Seasonal Variation of the Physico-chemical Parameters and Water Quality Index (WQI) of Danube Water in the Transborder Lower Danube Area

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Danube water assessment is a major concern in the international area of the Lower Danube which corresponds to Romania, Republic of Moldavia and Ukraine nearby to the industrial objectives and densely populated regions. Physico-chemical parameters, namely pH, TSM (Total Suspended Mater), filterable residue, Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, BOD (biochemical oxygen demand), (chemical oxygen demand) COD-Cr and phenols were monitored for the present study. The pollution in the monitored area is due to factors depending of upstream and local area. The monitoring was conducted seasonally between 2010 and 2012 and data interpretation was done using statistical analysis methods as: elemental analysis, the Principal Component Analysis (PCA) and the principal factor analysis (Varimax rotation). Water quality index (WQI) was also calculated. Statistical studies established the most important set of parameters to be measured for an optimal monitoring strategy to be effectively applied in this area of the Danube.

Keywords: Danube, water quality, physico-chemical parameters, WQI, PCA

Regular monitoring of water courses is essential for maintaining qualitative parameters within acceptable limits from the environmental point of view as well as for impact on life quality [1]. Different parameters and the statistical correlations between them are those which indicate the variation of water quality in the monitored stream [2-4]. Identification of interdependencies between few parameters it is used to determine sources of pollution, to adopt specific measures to decrease anthropic pressure, but also to determine the effectiveness of certain measures and investments, such as the municipal stations of wastewater treatment. Association of variables is established by using multivariate statistical techniques [5-7].

Periodic measurements in different monitoring stations represent a common program for water quality assessment involving a matrix of complex data in relation to a series of physico - chemical parameters describing water quality [8, 9].

WQI was calculated after the Weighted Arithmetic Water Quality Index Method [10, 11]. WQI is an adimensional number which combines more water quality parameters into a single number [12, 13]. WQI can reach values between 0 and 100, and according to this parameter, surface freshwaters can be classified into five categories (table 1), [14]. This classification could be associated with European Union Water Directives which use the same number of categories [15].

Table 1
WATER QUALITY RANGE IN COMPLIANCE WITH WQI

WQI values	Water quality range
0-25	Very good
25-50	Good
50-75	Moderate
75-100	Bad
>100	Very bad

Multivariate statistical analysis methods are applied to reduce the number of different monitored parameters (only relevant parameters are identified [16, 17]. These methods provide powerful tools which allow for a precise determination of possible correlations between various parameters. One of the applications consists in identifying the factors which influence aquatic ecosystems so as to establish an effective management and to identify solutions rapidly in case of pollution [18-21].

The present paper aims to determine the seasonal variation of water quality through WQI in the Lower Danube area, before it flows into the Danube Delta. The classification of Danube water in quality groups according to the Romanian legislation in force, [4, 23] was also envisaged.

Experimental part

In order to achieve a more accurate assessment of water quality in the Lower Danube area, the samples

Fig. 1. The geographic distribution of the sampling points (S1- Reni; S2- Scurta; S3- Grindu; S4- Isaccea; S5- Amonte Ivanova)

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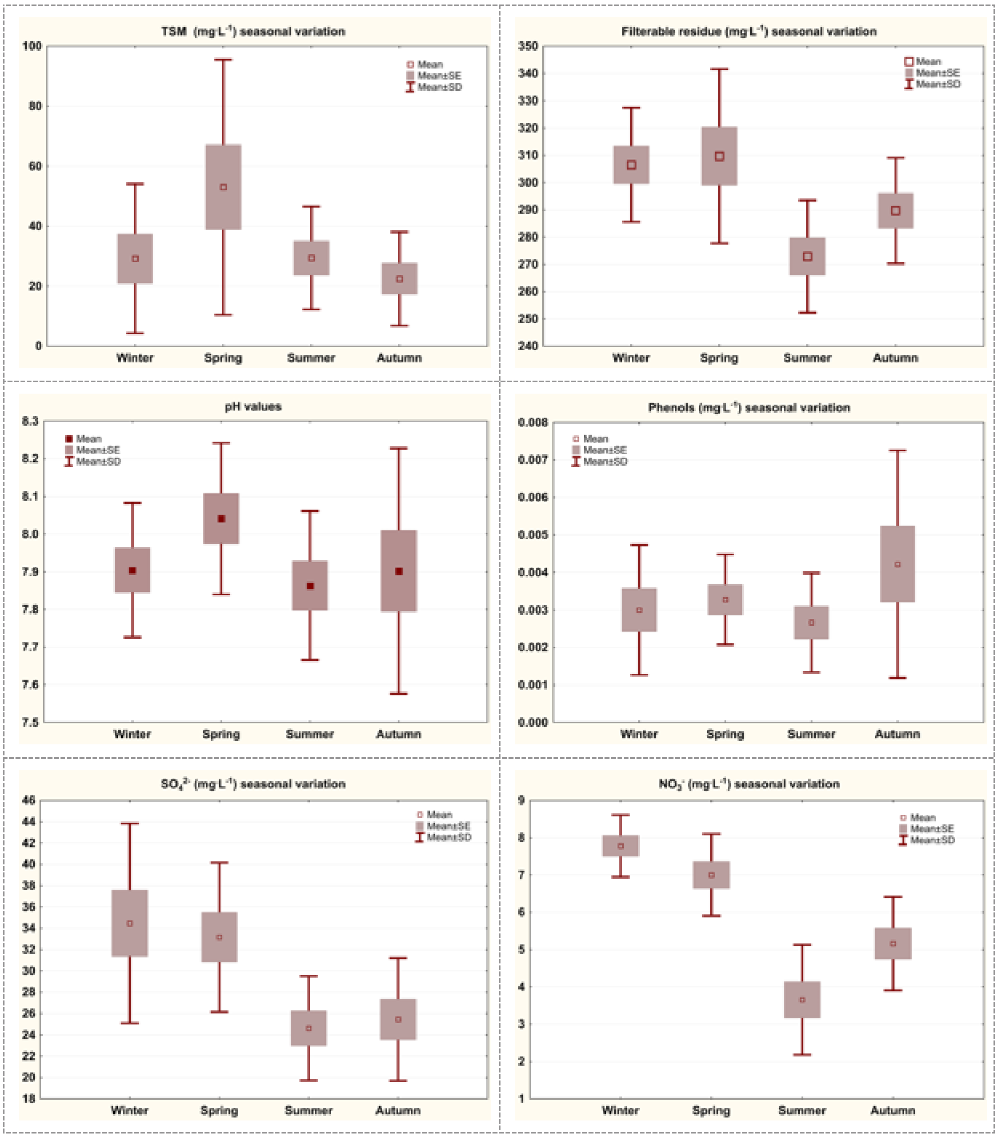

Fig. 2. Seasonal variation of physicochemical parameters: TSM, filtrable residue, pH, phenols, SO_4^{2-}, NO_3^-

analysed were taken from five monitoring key stations located upstream Tulcea and downstream the Prut River (fig. 1).Sampling was conducted at about 10 meters from the shore.

The samples were either analysed on the field or sent to the water testing laboratory (CREDENTIAL Center belonging to Dunarea de Jos University of Galati, Romania).

Physico-chemical parameters namely *p*H, TSM, filterable residue, Cl^-, $SO4^{2-}$, NO^{3-}, NH^{4+}, BOD, COD and phenols were monitored. Physico-chemical analyses were conducted in accordance with Romanian and international standards in force. BOD was made photometrically using Merck kits, (method in accordance with ISO 5815-1). COD was made photometrically using Merck kits (method in accordance with EPA 410.4 and SR ISO 6060). SO_4^{2-} – sulphate ion was also determined using Merck kits. This method is analogue with EPA 375.4 and in accordance with the EPA 9038/1996. Cl^- – ion chloride was determined photometrically using Merck kits (method in accordance with EPA 325.1 and ISO 9297:2001). Phenols were determined using Merck kits code 00856, method in accordance with SR ISO 6439:2001; SR EN ISO 11732:2005, for ammonium determination; SR EN ISO 11905-1:2003 for nitrogen from nitrate determination (Romanian Standards for Water Quality). pH measurements were made using HANNA HI 9828 multiparameter analyser. TSM was determined in accordance with the national standard STAS 6953-81.

Filterable residue determination was carried out in accordance with STAS 9187-84.

Results and discussions

Seasonal variation of the physico-chemical parameters monitored is presented by means of box plot diagrams (fig. 2 and fig. 3).

The *p*H of natural waters ranges between 6.5 and 8.5 *p*H units, a deviation from these values generally indicating the existence of pollution. The highest value measured of 8.35 *p*H units (sampling station 1, spring of 2011), the lowest value of 7.16 *p*H units (sampling station 1, December 2011). t-Test indicates confidence level below 0.05 in all cases.

BOD is conditioned by the amount of oxygen (mg/L), necessary for the oxidation by bacteria of organic substances existing in water. Average values reached approximately 1.77 mg $O_2 \cdot L^{-1}$, the lowest value of 0.59 mg $O_2 \cdot L^{-1}$, being recorded in station 3 in May and July 2012, and the highest value of 5.59 mg $O_2 \cdot L^{-1}$ in sampling station 1 in January 2012. According to the Romanian law, average values below 3 mg $O_2 \cdot L^{-1}$ allow for the inclusion of the water in this area in quality category I (fig. 3). This means that pollution with organic substances is relatively low, the organic load of the water increasing only for limited periods of time due to anthropogenic or natural factors. Values above the limit were registered only in station 1, which is the nearest to city of Galati. Moreover, different BOD values

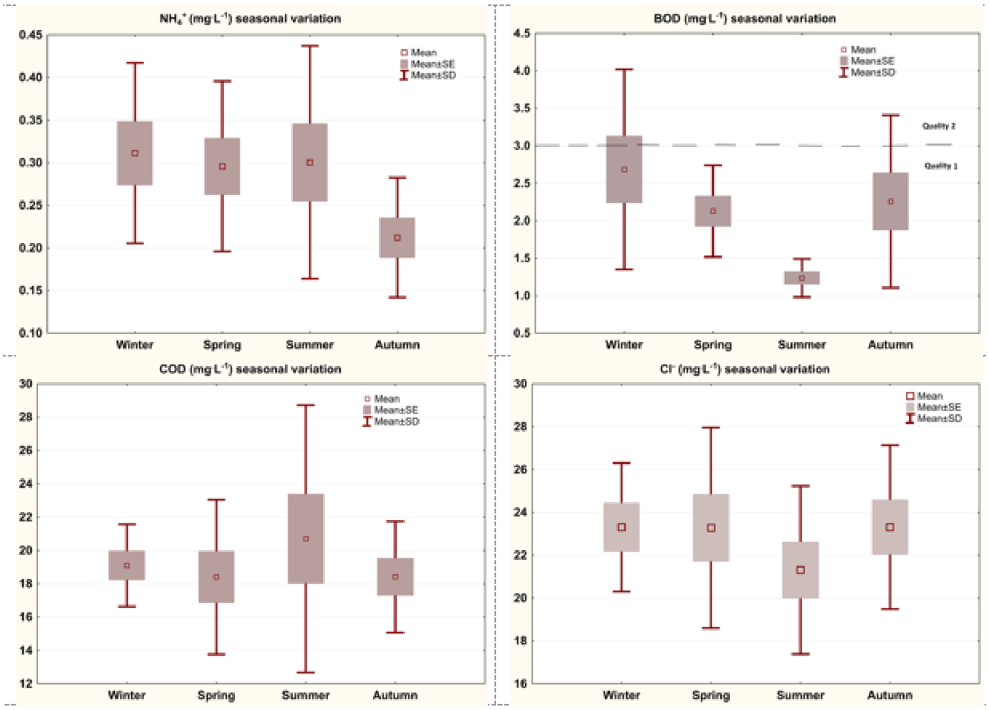

Fig. 3.Seasonal variation of chemical parameters: NH_4^+, BOD, COD,Cl^-.

in the monitored seasons were tested with the t-Test, the confidence level being below 0.05 in all cases.

COD indicator generally affects 60-70% of organic substances, the non-biodegradable ones included. Average values rose to approximately 19.106 $mg{\cdot}L^{-1}$, the lowest value of 13.21 mg $O_2{\cdot}L^{-1}$ being recorded in August 2010, and the highest one of 46.64 mg $O_2{\cdot}L^{-1}$ in August 2011. The latter value exceeds the multiannual average and categorizes the Danube water in the monitored sector in quality class III, indicating a possible pollution in the area at the time. The values obtained by using the t-Test method indicated a confidence level below 0.05.

This ammonium ion may be found in surface waters as a result of degradation of proteins and organic matter from vegetable and animal waste contained in the sediment, industrial and domestic water discharge, or in the underground waters where nitrate reduction occurs by autotrophic bacteria or by the ferric ions content [24 - Canadian Environmental Protection Act, 2001]. The mean value for the determinations made was 0.271 mg $N{\cdot}L^{-1}$, the maximum value of 0.539 mg $N{\cdot}L^{-1}$ being identified in January 2012 and the minimum one of 0.114 mg $N{\cdot}L^{-1}$ in October 2010. The separate values obtained revealed that Danube water in the monitored area corresponds to quality class I. The t-Test confirmed the obtained results, the confidence level being below 0.05.

The presence of nitrates in natural waters can be explained by water contact with the ground watershed or by water discharge from farmland. The average value of around 5.80 mg $N{\cdot}L^{-1}$ illustrated by figure 2 allows for the inclusion of the monitored water in quality class IV. The lowest value of 2.41 mg $N{\cdot}L^{-1}$ was recorded in August 2012 (quality class II), and the highest one of 10.13 mg $N{\cdot}L^{-1}$ in January 2012, (quality class IV). Nitrates values above the acceptable concentrations were recorded especially in spring, a possible explanation for this being the excessive use of fertilizers based on N for agriculture in the surrounding areas associated with important water flows resulting from snow melting on lands in the Danube basin or in those of the tributary rivers. The t-Test indicated confidence values below 0.05.

Sulphate ions can originate in natural sources such as minerals found in clays characteristic to the geology of the Danube basin, or in anthropogenic sources such as fertilizers used in agriculture or in the industries using H_2SO_4, (there is a steel mill downstream the monitored area which use H_2SO_4 for pickling). There were no records of values above the maximum acceptable concentration limits specific to quality class I during the 3 years of monitoring. One isolated value of 79, 05 $mg{\cdot}L^{-1}$ was recorded in station 2 in July 2011.

The phenols measurements made proved that the water monitored belongs to quality category II. A decrease in the phenol concentration was identified in 2012 in comparison with 2011 as result of closing down the Coking Plant having wastewater discharge the Siret River, upstream the monitored area.

Chloride values above the maximum allowable concentration for quality class I was recorded only in 2011 and only in one station (Station 2). The annual average was of 27.02 $mg{\cdot}L^{-1}$, which allowed for the inclusion of the water monitored in quality class II.

TSM represent the substances insoluble in water which can be separated by filtration, centrifugation or sedimentation (size of max. 2 mm expressed in $mg{\cdot}L^{-1}$) and it is closely conditioned by season and Danube debt [25, 26]. The mean, minimum and maximum values include the monitored water in quality category I.

As regards phenols, chlorides sulphates, TSM and filterable residue, the t- Test confirms the results, indicating confidence values below 0.05.

Taking into account the values obtained, the water monitored can be included in the category 'good' water quality. This is not the case with the summer months when, due to the low flow of the Danube, some parameters concentrations exceed the maximum allowable concentrations for water category II, and the WQI exceeds 50, the monitored water falling into the category poor water quality (fig. 4).

Figure 4 illustrates that the WQI average values are similar, but the values recorded in summer indicate a relatively high dispersion as compared to the other seasons (spring and winter). This variation can be explained by the action of natural and anthropogenic factors which are more important due to the activities carried out in the area

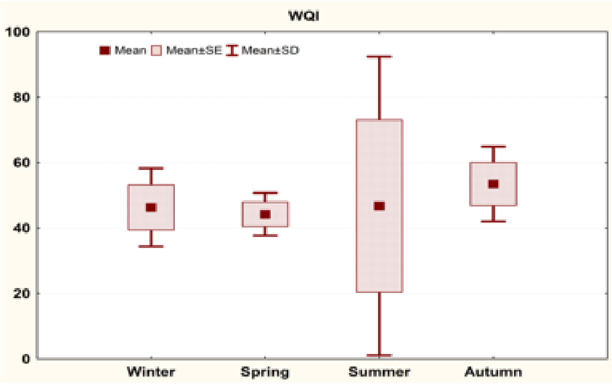

Fig. 4. Seasonal variation of WQI between 2010-2012

(agriculture, industry) and to the lower levels of the Danube in summer.

The seasonal variation of the monitored parameters was also evaluated and analysed using the Principal Component Analysis (PCA). This is a method meant to reduce a given data set which consists of numerous interconnected variables, preserving as much variability in the data set as possible [16, 25, 28-30]. Moreover, PCA allows for an evaluation of the correlation between the selected variables, which indicate the influence of individual chemical species on the most relevant factors [16, 29, 31].

The existence of a seasonal gradient in physico-chemical data set was checked by using the PCA. The diagrams show the grouping parameters depending on how they influence each other. For example, factor 1 is represented by the values of the SO_4^{2-}, Cl^-, NO_3^-, NH_4^+ ions, all of them having an influence on the pH value, which is part of the same group conditioning factor 1. Factor 2 includes the parameters: COD, BOD, phenol and filterable residue, this grouping being appropriate due to the fact that the values of the first two parameters are conditioned by the concentrations of the last two.

The angle between the directions corresponding to two parameters is generally conditioned by the value of the Pearson correlation coefficient and it is proportional to the value of the covariance between the two variables. Thus, the smaller the angle between the directions, the closer to value 1 is the correlation coefficients between the two variables. This means that the link between the parameters envisaged is stronger.

Thus, factor 1, which explains over 34% of the variance, includes the parameters COD, *p*H, NO_3^- and NH_4^+ in winter (fig. 5 a) and may be influenced by the Cl- and SO_4^{2-} ions, as well. As regards spring (fig. 5 b), the distribution changes, factor 1 being represented by pH, TSM, NO^{3-}si SO_4^{2-}. This variation in the parameters analysed can be explained by the high water flow during spring and the change in the degree of influence of natural and anthropic activities, respectively. The distribution undergoes a new change in summer, factor 1 being represented by SO_4^{2-}, phenols and NH_4^+. Factor 1 represents over 40% of the total variance of the monitored parameters in autumn and it includes a distribution represented by *p*H, filtrable residue, TSM, NO_3^- and SO_4^{2-}. The diagram changes significantly in the sense that, different from summer, phenols are negatively correlated, aspect which is characteristic to the high water flow seasons. These changes in the distribution of the two factors is attributed to water flow variation in an expanded basin whose hydrologic characteristics vary from one season to another and to the influence of anthropogenic factors, some of the activities carried out in the area (e.g. agriculture) being seasonal.

The PCA analysis was made taking into account the database of the WQI values. The results of the PCA analysis for two of the seasons i.e. winter and spring are presented in figure 6.

The analysis of correlations and connections between the parameters included in the database, illustrates the existence of some principal components with weights quite significant. Thus, for the values recorded in winter (fig. 6 a1), the factor 1 component covers 32.08% of the variance and includes parameters with a high degree of correlation between them, namely: NH_4, NO_3, *p*H. The factor 2 component, which explains 29.06% of the variance, correlates the WQI with TSM, SO_4 and Cl, etc. WQI correlates positively with TSM and negatively with filterable residue (fig. 6 a1). The relatively weak correlation between WQI and phenols can be explained by the low water flow in winter, which can modify the influences of the various components dissolved in water.

If the principal components of order 3 corresponding to winter and spring are taken into account (fig. 6 a2 and a3), the conclusion can be drawn that WQI is correlated with Cl^-, SO_4^{2-}, NH_4^+. Positive correlations were established between WQI and phenols, its influence being the most important. Correlations between WQI and Cl^-, SO_4^{2-}, NH_4^+ could be established in both cases.

As regards the analysis on the database including the records made in spring, WQI can be included factor1in factors group. This first principal component explains 44.65% of the total variance. Moreover, there are notable correlations between WQI, phenols and NH_4^+ and negative correlations between WQI, filterable residue; CCO-Cr and SO_4^{2-} (fig. 6 b1).

Considering the bidimensional representation of the principal components of orders 2 and 3 (fig. 6 b2 and b3), the fact may be noticed that there is a positive correlation between WQI and the concentration of phenols and NH_4^+, respectively. Moreover, there is a mainly negative correlation between WQI and *p*H, on the one hand and COD, filterable residue and Cl^-, on the other.

To sum up the aspects above, the phenol is the main parameter which influences the value of the WQI, its concentration conditioning the WQI value in all cases. Positive correlations between WQI and COD, BOD, NH_4^+ may also be noted, all these parameters indicating the degree of water pollution.

In order to have an additional confirmation of the results obtained by applying PCA, the factor analysis method (Varimax rotation) was used. This method provides a different grouping of the physico-chemical parameters allowing a simple and meaningful representation of the factors which diminish the contribution of the principal components, of the variables with minor significance and increase the contribution of the important ones [27, 30, 31]. The diagram in figure 7 illustrates the same grouping of parameters monitored by means of the PCA analysis.

Conclusions

The PCA analysis pointed out the fact that ions SO_4^{2-}, Cl^-, NO_3^-, NH_4^+ influence the pH value. As stated above, pH levels depend on important global factors such as temperature, organic loading, etc. Dependences could be established between sulphate and nitrogen ions, nitrate and ammonium, chloride and nitrate. If the sulphate ions are dominant, then pollution is of an anthropogenic nature. If nitrate or ammonium ions are more numerous, this indicates that pollution is of an agricultural nature (nitrate ions originating in fertilizers and ammonium ions originating in farming activity).

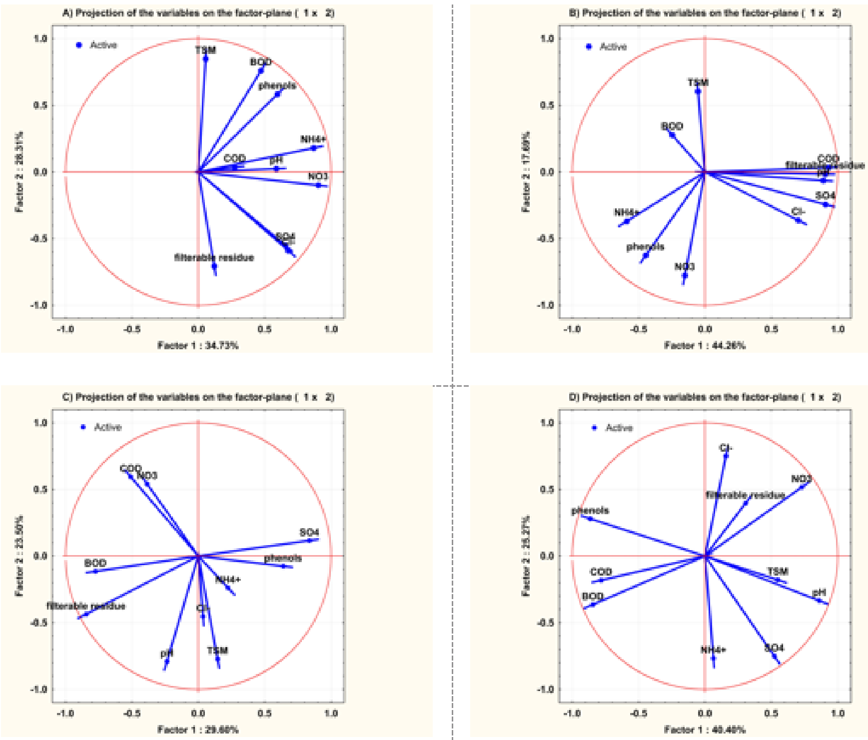

Fig. 5. Principal Component Analysis

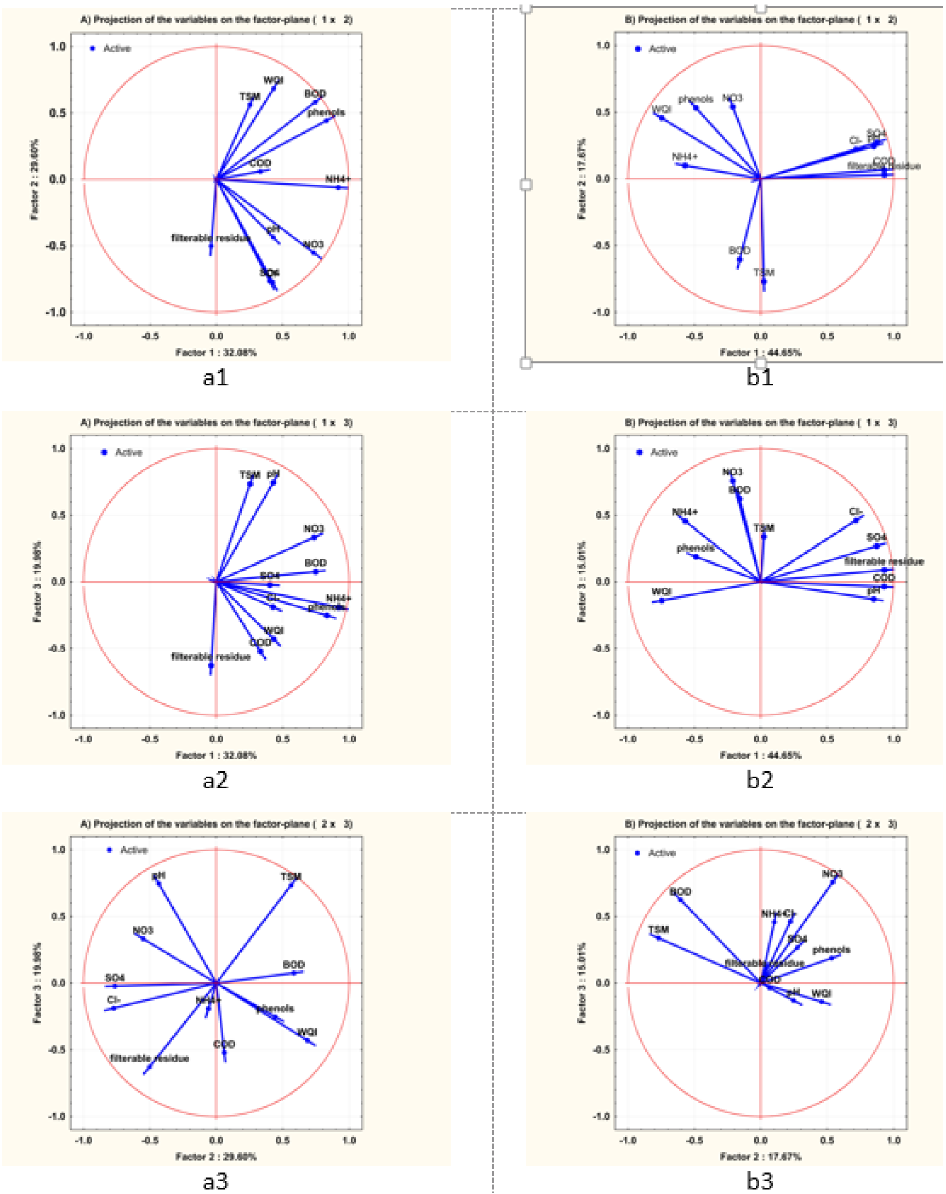

Fig. 6.PCA for WQI in winter (a1, a2, a3) and spring (b1, b2, b3)

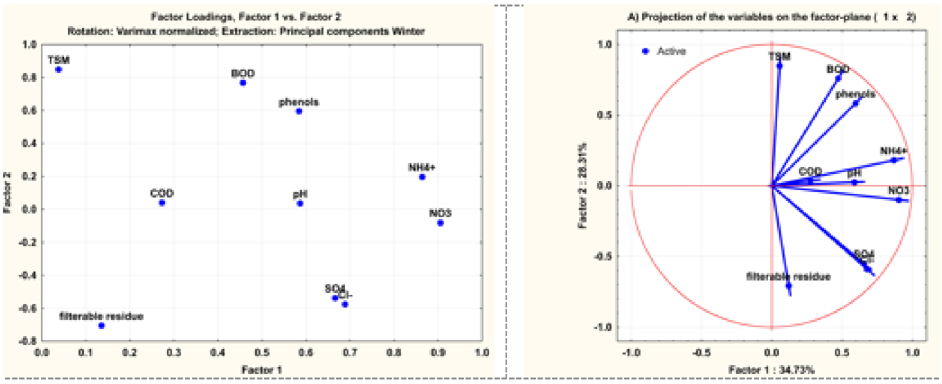

Fig. 7. Rotation of the principal components for winter season

The PCA analysis reveals that COD and BOD values depend on phenol and filterable residue values, conclusion which has been confirmed. Taking into account the results obtained (both the values of physico-chemical parameters and WQI), the monitored watershed falls into class quality II.

The present work is designed to improve monitoring methodology for large and very large rivers as Danube in a complex context containing anthropic influences but also important variability due to natural factors. Lower Danube area is also in the middle of the largest hydrographic basin in Europe and an improved methodology could serve not only for Romanian surface water but also for trans-border area limited by Republic of Moldavia and Ukraine.

For Lower Danube area the accurate monitoring technique serves not only to determine environmental parameters but also to define best treatment technologies for drinking water (Danube is the main source of drinking water for more than 700000 inhabitants in the area). WQI could be a good instrument for decision making institutions and structures in order to define strategies and budgets for all economic and social activities in the region.

Acknowledgment: Research was supported by the Project Black Sea Basin Joint Operational Programme, Innovative Instruments for Environmental Analysis in North Western Black Sea Basin (Black Sea e-EYE), MIS- ETC 1475.

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Manuscript received: 24.07.2015