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MULTIVARIATE STATISTICAL ANALYSES OF DANUBE RIVER WATER QUALITY AT GALATI, ROMANIA

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Abstract

This paper presents the research on the temporal variability of water quality parameters for the most important river system in Romania and Europe – Danube River. The data on the river water quality had been obtained during ten years. The investigation was systematic and complex. Using the Kolmogorov-Smirnov test, and traditional statistical methods based on correlation matrix - Principal Component Analysis (PCA) and Factor Analysis (FA), and ANOVA all the samples data sets were classified in order to determine the seasonal variability of the water quality state parameters and to identify the key quality factors that cause variability. The methodology for the systematic analysis due to the identification of the fundamental and the dependent parameters will not be exposed here, being the subject of another paper. These statistical analyzes showed that more than 70% of the total variance can be explained by three main factors: a) the first factor (**F1**) is the tutorial involving inorganic human influence type and flow variations and provides a natural buffer system perspective of the ecosystem; b) the second factor (**F2**) is the trophic factor; c) the third factor (**F3**) is related to the impact of anthropogenic activities. The analysis revealed that the weight of the three main factors is not the same over the course of the year. This work highlights two major aspects: the first one is due to the fact that the site of research is the meeting point of the borders of three countries: Moldova, Ukraine and Romania. The second significant issue is caused by the fact that the study was conducted in the predeltaic area of the Danube Delta. This study highlights the auto-filtering capacity of the Danube River. Research of this type is extremely useful because there are no other previous studies of this complexity.

Keywords: ANOVA, Danube River, Factor Analysis, Principal Components Analysis, temporal variability

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1. Introduction

Global deterioration of surface water quality was attributed to a couple of factors: human activities and natural processes, including hydrological variability, climate change, weather characteristics, and adjacent land use. The category of human activities can include the influence of municipal wastewater discharged through drains, both the untreated wastewater and the treated water discharges in wastewater treatment plants (Arain et al., 2008; Gantidis et al., 2007; Kundewicz et al., 2007; Ravichandran, 2003; Zaharia and Jufa, 2017). From this point of view, there are two important factors which can be considered: the climate change on the one hand and the human influence on the other hand. These two major aspects have caused, over time, significant changes on hydrological regimes and water quality.

In the area included in the case study, during the last decades, with the rapid development of industries and agriculture, a large amount of pollutants was produced and discharged into rivers and lakes. From this point of view, this caused a severe degradation of water quality. Further, as a direct consequence, there is a strong influence and a major restriction on the sustainable development of the local economies (Popa et al., 1998). In this respect,

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investigations on water quality and on the pollution sources are essential for the implementation of certain sustainable management strategies (Crosa et al., 2006; Sarkar et al., 2007; Zhou et al., 2007). For this purpose, many methods and investigation procedures were considered over time. For example, by using analysis of variance (ANOVA), which is robust enough to be used in the case of the moderate departures of normality (Kuzma et al., 2004), many authors indicated significant spatial variability for pH, and other chemical parameters which cause significant changes regarding water quality (Li et al., 2008). The investigation of cyclical variation had been developed further. Many authors indicated that, due to the seasonality of river water flows, the assessment of temporal variations of the water quality could be made (Ouyang et al., 2006; Sundaray et al., 2006). In this respect, these seasonal variations are an important aspect of the physical and chemical characterization of aquatic environments and every investigation should include this research (Barbone et al., 2012; Ouyang et al., 2006; Sundaray et al., 2006; Vasiliniuc et al., 2013).

A number of investigations on spatial and temporal variations of the parameters for the rivers water quality assessment were carried out during the last years (Afifi et al., 2004; Liu et al., 2001; Wong et al., 2002). By investigating the spatial and seasonal variability of the quality of water, these authors showed a series of important aspects and the connection between them. For example they revealed that eutrophication is directly dependent on the use of waterside land (Bu et al., 2010; Caccia and Boyer, 2005). In this context, previous studies demonstrated a direct and significant relationship between urbanization and surface water quality (Hatvani et al., 2014; Wang et al., 2008). In the literature there are several references that quantify the relationship between the level of land use and the water quality (Wang et al., 2008). The investigation methods can be extended even to the case of marine estuaries and lagoons, such as Laguna of Venice, where the studies recorded an evolution of trophic water (Solidoro et al., 2004). A number of water quality level investigations have identified other potential pollution sources and influences. These causes of potential pollution are the result of natural processes and other anthropogenic activities, and show definite present spatial and temporal variations (Kannel et al., 2008; Mendiguchià et al., 2007; Pillsbury and Byrne, 2007).

In Romania, numerous studies have focused only on a few rivers crossing urban, rural or industrial areas, especially in the regions of Transylvania (Oprea et al., 2013) and Moldova (Georgescu et al., 2010a, 2010b; Voiculescu et al., 2011). Systematic studies focused on large natural river systems are relatively rare in the Romanian literature. At the same time, a global analysis, considering the entire set of pollution sources, has never been made in the case of the Danube. The Danube was selected for water quality assessment in order to succeed in reflecting the typical pattern of a drainage basin in the vicinity of the Danube Delta, which include~~s~~ several protected areas. The main research hypothesis states that the pollution factors affecting the Danube hold temporal variability. The major aims of this study were to (i) determine seasonal variability in water quality and to (ii) identify the key quality factors that control this variability.

The present study will fill the current gap in knowledge regarding the Danube, one of the largest rivers in Europe and being a significant environmental component in the region. Thus, the results of this study will be used for future projects for ecological restoration and protection of surface water quality in the region of Eastern Europe.

2. Material and methods

2.1. Study area

The Danube is the second longest river of Europe (after the Volga) and it is the only European river that flows from West to East (Fig. 1) through 10 countries (Germany, Austria, Slovakia, Hungary, Croatia, Serbia, Romania, Bulgaria, Moldova and Ukraine) with seven tributaries before reaching the Black Sea, where it has created the only delta in Europe - the Danube Delta.

The interest for this area is significant because the Delta entered the United Nations Educational, Scientific and Cultural Organization World Heritage Biosphere Reserve in 1991. Because it passes through four state capitals: Vienna, Bratislava, Budapest and Belgrade, the Danube is very important for river transport and for tourism. This important European water stream - the Danube River has a length of 1,075 km between the entry point – Bazias - and Sulina. This river represents the border with Serbia (235.5 km), Bulgaria (469.5 km), Moldova (0.6 km) and the Ukraine (53.9 km). Except for the rivers flowing in Dobrogea, the Danube River collects the majority of the rivers in Romania, transporting annually about 60 million tons of silt and 200 billion m^3 of water (National Administration of Romanian Water, 2013). The Danube course covers an important area in Europe (Fig. 1).

2.2. Analytical approach

The water samples were collected monthly, during 1990-1998, near Galati, on the left bank of the river. The most important quality indicators for the river water quality assessment taken into account are: chemical parameters, nutrients, and tracing elements. The water samples were collected in polyethylene containers which met the standard requirements and then were subjected to analysis according to standardized methods in use in Romania.

All samples were analyzed immediately after being collected. A list of the methods that were used for the analysis of each parameter as well as the corresponding measure units are presented in Table 1.

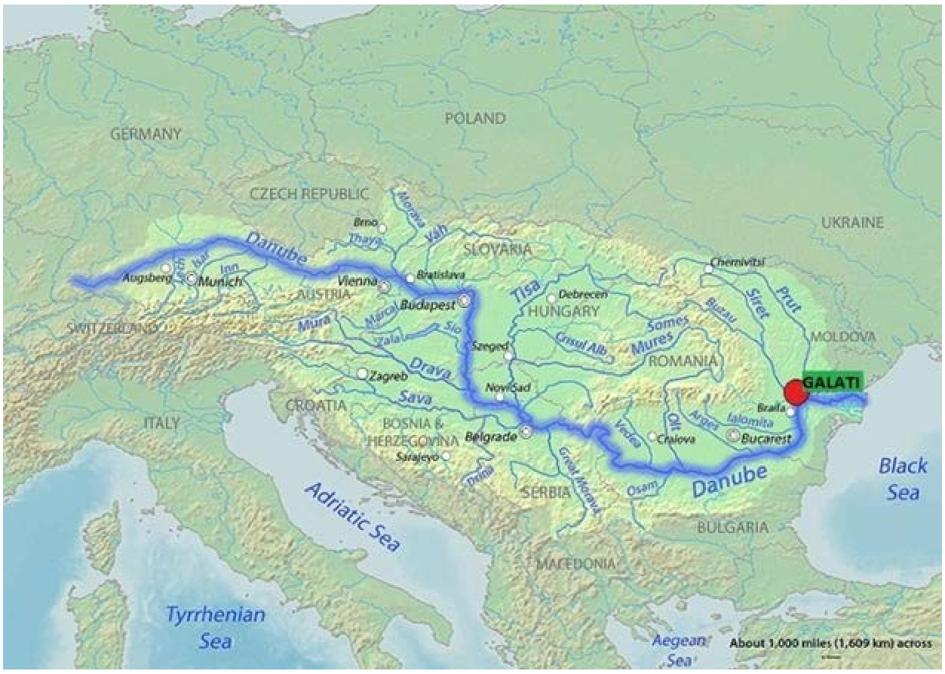


Fig. 1. The Danube River map (red circle – the monitoring point)

2.3. Statistical approach

In general, every statistical study has to be based mainly on massive recorded data series, which represent the explored water body in order to succeed in discovering laws that govern the related phenomena.

Table 1. Parameters and methods of analysis

Methods	*Parameter*	*Measurement unit*
Electrometrical	pH	upH
Volumetric	COD-Mn	mg $O_2 \cdot L^{-1}$
	Ca^{2+}	$mg \cdot L^{-1}$
	Mg^{2+}	$mg \cdot L^{-1}$
	Cl^-	$mg \cdot L^{-1}$
	CO_3^{2-}	$mg \cdot L^{-1}$
	HCO_3^-	$mg \cdot L^{-1}$
	Alkalinity	$mval \cdot L^{-1}$
	W. hardness	^{0}dH
Mathematic	Ca^{2+}/Mg^{2+}	-
Spectrophotometric	Fe_{total}	$mg \cdot L^{-1}$
	NO_2^-	$mg \cdot L^{-1}$
	NO_3^-	$mg \cdot L^{-1}$
	PO_4^{3-}	$mg \cdot L^{-1}$
	NH_3	$mg \cdot L^{-1}$
	NH_4^+	$mg \cdot L^{-1}$
Gravimetric	SO_4^{2-}	$mg \cdot L^{-1}$
	Rf_{105}	$mg \cdot L^{-1}$
	TSM	$mg \cdot L^{-1}$

In this paper, the data series set contained 2376 records. In this way, a number of methods of analysis were considered, in order to identify the main relationships and the causal connection between the measured parameters (Alhassan et al., 2016; Li et al., 2008; Skoulikidis et al., 2006).

2.4. Data analysis

The Kolmogorov-Smirnov test was used for testing for normal distribution of the experimental data set. This non-parametric method is used to decide if a sample comes from a population with a specific distribution. An important feature of this test is that the distribution of the K-S test statistic itself does not depend on the underlying cumulative distribution function being tested.

The computed values are the following: pH (Kolmogorov-Smirnov test value d = 0.10330, $p < 0.01$), Ca (d = 0.19493, $p < 0.01$), Mg (d = 0.09570, p = n.s.), Fe_{total} (d = 0.49753, $p < 0.01$), Cl concentration (d = 0.14666, $p < 0.05$), SO_4 concentration (d = 0.24012, $p < 0.01$), HCO_3 concentration (d = 0.14084, $p < 0.05$), NO_2 (d = 0.28445, $p < 0.01$), NO_3 (d = 0.12080, $p < 0.10$), PO_4 (d = 0.12903, $p < 0.10$), NH_3 (d = 0.18531, $p < 0.01$), NH_4 (d = 0.20456, $p < 0.01$), Alkalinity (d = 0.16296, $p < 0.01$), Dg (d = 0.19036, $p < 0.01$), Rf 105 (d = 0.09862, p = n.s.), TSM (d = 0.18534, $p < 0.01$).

From the Kolmogorov-Smirnov table it can be seen that almost the entire experimental data set is suited due to the normal distribution (with $p<0.1$ and respectively $p<0.05$).

On another hand, the correlation matrix investigation shows certain seasonal differences. During winter, all parameters' correlation coefficients represent high value, except for the Ca, Mg and SO_4 concentrations and respectively for the Cl and HCO_3 concentrations. This probably occurs due to low flow values and small temperatures. During spring, the correlations between the measured parameters are very low, except for links between the COD-Mn and CO_3^{2-}, pH and NH_3 concentration, HCO_3^- and

Alkalinity and respectively for the group of TSM, NO_3^- and PO_4 concentrations.

During summer, the correlations between the measured parameters are changed and have low magnitudes, except for links between the pH values and Ca concentration, COD-Mn and Alkalinity, Ca, Mg and W. hardness, SO_4, CO_3 concentrations and Rf_{105} values. During autumn, the correlations between the measured parameters are changed again having high magnitudes except for COD-Mn, Ca and Mg with SO_4, CO_3, HCO_3, NO_3, PO_4, NH_3, NH_4, Rf_{105} and TSM. In the initial phase, the analysis of variance method (ANOVA) was applied, and, before that, the FA procedure and PCA analysis.

2.4.1. Analysis of variance

ANOVA is a general method that can separate the contributions of each parameter from a set of experimental data and test the significance of each contribution. Each source of variation is characterized by the sum of squares (SS), the number of degrees of freedom (DF) and mean square (MS). Generally speaking, the MS and DF are for general variations and SS and DF for some contributions from sources of variance (Astel et al., 2006). The statistical analysis uses FA and PCA methods in order to regroup measured parameters on the base of reciprocal correlations. ANOVA completes these analyses in order to take into account the weight of reciprocal dependence within identified groups.

ANOVA (specifically, two-way ANOVA test) was performed to estimate the analyzed parameters which are grouped seasonally and temporally (Mendiguchià et al., 2007; Moore and Cobby, 1998). ANOVA was mainly applied in order to achieve the variability for the data sets on seasons and even months, in order to highlight seasonal variations in water quality in the ecosystem. ANOVA and ***t***-test (applied sequentially, for each analyzed parameter and for each sequence of two seasons) have shown a significant variation ($p<0.05$) for pH transition between winter (and) spring, NO_3^- and NH_4^+ (autumn/winter) and Rf_{105} - TMS (autumn/winter).

These substantial changes indicate the existence of groups of factors that combine differently and present temporal changes (Skoulikidis et al., 2006). The dependent variables were chosen for each group factor, taking into account the chemical interdependencies: e.g. HCO_3^- regulates level of calcium and magnesium ions solubility.

In order to complete the image on dynamics of the interdependencies, the ANOVA is accomplished with a graphical representation using the least square method (LSM) obtained through MAPLE Maplesoft 6 software. The problem is more complex due to the link between the various biotic and abiotic processes. In the last category we may consider: the disintegration of rocks, erosion, sedimentation, evaporation, the processes of adsorption and desorption and washing etc. (Popa et al., 1998). To these items we must add human interference with river water, coastal areas, etc. (Popa et al., 1998).

The identification of geological and hydro-geological parameters forces acting on temporal variation of soil and water composition is a complex issue and requires special approaches (Interlandi and Crockett, 2003; Markich and Brown, 1998; Meybeck and Helmer, 1989; Skoulikidis, 1993; Skoulikidis et al., 2002; Stallard, 1980; Zobrist and Stumm, 1981). The procedure for the systematic analysis due to the identification of the fundamental and the dependent parameters will not be exposed in this article. This is the subject of another paper.

2.4.2. FA and PCA

The FA method is often used in order to identify the main pollution factors which affect the water quality (He et al., 2001; Wu et al., 2010). It is preferable to use the correlation matrix and not the covariance matrix because standardization may cause distortions in the results due to the fact that it changes the deviations (Magyar et al., 2013).

The PCA method was used to verify and to identify the factors which affect the water quality (Mei-Lin et al., 2010; Rencher and Christensen, 2012; Zhang et al., 2008). Like other (Güler et al., 2002), all statistical analyses were performed using StatSoft STATISTICA 10 (StatSoft, Inc., USA). For each measured parameter and for each season observation, the box plots method was used in order to present the mean values, standard deviation and standard error magnitude etc.

Because the PCA method is based on the reference axis rotation around the center of mass of the experimental data set in order to minimize the squares sum and the FA method used to decrease the correlation matrix components along the axes of reference, the obtained results sometimes could be different. Because the study period is extended and the measured parameters' variations are quite important, these analyzes were done with caution. Applying both methods could highlight that our seasonal approach with few exceptions, proved to be coherent.

3. Results

3.1. Study of flow variation

The Danube flow shows a significant seasonal variation, at the Galati monitoring point (Fig. 2). Recordings made over a period of approximately 80 years show that there is a significant seasonal variation. Naturally, high values in spring flow are due to melting snow and heavy rains. In fact, in the upper and middle course of Danube River increases of flow are recorded, especially in March-April. In May-June decreases of flow are recorded (Simeonov et al., 2001). Statistically, the average flow values change from month to month. During spring and winter, the flow average values have an increasing trend. This fact proved that in this period, due to rainfalls and water intakes, the average is greater and could explain this variation.

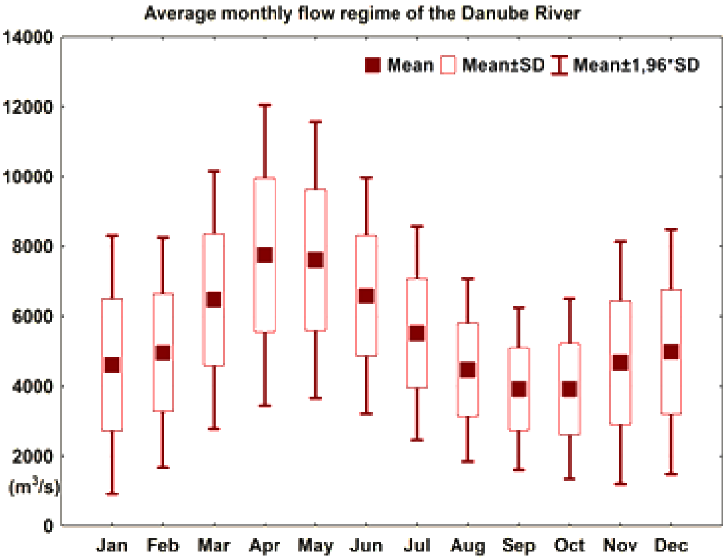


Fig. 2. The Danube River monthly average flow magnitudes

In summer, the average begins to trend downward. This trend persists in the autumn. During winter, a relatively low flow of Danube is recorded. The significant peaks are recorded in April and May, during the spring season. This can be correlated with changes in various factors which may characterize in terms of river water quality.

The recorded temperatures in the Danube are directly influenced mostly by the air temperature. This parameter was not considered in this investigation because the obtained results are acceptably explained by the chemical state parameters indicated above. In the Galati area, the difference between the air temperature and the water temperature is significant, thus the water flow which is an important parameter is influenced by the upper stream characteristics. As a specific aspect of the Danube River, we can note that floes or ice may occur as early as the first part of December until early March. This indicates that the temperature significantly varies each year. Ice bridges may persist 45-50 days on average (National Institute of Hydrology and Water Management newsletter, 2013).

3.2. Study of the quality parameters' variation

There were 108 monthly sampling sessions covering 19 parameters (Table 1). Recorded values of the considered parameters show certain variability over the 4 seasons. In Fig. 3 are presented the seasonal mean values box-plot for the measured parameters. Certain seasonal variations could be easily be observed. Statistical t –test applied sequentially, for each data set, shows that there is a significant seasonal variation ($p<0.05$).

Some preliminary comments should be made here. According to Fig. 3 the large range of values was recorded for SO_4^{2-}, NO_2^- and Rf_{105} in spring - probably due to extremely high flow compared to other seasons (Al-Khashman, 2007; Takiguchi et al., 2006). On the other hand, Fe_{total}, Cl^-, NO_3^- and PO_4^{3-} have the large range value in summer - probably due to the sharp decrease of flow, caused by anthropogenic influence intake (Al-Khashman, 2007, 2008).

According to different authors, small amounts of NO_3^- are attributed to intense photosynthesis that occurs in the rivers in summer (Skoulikidis et al., 2006). The large amounts of NO_3^- are attributed to the water discharges of municipal waste water. The most of the analyzed parameters (pH, Ca^{2+}, Mg^{2+}, HCO_3^-, Alkalinity, W. hardness, NH_4^+ and COD-Mn) registered a large range of values in autumn. Their variations are against the variations found by Skoulikidis (2006) and Al-Khashman (2007).

The number of parameters that have high values and their diversity should be associated to the specific behavior of natural aquatic ecosystems. These parameters mark the reduced biological activity of the aquatic ecosystem in the Danube River (Murariu et al., 2011). Also, NH_3 and TSM have a large range of values in winter (Fig. 3). This aspect might be due to low flow of the river, and it is a general feature as it has been highlighted by others (Al-Khashman, 2007, 2008). The highest mean values in **winter** were recorded for NH_3, and TSM (Fig. 3). In **spring** the highest mean values were recorded for pH, Rf_{105}, NO_2^- and NO_3^-(Fig. 3). In **summer** (were recorded) the highest mean values were recorded for two parameters: Cl^- and SO_4^{2-}. In **autumn**, three of the analyzed parameters have higher mean values then the other seasons (Fig. 3). These are: COD-Mn, $Ca^{2+}$and NH_4^+.

Some analyzed parameters such as Mg^{2+}, Ca^{2+}/Mg^{2+} and HCO_3^- have a constant variation of their mean values in all seasons. PO_4^{3-}, NH_3, Alkalinity and W. hardness have a constant evolution of their mean values except during winter when they present maximum mean values.

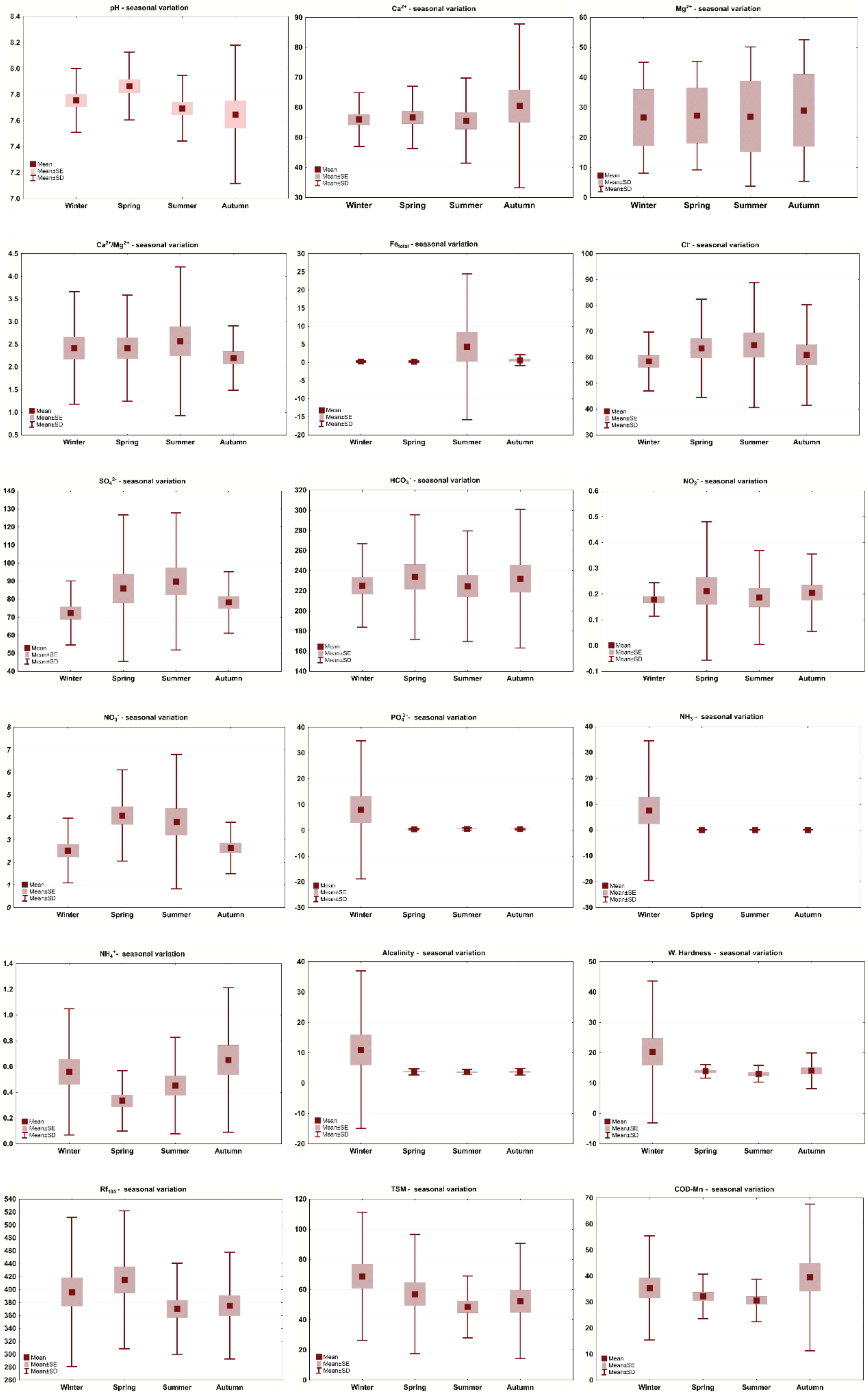


Fig. 3. The box-plot diagrams for the measured parameters during the 9 years monitoring observation period

The behavior of Fe_{total} is similar to the three parameters that were previously presented except the fact the maximum value of mean is in summer.

The parameters which present minimum values of mean in **winter** are: SO_4^{2-}, NO_3^-, and Cl^- probably due to the lower flows (Fig. 3). During **spring**, minimum values of mean are recorded for NH_4^+. This behavior is probably due to the increased river flow. It is interesting to note that in **summer** the mean values of COD-Mn, TSM, RF_{105}, NO_2^- and Ca^{2+} have the minimum values. In **autumn** there are minimal variations for the pH.

3.3. PCA, FA methods and multidimensional regression analysis

Intra-annual variations in climatic and discharge rates are major drivers of the hydro-chemical fluctuations in rivers. In order to assure the consistency and cross checking of the interpretations both FA and PCA were used.

A short observation should be included here. From literature, was exposed that the seasonal regime of solute concentrations in river water is controlled by three main processes that are governed by hydrological factors: (i) dilution during spring and selectively during winter, (ii) concentration due to evaporation and base flow contribution during the dry season (in summer, river water is practically represented by groundwater) and (iii) enrichment due to the flushing of soil-salts (Edwards, 1973; Semkin et al., 1994; Walling and Foster, 1975), following flood events, occurring in autumn, winter and rarely in spring (Skoulikidis, 1993). In addition, as an original aspect, this paper emphasizes the existence of the four factors that contribute significantly to seasonal variation of chemical species' concentrations in river water and is due to human influence conurbations along the water. An example is shown as a case study for the Danube (River) in the SE region of Romania. A similar study on this area was never made before.

The sequentially applied PCA method for each season separately revealed the possible existence of four main factors. The first three provide an explanation of over 80% of the total variance. The weight identified factors could vary throughout the year, so it cannot establish a hierarchy during the year.

The weights of these factors, along seasons are not constant (Figs. 4a -4d). The weights of factors and the variability in aquatic ecosystems are graphical represented in order to succeed in understanding their evolutions (Fig. 5). This depiction is based on the correlations between key stakeholders and seasonality analysis. In this respect, in winter, the variability of the system shows only 2 factors (**Fl** and **F2)** having a significant weight. In other seasons, the weight of factors **F1**, **F2** and **F3** decrease dramatically.

Thus, one can see three main factors: (*i*) *the **F1** factor* - is attributable to the natural buffer system of surface waters and includes the following analytical species: pH, Ca^{2+}, Mg^{2+}, HCO_3^-, Alkalinity and W. hardness; (*ii*) *the **F2** factor* - is the factor that characterizes anthropogenic nutrient pollution (biological) in the area and includes the following parameters: pH, NO_2^-, NO_3^- and NH_4^+; (*iii*) *the **F3** factor* - can be attributed to anthropogenic activity-generated inorganic and organic pollution includes pH, Rf_{105}, TMS, COD-Mn. The multifactor ANOVA analysis highlights the seasonal dependence of the some dependent parameters (such as HCO_3^-, Alkalinity, NO_3^-, NO_2^-, Rf_{105}) versus the other considered as independent parameters (such as pH and Ca^{2+}, Mg^{2+} and pH, W. hardness and pH, NH_4^+ and pH, NH_4^+ and pH, TSM and pH). In Table 2 are presented the results of multifactor ANOVA analysis showing the seasonal dependence of: (*i*) HCO_3^- versus the independent parameters Ca^{2+} and pH; (*ii*) HCO_3^- versus the independent parameters Mg^{2+} and pH; the choices of the dependent parameters were made basing on previous studies on the local rivers water quality investigations (Popa et al., 1998).

In brief, the most significant association between parameters was obtained by different tests and where transposes into the response surfaces by multidimensional regression analysis. The synthetic results of all statistical methods that were used led to the possibility of specifying which parameter is dependent and which is independent. (*iii*) Alkalinity versus the independent parameters W. hardness and pH; (*iv*) NO_2^- versus the independence parameters NH_4^+ and pH; (*v*) NO_3^- versus the independence parameters NH_4^+ and pH; (*vi*) Rf_{105} versus the independent parameters TSM and pH.

For a complete representation, the calculated values for R^2 and adjust R^2 should be taken into account, for all the 6 groups of analyzed parameters (Table 3) in order to succeed in obtaining a coherent and complete picture of the investigation. From Table 2 it can be seen that the p coefficient's values generally follow the required confidence level and the multi-linear model coefficients are given by the beta values.

According to Table 3 the values of the significance coefficient **p** are small enough ($p \leq 0.05$) and the size of F test also shows a correlation between the parameters mentioned above.

4. Discussion

4.1. Seasonal weight factors dynamics

The results presented in the section above allow the observation of several important characteristics. In general, the water quality dynamics is related, on the one hand, directly to the natural cycle of the biological activity of the ecosystem and to the human activity impact, and, on the other hand, is linked to the Danube flow's seasonal variations (Fig. 2). By combining the ANOVA factorial results with the least square method representations for the interdependence relations, suggestive pictures can be obtained in order to succeed in explaining the observed seasonal dynamics for all the 3 identified factors - **F1**, **F2** and **F3**.

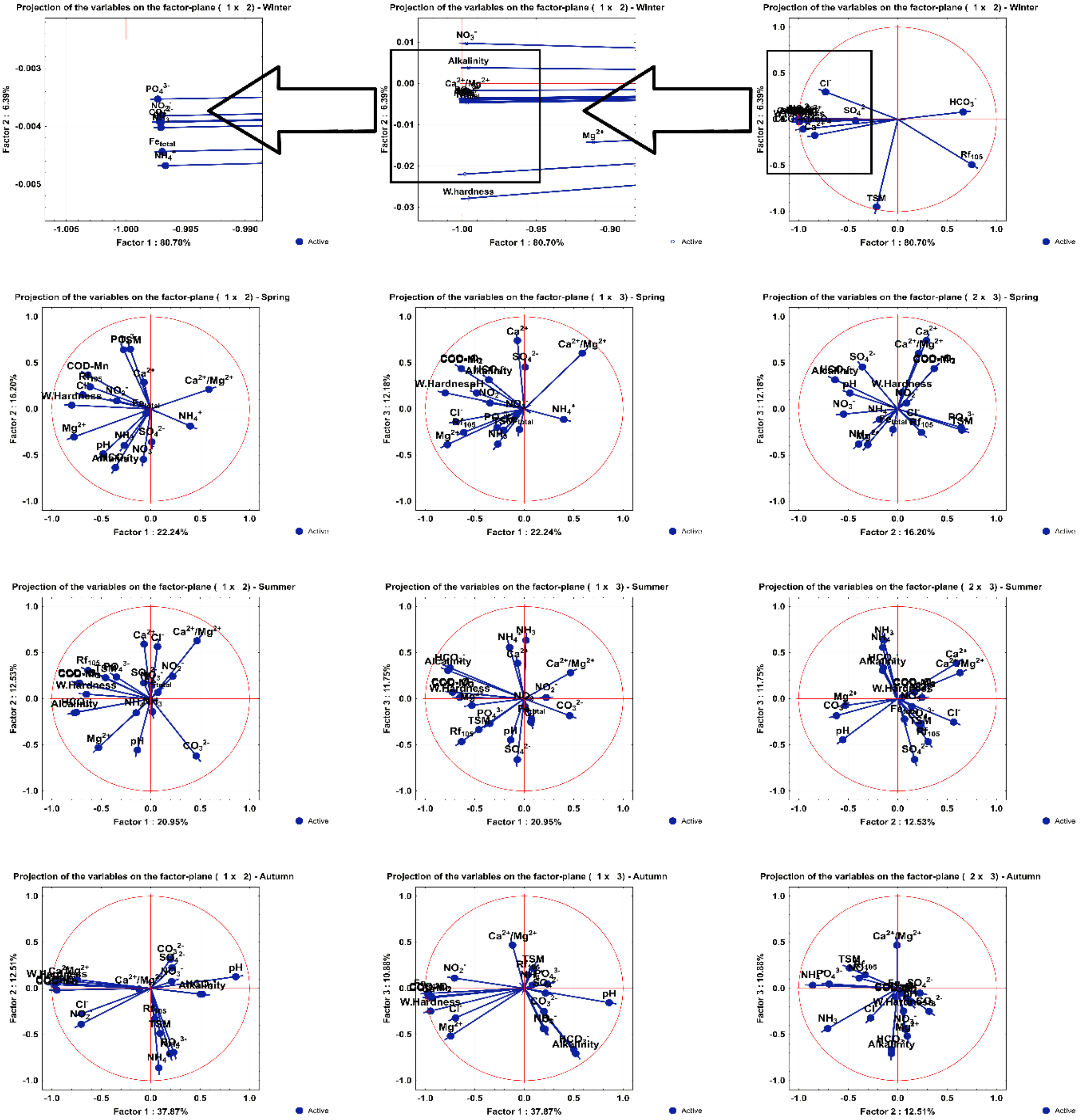


Fig. 4. The seasonal PCA results for the main three factors

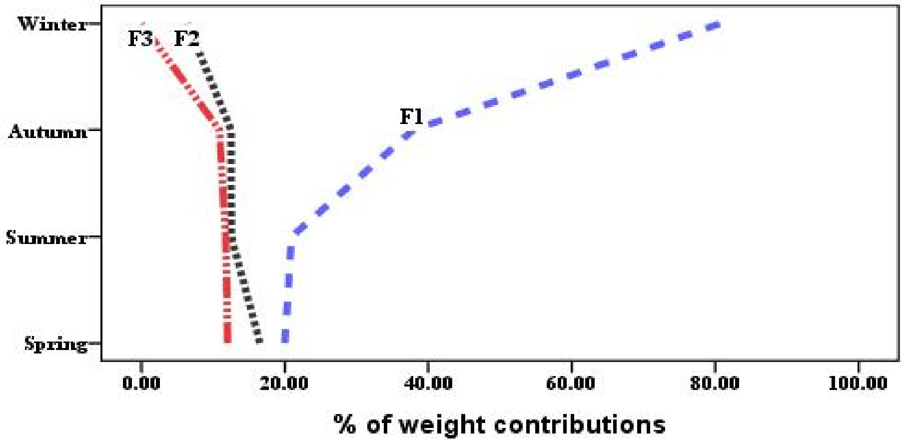


Fig. 5. The seasonal factors' computed weights

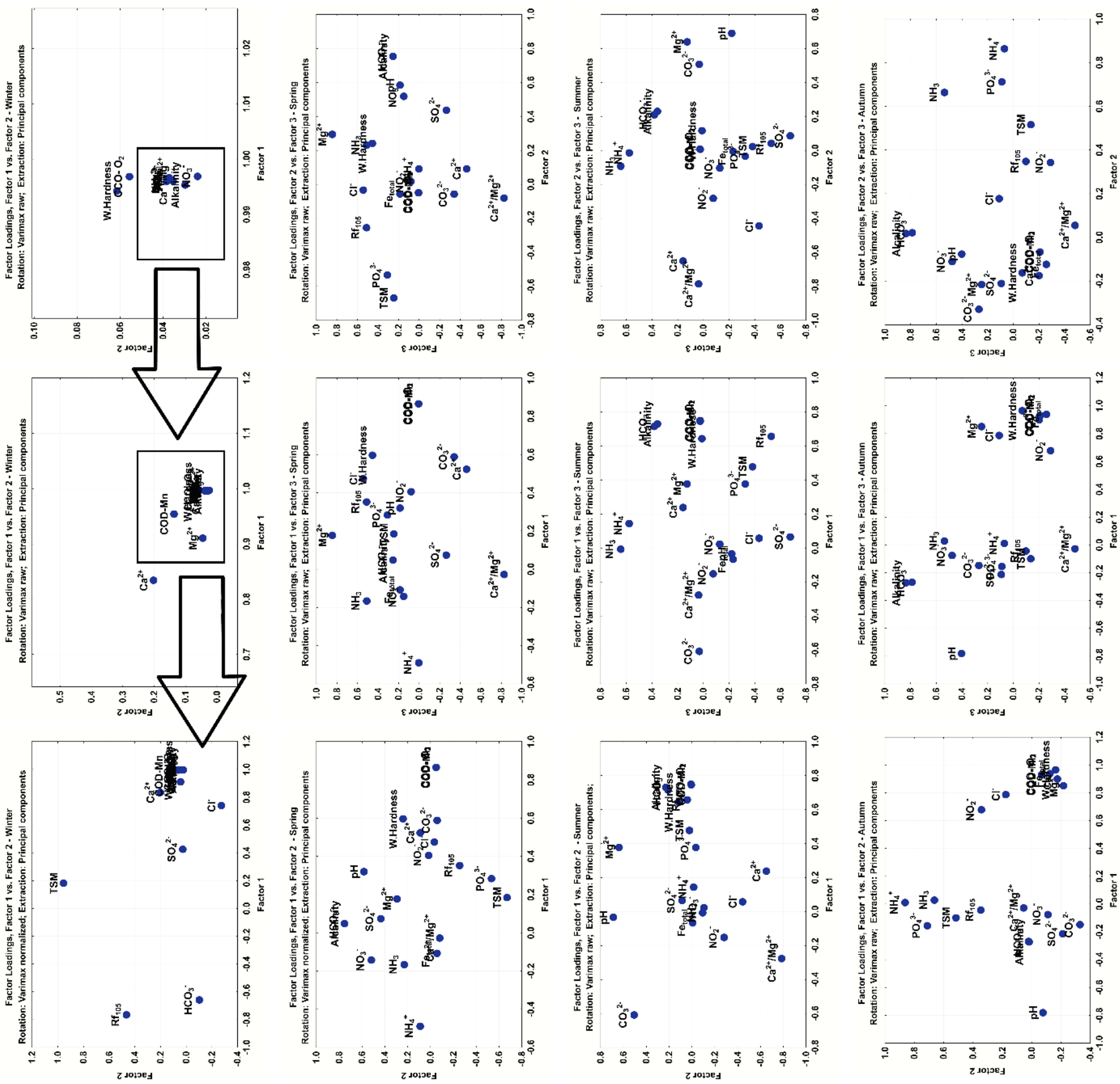


Fig. 6. The distribution of factorial variables weights on seasonal variation

Table 2. ANOVA analysis seasonal results for different dependences of analyzed parameters

Parameters	*Season*	*Variables*	*Beta*	*Std. Err. of Beta*	*B*	*Std. Err. of B*	*t(24)*
HCO$_3^-$ vs. Ca^{2+} and pH	Winter	Intercept	-	-	323.538	47.18003	6.85754
		pH	-0.24645	0.25298	-0.5135	0.5271	-0.97418
		Ca^{2+}(mg/L)	-0.48044	0.25298	-1.6866	0.88811	-1.89908
	Spring	Intercept	-	-	-190.621	318.3603	-0.59876
		pH	0.254875	0.19737	51.917	40.203	1.291375
		Ca^{2+}(mg/L)	0.041091	0.19737	0.25	1.2014	0.208197
	Summer	Intercept	-	-	65.86279	316.755	0.20793
		pH	0.104286	0.22820	17.39263	38.0591	0.45699
		Ca^{2+}(mg/L)	0.117347	0.22820	0.45934	0.8933	0.514226
	Autumn	Intercept	-	-	-81.5311	324.7291	-0.25107
		pH	0.318804	0.28366	42.5052	37.8201	1.123878
		Ca^{2+}(mg/L)	-0.10331	0.28366	-0.2703	0.7422	-0.36420
HCO$_3^-$ vs. Mg^{2+} and pH	Winter	Intercept	-	-	228.5142	20.58811	11.09933
		pH	-0.76854	0.37820	-1.6013	0.78797	-2.03211
		Mg^{2+}(mg/L)	0.143336	0.37820	0.3407	0.89885	0.379
	Spring	Intercept	-	-	-89.5668	304.2838	-0.29435
		pH	0.165217	0.196237	33.6542	39.9708	0.841969
		Mg^{2+}(mg/L)	0.312858	0.19623	2.0999	1.3171	1.594364

Parameters	***Season***	***Variables***	***Beta***	***Std. Err. of Beta***	***B***	***Std. Err. of B***	***t(24)***
	Summer	Intercept	-	-	266.5766	246.0628	1.083368
		pH	-0.07103	0.19796	-11.8459	33.0151	-0.35880
		Mg^{2+}(mg/L)	0.398729	0.19796	1.8341	0.9106	2.014217
	Autumn	Intercept	-	-	-81.5311	324.7291	-0.25107
		pH	0.318804	0.28366	42.5052	37.8201	1.123878
		Mg^{2+}(mg/L)	-0.10331	0.28366	-0.2703	0.7422	-0.36420
Alkalinity vs. W. hardness and pH	Winter	Intercept	-	-	3.268914	0.917346	3.56345
		Alkalinity	0.9241	0.080217	0,886060	0.076915	11.51994
		W. hardness	0,075484	0,080217	0,080372	0,085413	0,94099
	Spring	Intercept	-	-	7.097943	0.384237	18.47283
		Alkalinity	0.19006	0.196011	0.056883	0.058664	0.96964
		W. hardness	0.269517	0.196011	0.036386	0.026462	1.37501
	Summer	Intercept	-	-	7.531776	0.355647	21.17766
		Alkalinity	0.067729	0.230072	0.026162	0.088872	0.29438
		W. hardness	0.005034	0.230072	0.000582	0.026596	0.02188
	Autumn	Intercept	-	-	8.109542	0.330193	24.56004
		Alkalinity	0.223753	0.1335	0.103823	0.061945	1.67604
		W. hardness	-0.68429	0.1335	-0.059771	0.011661	-5.12575
NO_3^- vs. NH_4^+ and pH	Winter	Intercept	-	-	7.117884	0.182126	39.08228
		NO_3^-(mg/L)	0.05999	0.079712	0.056731	0.075382	0.75259
		NH_4^+(mg/L)	0.939882	0.079712	0.872534	0.074	11.79096
	Spring	Intercept	-	-	7.689268	0.159599	48.17881
		NO_3^-(mg/L)	0.292053	0.195339	0.042633	0.028515	1.49511
		NH_4^+(mg/L)	-0,08308	0.195339	-0.105321	0.247623	-0.42533
	Summer	Intercept	-	-	7.653828	0.143804	53.22396
		NO_3^-(mg/L)	-0.0732	0.206439	-0.008207	0.023143	-0.35461
		NH_4^+(mg/L)	0.032364	0.206439	0.02708	0.172734	0.15677
	Autumn	Intercept	-	-	7.335244	0.281103	26.09448
		NO_3^-(mg/L)	0,286153	0,195602	0.133295	0.091115	1.46294
		NH_4^+(mg/L)	-0.045188	0.195602	-0.043103	0.186577	-0.23102
NO_2^- vs. NH_4^+ and pH	Winter	Intercept	-	-	7.595498	0.069088	109.9395
		NO_2^-(mg/L)	1.013807	0.120767	0.937657	0.111696	8.3947
		NH_4^+(mg/L)	-0.013862	0.120767	-0.012869	0.112113	-0.1148
	Spring	Intercept	-	-	7.777553	0.131284	59.24203
		NO_2^-(mg/L)	0.24637	0.207714	0.286674	0.241695	1.1861
		NH_4^+(mg/L)	-0.04097	0.207714	-0.051939	0.26331	-0.19726
	Summer	Intercept	-	-	7.671424	0.12142	63.18066
		NO_2^-(mg/L)	-0.160391	0.201335	-0.294086	0.369159	-0.79664
		NH_4^+(mg/L)	0.048851	0.201335	0.040875	0.168463	0.24264
	Autumn	Intercept	-	-	8.02651	0.149953	53.52685
		NO_2^-(mg/L)	-0.689541	0.165165	-2.44416	0.585445	-4.17487
		NH_4^+(mg/L)	0.200365	0.165165	0.19112	0.157544	1.21312
Rf_{105} vs. TSM and pH	Winter	Intercept	-	-	69.83666	9.672226	7.22033
		Rf_{105}(mg/L)	-0.85529	0.110442	-0.18462	0.02384	-7.74428
		TSM(mg/L)	0.445044	0.110442	0.26116	0.064809	4.02967
	Spring	Intercept	-	-	7.447871	0.20237	36.80322
		Rf_{105}(mg/L)	0.576236	0.197811	0.00163	0.00056	2.91307
		TSM (mg/L)	-0.703025	0.197811	-0.005367	0.00151	-3.55403
	Summer	Intercept	-	-	7.430309	0.354365	20.96797
		Rf_{105}(mg/L)	0.259942	0.267607	0.001183	0.001218	0.97136
		TSM(mg/L)	-0.306096	0.267607	-0,004796	0.004193	-1.14383
	Autumn	Intercept	-	-	8.037314	0.577093	13.92725
		Rf_{105}(mg/L)	-0.172832	0.30146	-0.001082	0.001887	-0.57332
		TSM(mg/L)	0.033756	0.30146	0.000456	0.00407	0.11198

Table 3. The coefficient significance parameter from ANOVA analysis for seasonal dependence of analyzed parameters

Parameters	***Season***	***R***	***R^2***	***Adjusted R^2***	***F(2,24)***	***p***	***Std. Error of Estimate***
HCO_3^- vs. Ca^{2+} and pH	Winter	0.6961348	0.4846037	0.441654	11.283	< 0.00035	38.744
	Spring	0.2603197	0.0677663		0.87231	< 0.43082	61.737
	Summer	0.1158164	0.0134134		0.16315	< 0.85040	55.432
	Autumn	0.4023255	0.1618658	0.0920213	2.3175	< 0.01202	65.39
HCO_3^- vs. Mg^{2+} and pH	Winter	0.6408444	0.4106816	0.3615717	8.3625	< 0.00175	41.429
	Spring	0.3943683	0.1555264	0.0851535	2.21	< 0.13153	58.759

	Summer	0.3831139	0.1467763	0.0756743	2.0643	< 0.14885	51.549
	Autumn	0.4023255	0.1618658	0.0920213	2.3175	< 0.01202	65.39
Alkalinity vs. W. hardness and pH	Winter	0.9992395	0.9984796	0.9983529	7880.4	< 0.0000	1.01
	Spring	0.3661127	0.1340385	0.0618751	1.8574	< 0.17782	0.29211
	Summer	0.7836963	0.6141798	0.5820281	19.103	< 0.00001	0.33276
	Autumn	0.4023255	0.1618658	0.0920213	2.3175	< 0.01202	65.39
NO_3^- vs. NH_4^+ and pH	Winter	0.9997964	0.9995928	0.9995588	29455	< 0.0000	0.52272
	Spring	0.3133543	0.0981909	0.0230402	1.3066	< 0.28932	0.2981
	Summer	0.0849611	0.0072184		0.08725	< 0.91674	0.33341
	Autumn	0.2880641	0.082981	0.0065627	1.0859	< 0.35362	0.51301
NO_2^- vs. NH_4^+ and pH	Winter	0.9999471	0.9998941	0.9998853	1133	< 0.0000	0.26656
	Spring	0.2622649	0.0687829		0.88636	< 0.42522	0.30292
	Summer	0.1665127	0.0277265		0.34221	< 0.71361	0.32995
	Autumn	0.6491547	0.4214018	0.3731853	8.7398	< 0.00141	0.4075
Rf_{105} vs. TSM and pH	Winter	0.8531268	0.7278253	0.7051441	32.089	< 0.00000	13.513
	Spring	0.6042638	0.3651348	0.3122294	6.9016	< 0.00429	0.25011
	Summer	0.2335082	0.0545261		0.69205	< 0.51026	0.32537
	Autumn	0.1494762	0.0223431		0.27424	< 0.76250	0.5297

The graphical structure is the following: on the horizontal axis the magnitudes of the considered independent parameters are represented and meanwhile, on the vertical axis the results that were obtained subsequently by the method of the least squares surface response.

The ***F1** factor* named *the natural buffer system* includes the following analytical species: pH, Ca^{2+}, Mg^{2+}, HCO_3^-, Alkalinity and W. hardness. This factor has a certain dynamics, with components related to each other with definite seasonal variability. For exemplification, we investigated the following 3 groups of ***F1** factor components*: Ca^{2+} and pH versus HCO_3^-, Mg^{2+} and pH versus HCO_3^-, Alkalinity and W. hardness versus pH. These two parameters were identified as having the significant influence on the vertical axis parameter (Fig. 4) while the HCO_3^- is an excellent equilibrium state indicator (Popa et al., 2008).

The least square regressive method approach based on factorial ANOVA results for Ca^{2+} and pH versus HCO_3^- reveals noteworthy aspects (Fig. 7). During winter as during summer, a stable equilibrium state shape is noticeable, with the representation points grouped on the main trend line. For the spring and autumn, the shape form is dramatically changed. The shape's forms lead to the conclusion that opposed processes are involved in a dynamical balance, in a strong correlation with the seasonal (Danube River) water flow magnitudes. Using these representations the driving processes could be suggested. During winter, the variation in the concentration of Ca^{2+} and HCO_3^- is due to chemical, rather than biological processes. In this respect, it can be observed the certain tendency for the minimum values of Ca^{2+} concentration. As such, the concentration of HCO_3^- decreases as the concentration of Ca^{2+} rises, due to the shifting of the chemical equilibrium towards the formation of insoluble $CaCO_3$ instead of $Ca(HCO_3)_2$ (Beral and Zapan, 1973).

As the concentration of Ca^{2+} is raised even further, the formation of soluble $Ca(HCO_3)_2$ is favored, resulting in the release of HCO_3^- ions as the salt is hydrated (Fig. 7). During spring, the concentration of Ca^{2+} does not influence the concentration of HCO_3^-, as the dominant processes are the formation and decomposition of carbonic acid. The concentration of HCO_3^- drops as the magnitude of the water's pH decreases due to the chemical equilibrium being shifted towards the formation of non-dissociated carbonic acid (Beral and Zapan, 1973).

The decrease in the concentration of HCO_3^- drives the increase in pH, as in this case carbonic acid is formed and is then decomposed into H_2O and CO_2, followed by the removal of the CO_2 from the medium by photosynthesizing micro-organisms (Mazareanu and Pricope, 2007). The least square regressive method approach based on factorial ANOVA results for Mg^{2+} and pH versus HCO_3^- reveals once more suggestive aspects (Fig. 8). This discussion should be made by the correspondence arguments.

A similar behavior can be observed in winter and summer, which corresponds to a stable dynamic equilibrium type, which is a certain characteristic action of antagonistic factors. Such a situation was previous discussed in literature (Murariu et al., 2010, 2013b). During spring, the shape of the response surface is changed and it corresponds to an appropriate type of unstable dynamic equilibrium. In winter and summer respectively, there are two factors that influence the hydrogen carbonate ion concentration and these factors are influenced by the reduced flow magnitude of the Danube River (Kannel et al., 2007).

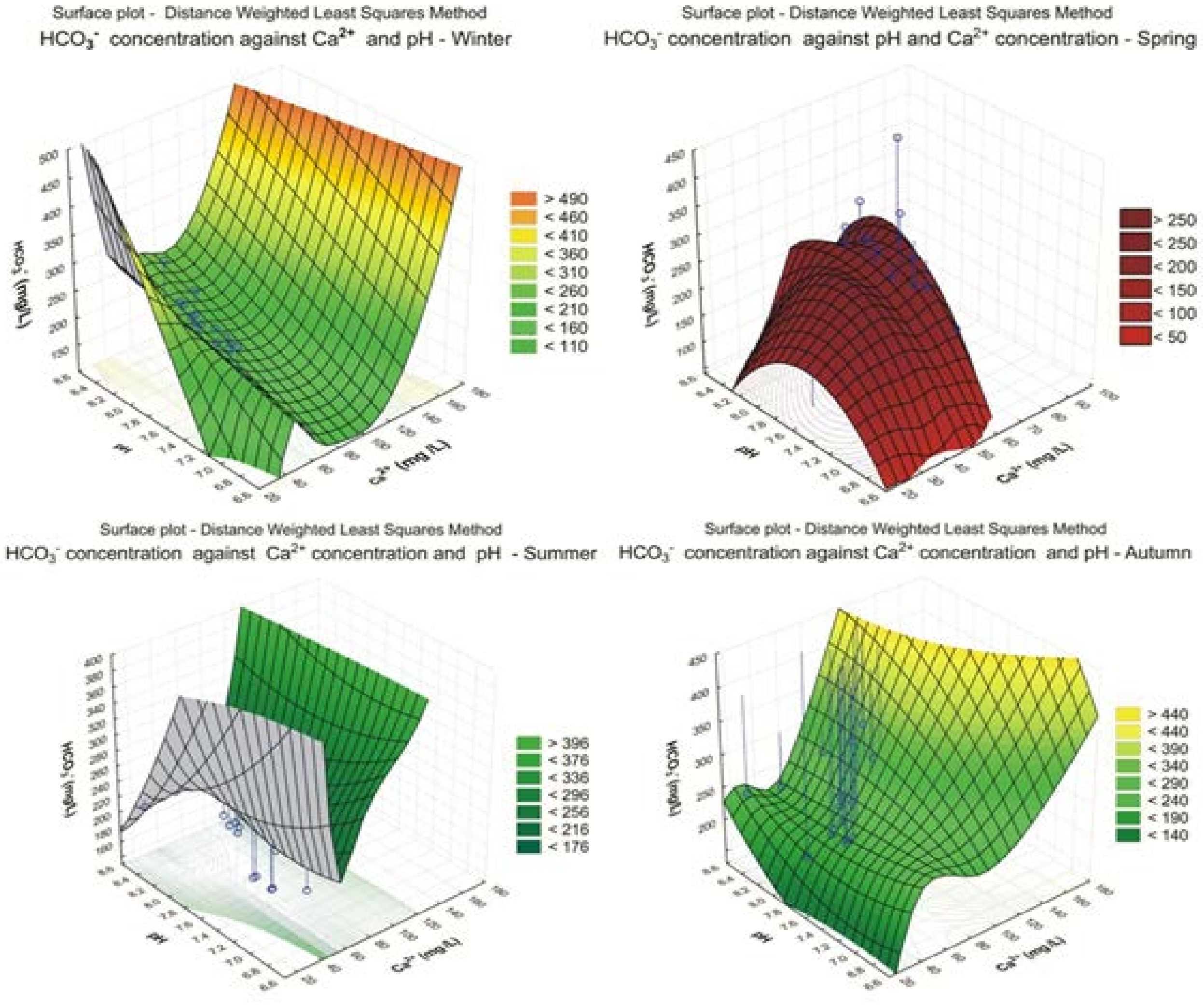
Thus, if HCO_3^- is a negatively correlated factor with the Ca^{2+} ion concentration, taking into account that the river flows recorded low levels in this season, there will be an upward trend in the concentration of this ion and thus the effect is translated through a positive correlation between these parameters (Fig. 7).

In the diluted water such as the case of the large flow of the Danube, a trend of increasing amounts of Ca^{2+} and HCO_3^- is visible. This is not surprising if river waters have contributions/inputs from rain water or bedrock disaggregation and therefore a Ca^{2+} and a HCO_3^- influx (Railsback, 2006). The surface response instability is evident in spring and autumn. It can be easily observed that there are complementarities between the Ca^{2+} and Mg^{2+} concentration (Fig. 7 and Fig. 8). In this way, when Ca^{2+} ion concentration increases, there is a correspondent decrease in Mg^{2+} concentration. This interesting phenomenon can be observed along all seasons, and shows that the hardness is due predominantly by the Ca^{2+} - calcium hardness. In the summer and winter the phenomenon is caused predominantly by the ionic strength Mg^{2+} - magnesium hardness.

Further, we applied the least square regressive method approach based on factorial ANOVA results for the independent factors Alkalinity and W. hardness versus pH regarded as dependent variable (Fig. 9). These two parameters were identified as having the significant influence on the vertical axis parameter (Fig. 4). Using these representations the driving processes could be suggested. Relative to the first independent factor, we can see a similar behavior in autumn, winter and spring, corresponding to a dynamic equilibrium type. The presented characteristics show again action of two main antagonistic factors. For winter, the surface allure corresponds to a stable dynamic equilibrium type (Murariu et al., 2013a).

During summer, the ecosystem response surface shape changes significantly, corresponding to an unstable dynamic equilibrium type. The variability for the ecosystem aquatic parameter pH is evident in the summer when flows are at lowest values and when the amount of wastewater discharged into the river flow is relatively constant. There is a trend of increasing values of this parameter.

The ***F2** factor* characterizes *the anthropogenic nutrient pollution in the area* and includes: pH, NO_2^-, NO_3^- and NH_4^+. This factor (F2) highlights seasonal changes depending on how its components relate to each other. For example, were examined the following 2 groups of parameters: NO_3^- and NH_4^+ versus pH, respectively $NO_2^-$and NH_4^+ versus pH. The choices were made basing on previous observation (Fig. 4). The results of the regression analysis method when we consider as independent factors NO_3^- concentration and NH_4^+ concentration and the dependent factor is pH reveals interesting facts (Fig. 10). Taking into account the second factor a similar behavior can be observed during spring and autumn, behavior that corresponds to a dynamic equilibrium type.


Surface plot - Distance Weighted Least Squares Method
HCO_3^- concentration against Ca^{2+} and pH - Winter

Surface plot - Distance Weighted Least Squares Method
HCO_3^- concentration against pH and Ca^{2+} concentration - Spring

Surface plot - Distance Weighted Least Squares Method
HCO_3^- concentration against Ca^{2+} concentration and pH - Summer

Surface plot - Distance Weighted Least Squares Method
HCO_3^- concentration against Ca^{2+} concentration and pH - Autumn

Fig. 7. Response surfaces of multidimensional regression analysis for Ca^{2+} and pH versus HCO_3^- for all seasons

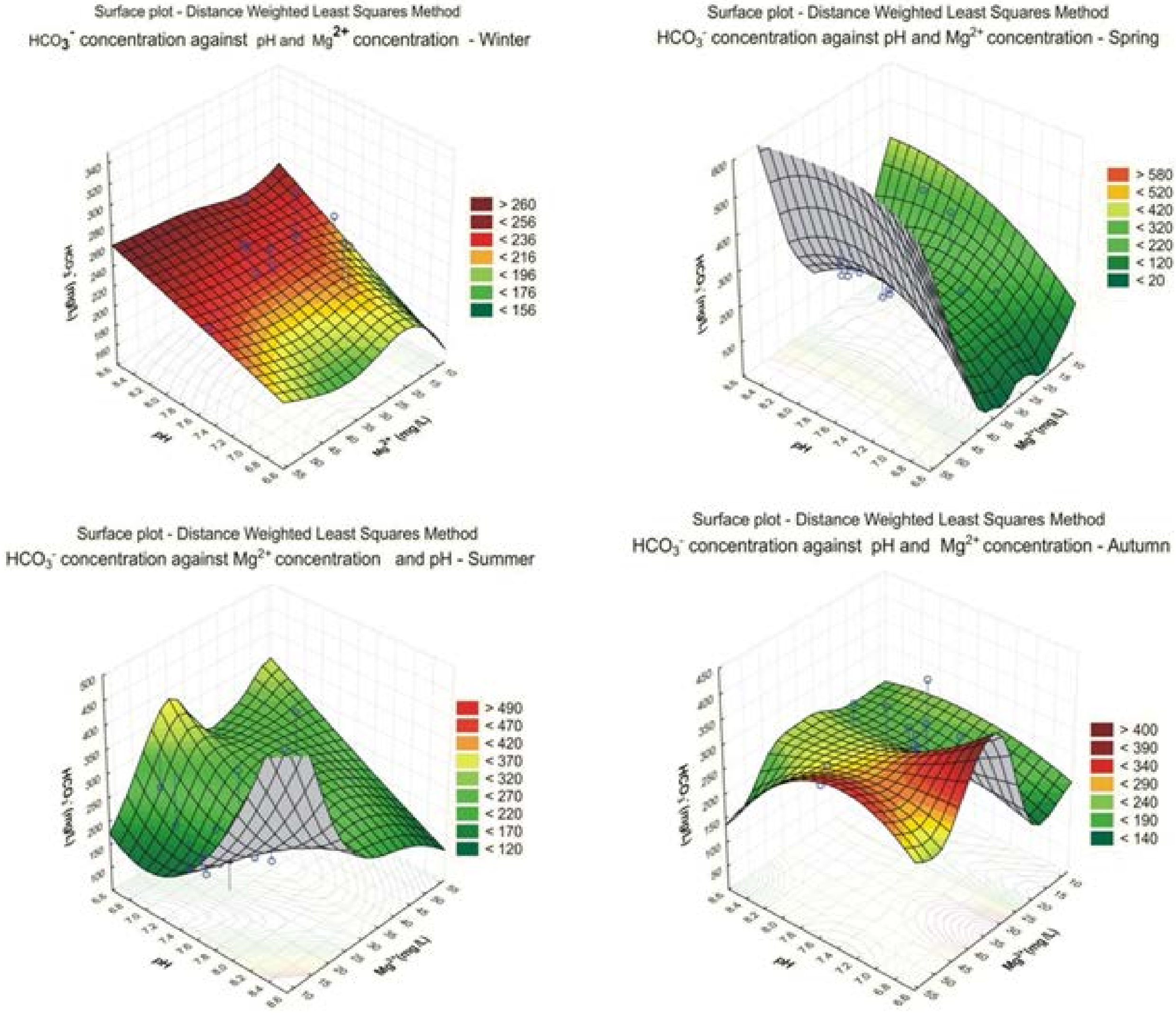


Fig. 8. Response surfaces of multidimensional regression analysis for Mg^{2+} and pH versus HCO_3^- for all seasons

During summer, the ecosystem response‘s surface shape changes significantly, corresponding to a specific unstable dynamic equilibrium. In this case, the system parameter - pH has an evident variability over the summer, when flows record their lowest values and the amount of wastewater discharged into the river flow is relatively constant. The least square regressive method approach based on factorial ANOVA results when we consider the independent factors NO_2^- concentration and NH_4^+ concentration and dependent parameter is pH (Fig. 11).

Taking into consideration the second factor, a similar behavior can be seen in the autumn and winter, corresponding to a dynamic equilibrium type, that is a characteristic action of two antagonistic factors (Mazareanu and Pricope, 2007). During spring, the ecosystem response surface shape changes significantly, corresponding to an unstable dynamic equilibrium type.

Again, the pH is the system parameter with an evident variability over the spring and summer, when flows are variable and decreasing and the flow (Beral and Zapan, 1973; Mazareanu and Pricope, 2007). The ***F3** factor* characterizes *the inorganic and organic pollution due to anthropogenic activities*, mainly due to fertilizer use in agricultural riparian area and includes: pH, Rf_{105}, TSM.

Pollution refers to situations in which some material or some form of energy occurs in larger quantity than can be tolerated by humans, plants, or animals without suffering some kind of harm. Human-caused pollution is sometimes referred to as anthropogenic pollution. Anthropogenic pollution has existed for centuries. People living along the Danube for example, were exposed to huge quantities of noxious gases in the air and dangerous levels of harmful pollutants in their water supplies.

The least square regressive method approach based on factorial ANOVA results when as independent factors are considered Rf_{105} and TSM and the dependent parameter is considered pH (Fig. 12). Taking into account this third factor certain differential seasonal behaviors can be observed. The most pronounced differences are recorded in the winter season when water flow is small and external wastewater influence is most strongly felt.

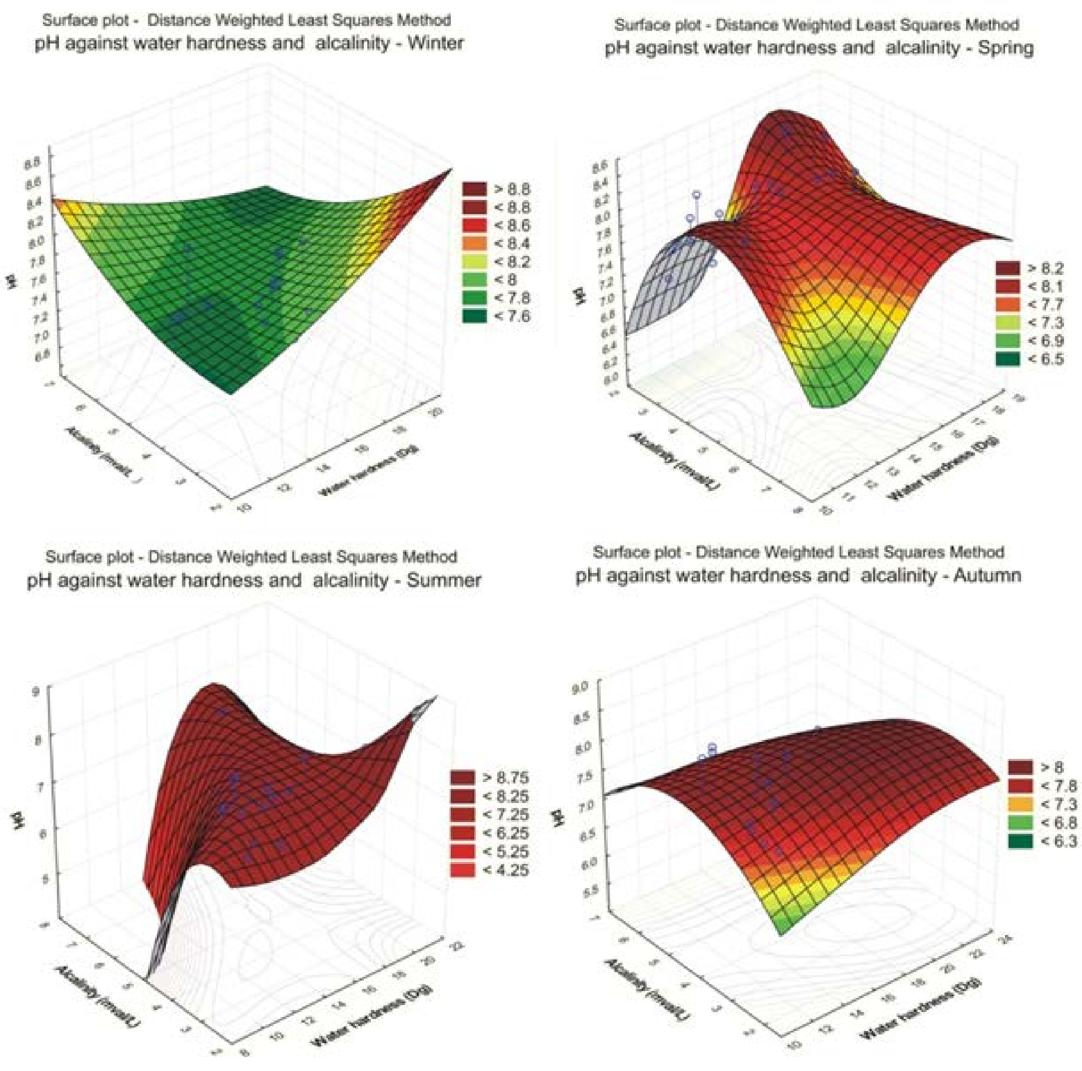


Fig. 9. Response surfaces of multidimensional regression analysis for Alkalinity and W. hardness versus pH for all seasons

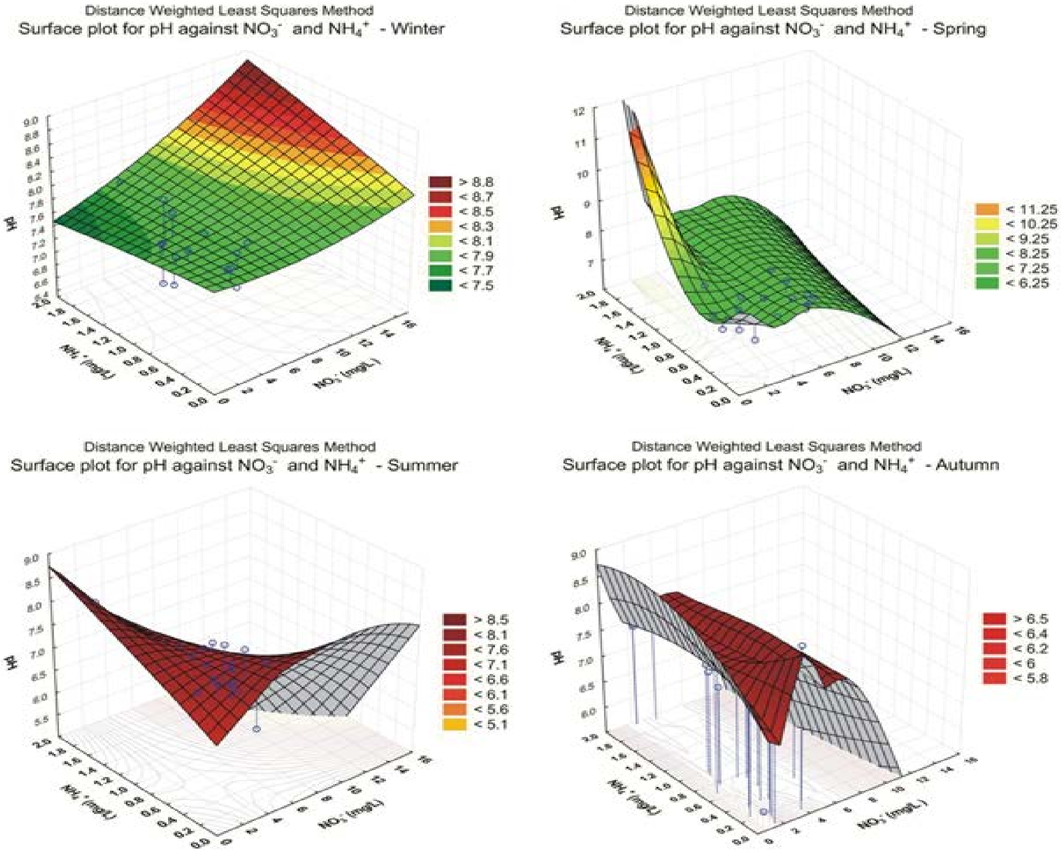
The ecosystem response surface shape changes significantly, corresponding to an unstable dynamic equilibrium type. As it was highlighted before, the considered parameter pH registered an obvious variability in the system, especially when the amount of wastewater discharged into the river flow is relatively constant (Mazareanu and Pricope, 2007).

5. Conclusions

In this paper we presented a statistical analysis through which we can identify three important factors that directly influence the water parameters. These three main key identified factors show different weights during the year, based on a certain seasonal variability. In this respect, in winter, because the flow and temperature are normally low a strong correlation was found between the analyzed water parameters of the Danube River. In spring, due to increased flow, strong changes of the correlation matrix were noticeable and the three identified factors have different loads. During the summer the anthropogenic footprint on water quality ecosystem of the Danube was highlighted. In the fall, the reduction or even absence of the natural biological activity leads to decrease of pollution caused by natural sources of the region.

The PCA method enabled us to group the water parameters of the Danube River in factors and allowed us to succeed in obtaining the response surfaces by applying least square regression procedure. In order to complete the image on dynamics of the interdependencies, the ANOVA is accomplished with a graphical representation using the least square method.

The methodology for the systematic analysis due to the identification of the fundamental and the dependent parameters was not exposed in this article because it is the subject of another paper. In this prolonged period that spanned the study, it is clear that the Danube has a remarkable capacity for self-filtering.

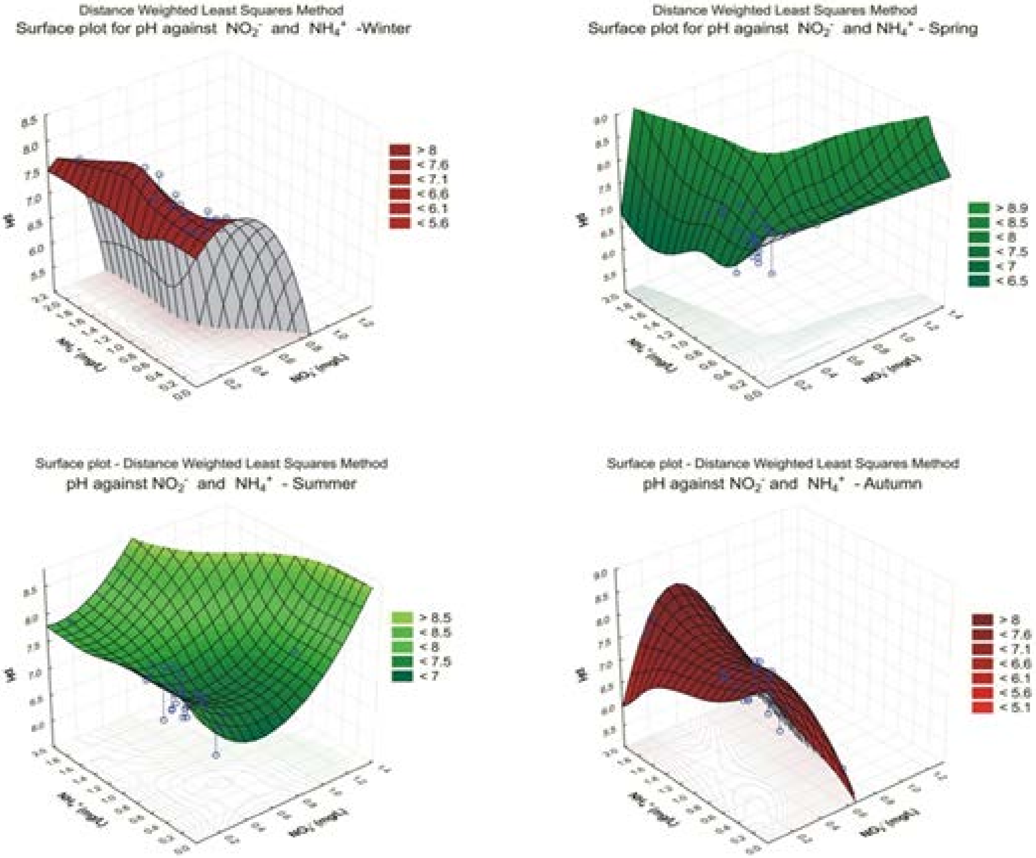

Distance Weighted Least Squares Method
Surface plot for pH against NO_3^- and NH_4^+ - Winter

Distance Weighted Least Squares Method
Surface plot for pH against NO_3^- and NH_4^+ - Spring

Distance Weighted Least Squares Method
Surface plot for pH against NO_3^- and NH_4^+ - Summer

Distance Weighted Least Squares Method
Surface plot for pH against NO_3^- and NH_4^+ - Autumn

Fig. 10. Response surfaces of multidimensional regression analysis for NO_3^- and NH_4^+ versus pH for all seasons


Distance Weighted Least Squares Method
Surface plot for pH against NO_2^- and NH_4^+ -Winter

Distance Weighted Least Squares Method
Surface plot for pH against NO_2^- and NH_4^+ - Spring

Surface plot - Distance Weighted Least Squares Method
pH against NO_2^- and NH_4^+ - Summer

Surface plot - Distance Weighted Least Squares Method
pH against NO_2^- and NH_4^+ - Autumn

Fig. 11. Response surfaces of multidimensional regression analysis for NO_2^- and NH_4^+ versus pH for all seasons

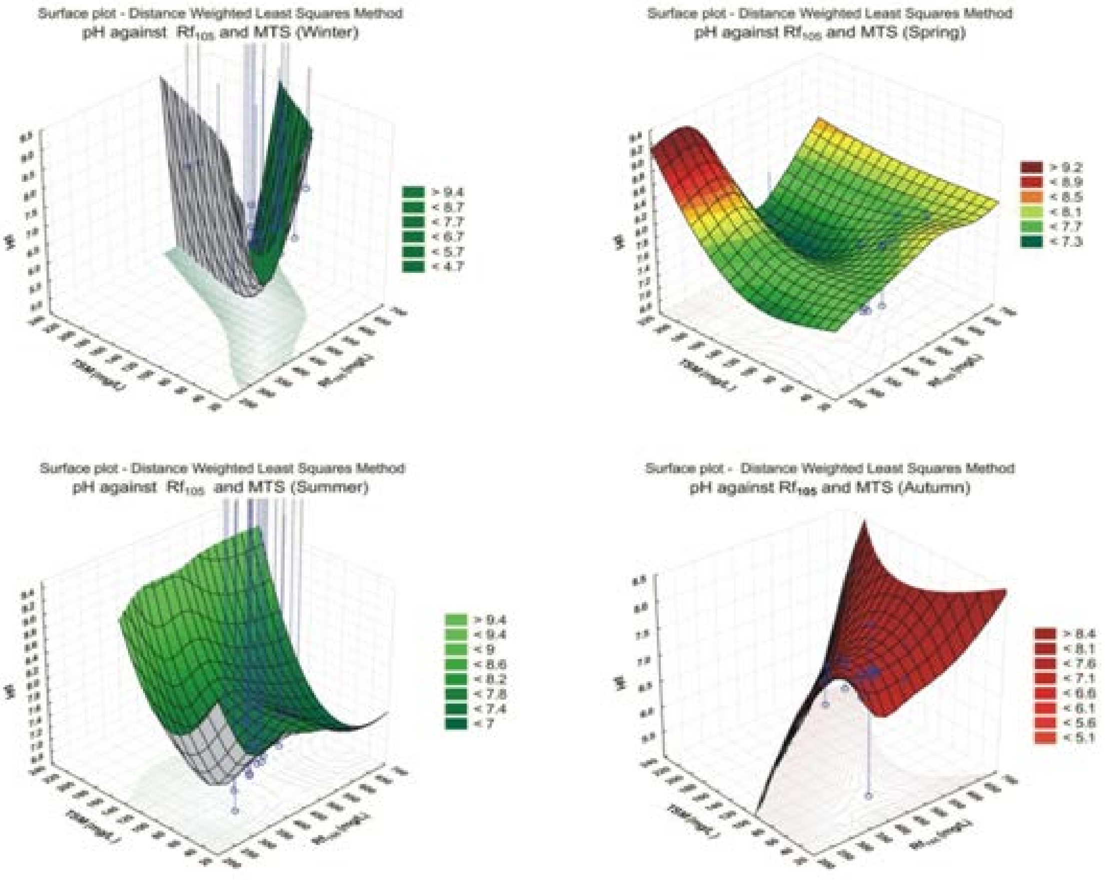


Fig. 12. Response surfaces of multidimensional regression analysis for TSM and Rf_{105} versus pH for all seasons

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