10.	WINTER 2013	41.74	51.46	47.17	48.95	40.51
11.	SPRING 2013	44.01	52.18	49.22	53.58	40.39
12.	SUMMER2013	40.43	52.37	48.2	50.65	40.2

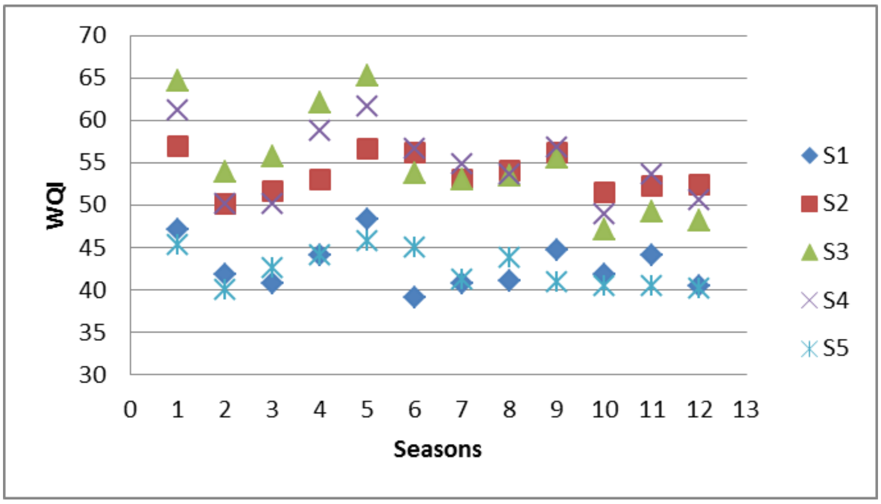

Figure 2. WQI Variation

The values recorded in the S2, S3 and S4 points are over 50, aspect which leads to the inclusion of the water in these points in the “poor water” category. The S2 sampling point is situated at the Siret and Danube Rivers confluence. The influence of the intake water is more significant in this point because the level of pollution is higher on the Siret than on the Danube. The fact could be noticed that the nutrients intake, especially the nitrites, is higher during spring and summer and nitrogen- and phosphorus- based fertilizers are used for agricultural activities. In addition, the position of the S2 sampling point upstream the ore port favours the presence of higher Fe levels than the standard values legally accepted. The same may be said in relation to the Prut, the S4 sampling point being situated at the confluence of this river with the Danube and after the city sewer line.

The highest WQI values were recorded in the S3 sampling point (Fig. 3) which is situated close to the point where Municipal Wastewater is spilt in the Danube. The maximum levels acceptable for second category waters were exceeded in the case of COD, BOD, SO_4 and heavy metals. The Waste Water Treatment Plant (WWTP) activated in 2012 led to a decrease in the WQI below 60 in the S3 and S4 sampling points. The WQI values slightly increased in the S2 sampling point as a result of the sewage water treated in the WWTP spilt in the Siret River and of the subsequent increase in the COD, BOD and heavy metals levels.

Analysing the results obtained for each season, the fact could be noticed that the lowest values were recorded during winter (Fig. 4) when the dissolved oxygen (DO) level is higher and the nutrients level is lower, whereas the highest values were recorded during autumn.

Considering the aspects mentioned above, the assessment of the WQI proves extremely useful for analysing the water quality management, especially in the case of surface waters which are influenced both by anthropogenic and natural factors. The WWTP in Galati, the first significant investment of this type in our city, has already proved its usefulness, despite the fact that at the moment when the present study was conducted this plant was strictly used for mechanic water treatment (sediment removal). The development of this investment by adding chemical and biologic water treatment will definitely have a significant impact on the Danube water quality, and will most probably represent the subject of further research.

The WQI values point out the fact that the river flow plays an important part in the results obtained. Thus, the highest values were recorded during autumn (Fig. 5) after a period of low river flows (especially during August), and the lowest values were recorded during winter, due to higher river flows, to lower temperatures and to less intensive agricultural activities in the Prut – Siret hydrographic areas.

The Principal Component Analysis was used to check if there is any seasonal gradient in the chemical data obtained in the various sites and seasons considered. The first axis explained 28.75 % of the total variance of chemical parameters among seasons. The second axis explained an additional 21.49% of this variance. A clear separation was identified in the winter and spring of 2011.

Figures 8 and 9 illustrate the PCA for 2012 and 2013, but the distinction is not clear because some of the physico–chemical parameters monitored are within normal limits, most probably due to the functioning of the municipal wastewater treatment plant. In 2012 (Fig. 8) first axis of the PCA explained 27.58% of the variance and the axis two 22.09% but the analyses did not revealed any clear gradient and can this finding can be explained by a high variability of chemical parameters among seasons and sites.

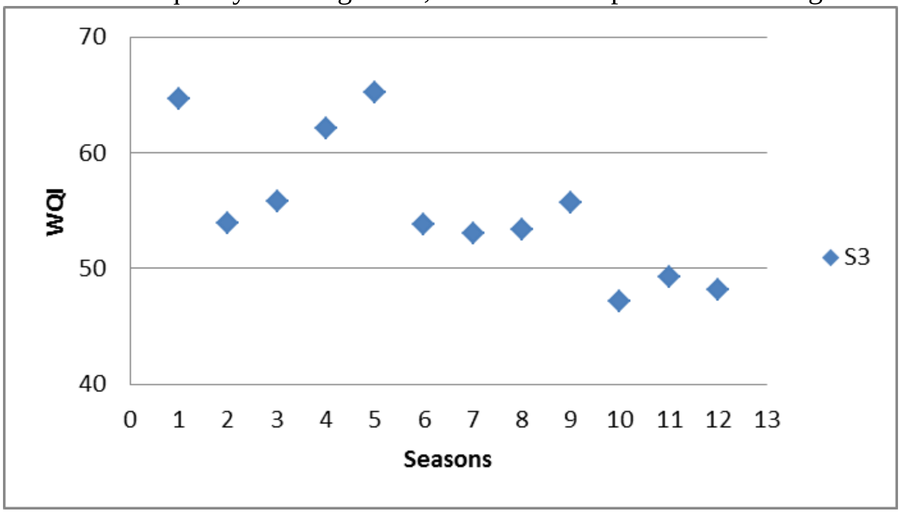

Figure 3. WQI Variation in S3 sampling point between 2010– 2013

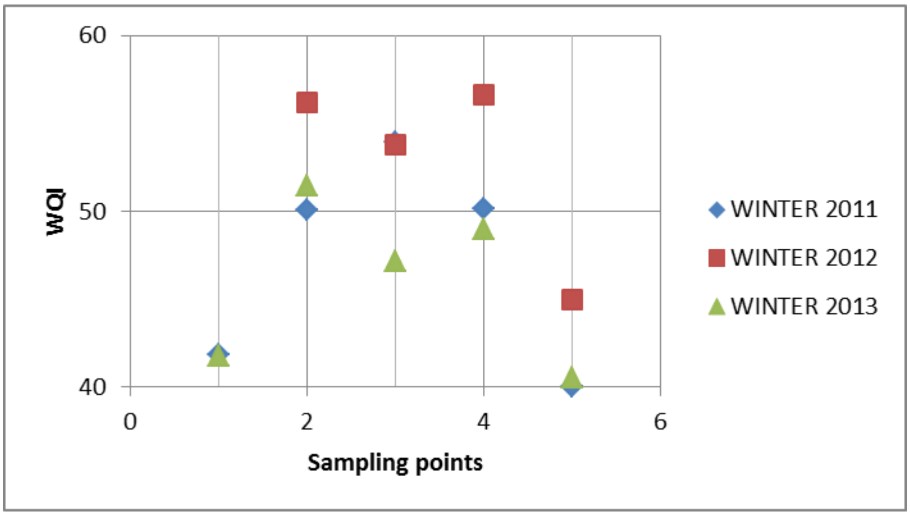

Figure 5. WQI Variation in the winters of 2011 – 2013

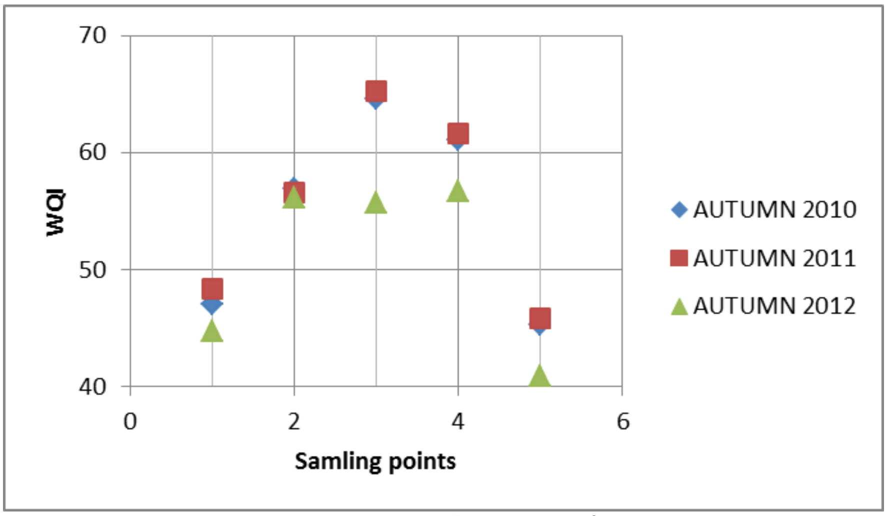

Figure 6. WQI Variation in the autumn of 2010 – 2012

In 2013 (Fig. 9) first axis of the PCA explained 38.93 % of the variance and second axis 20.83 %. PCA revealed that in station 5 at Reni, in spring and winter season, chemical parameters registered approximately the same seasonal variation. Anthropic influence it's decreasing in this site because he is situated away from sources of pollution emphasizing self-cleaning capacity Danube water. Overall and considering the other stations box plot shows that water quality registers an improvement in the winter season.

5. CONCLUSIONS

The results of the present research point out the necessity of systematically observing the hydrograhic basins situated close to urban areas where water quality has a significant impact on both the human health (the rivers in these basins being a major source of drinking water) and the sensitive ecosystems nearby (in our case the Danube Delta, one of the most important natural reservations in the world).

In addition, the WQI methodology has proved its usefulness as an instrument used for the surface waters global management and for calculating the cost/effectiveness report in the case of certain major investments such as the WWTP in Galati, built mainly from EU funding.

Effective results in water quality monitoring can be obtained if the number of parameters included in the WQI analysis is high and if this analysis takes into consideration chemical species with the same order concentrations. The latter condition allows for a reasonable statistic distribution of the parameters envisaged when globally assessing the quality of the waters analysed.

Another important conclusion is related to the necessity of making complex research which is centred not only on water quality, but also on the quality of the associated sediments.

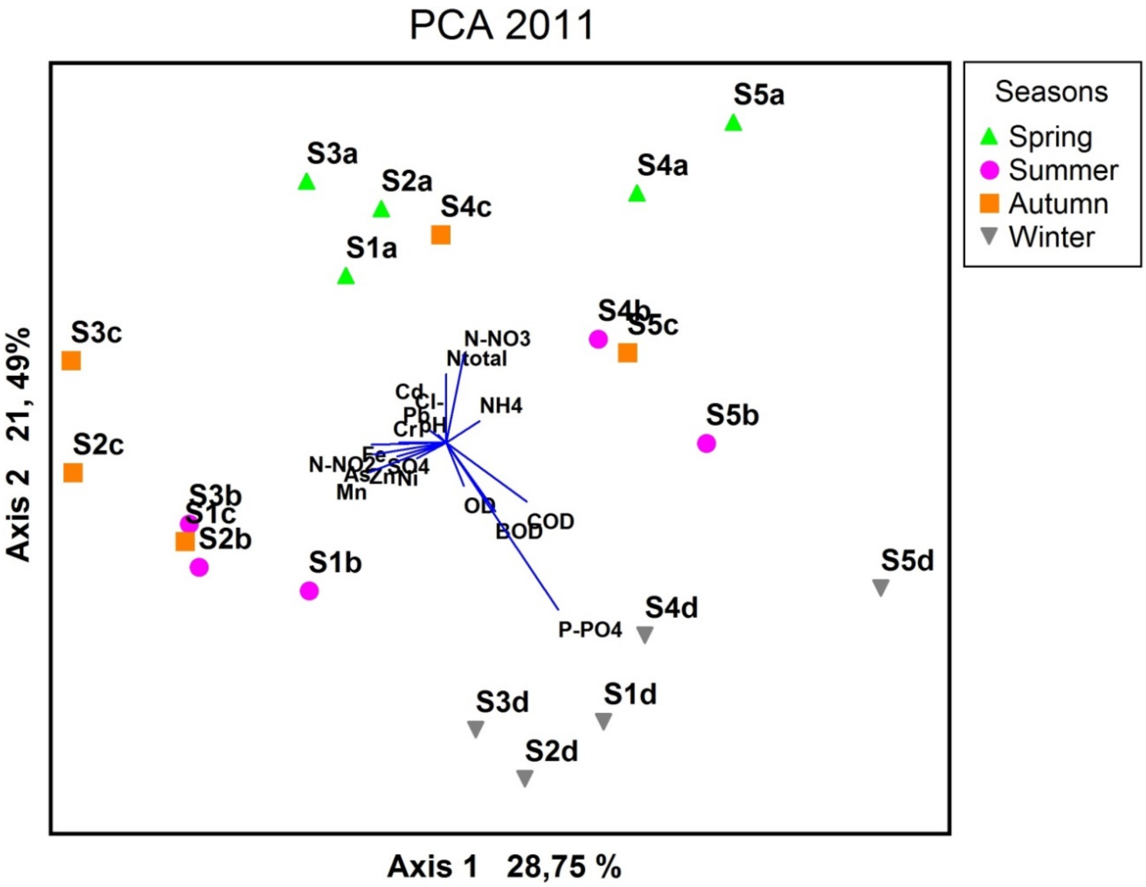

Figure 7. Principal Component Analysis for seasons and parameters measured in 2011

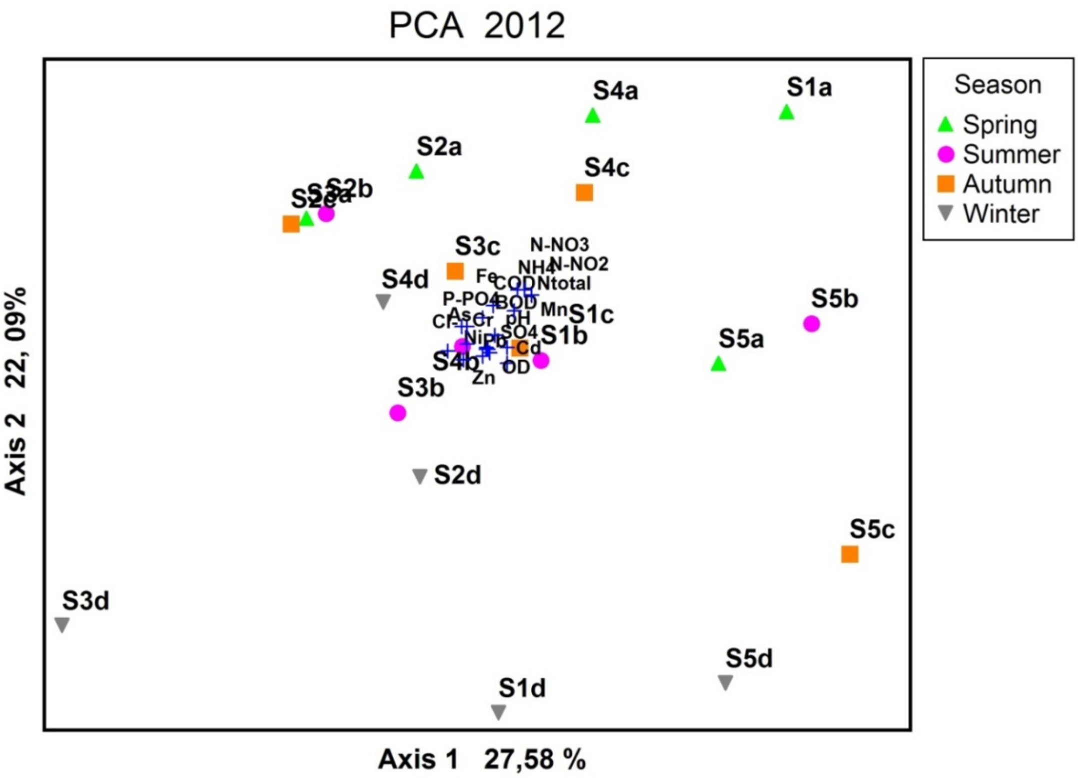

Figure 8. Principal Component Analysis for chemical parameters monitored in four seasons in 2012

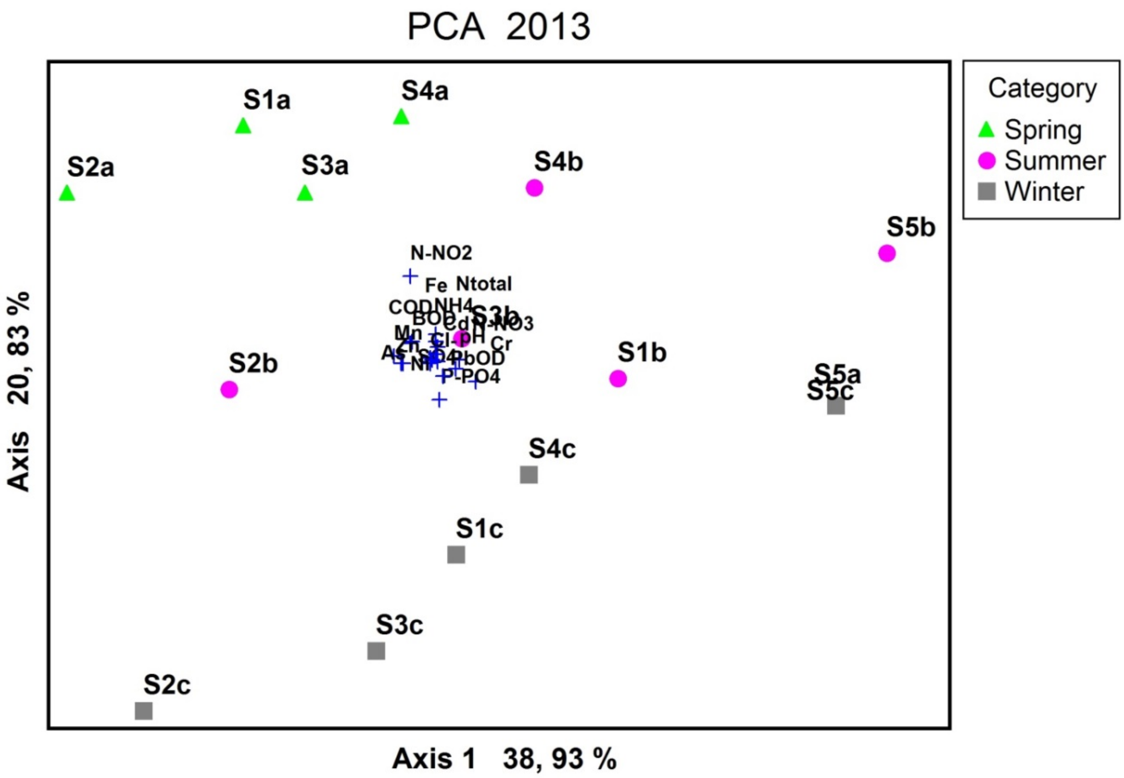

Figure 9. Principal Component Analysis for chemical parameters monitored in three seasons in 2013

Water quality seems to improve after the areas affected by anthropogenic factors, the water pollutants being traceable in sediments, in the vegetation, as well as in the biologic systems specific to the benthos. The water treatment process may become more effective by closely observing the presence of sensitive species in the associated sediments.

There are specific and multiple environmental pressures on water quality in the Lower Danube area, the industrial, agricultural and domestic sources being mainly responsible for this situation. Taking into account the specificity of sensitive water ecosystems, it is necessary to ensure long-term monitoring of chemical parameters, but not only. It is also compulsory to extend the monitoring process on biological parameters and on soil quality, as well as to identify the environmental impact of different sources. The present paper gives an overall description on the impact of existing measures (new waste water treatment plant) and it suggests further investments in water treatment plants so as to identify the main pollutants and their impact on Danube water quality.

Finally, considering the position of the area analysed on the borders of the Republic of Moldova and Ukraine, the systematic observations have to be made on larger areas which will include adjacent territories of riverain countries.

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