

The Analysis of Correlation of some ions concentration in rainwater in an urban area

Alina Bărbulescu

Abstract— In the framework of urban environmental control, it is necessary to know the effect of different types of pollutants on air and water quality. The precipitation is the main factor of water circulation, so it can contribute to the pollutants transportation from atmosphere into the soil and surface water.

In order to determine if the air pollutants have a major impact on the quality of surface water, in an urban area, we developed a study on Constanta city, Romania. In this paper we present the results of the analysis of annual and monthly indicators of the rainwater quality and the study of correlation between the rainwater indicators and the Tăbăcărie Lake quality indicators.

Keywords — impact, indicators, precipitation, variation, water quality.

I. INTRODUCTION

CONSTANTA (pronounced *Constantza*) is a coastal Black Sea town in southern Dobruja, Romania, the second most important city in the country. It is the capital of the Constanta county (Fig.1) and Romania's largest seaport.



Fig.1. Constanta county

Constanta (Fig.2), being founded as a city almost 2600 years ago, it is the oldest attested city in Romania, the biggest port at the Black Sea (third largest in Europe) and also the third largest city in Romania with its 400,000 inhabitants. It

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Alina Bărbulescu is with Ovidius University of Constanta, Department of Mathematics and Computers Science, 124, Mamaia Blvd, 900527 – Constanta, ROMANIA (phone: 0040- 241- 606242; e-mail: alinadumitriu@yahoo.com).

was founded by the Greeks as a port on the Black Sea Coast for trading with inland people and called *Tomis* (VIth C. BC). The city was renamed later after Constantina, niece of Constantine the Great (274-337). It was still a flourishing port city in the Xth and XIth centuries trading with the Byzantine Empire and the city of Genoa. [1]

The climate in this area is moderate continental, strongly influenced by both the Black Sea and Mediterranean Sea. Recently, changes in temperature, as well as the pollution increase were registered in Constanta.



Fig. 2. Constanta and its coastal lakes

Tăbăcărie Lake (Fig.2), located at 44.12⁰N latitude and 28.38⁰E longitude, is a 99 ha surface fluvial-marine haven near the shore of Black Sea. Due to its formation, its level is 125 cm higher than the sea level, so that communication between them is well established. The lake is also connected to the Siutghiol Lake, whose water ensures the feed of

Tăbăcărie. Still, the lake's water is brackish and is not drinkable, but is satisfactory for recreation. At the present time, the lake needs urgent attention.

For the last years, its color has been green, because of algae development.

An important amount of waste water from the city still goes in Tăbăcărie Lake without appropriate treatment, so water quality has been decreased in the past years to the hypereutrophic stage.

The enrichment of coastal water with nutrients leads to the lakes eutrophication. The main eutrophication causes, in this case, are the discharge of waste water from Constanta city and the combustion of fossil fuels in the urban agglomeration. Other causes include agriculture in the neighborhood villages, with excessive use of mineral fertilizers which eventually leads to water contamination, chemical industry and its atmospheric emissions of nitrogen oxides, their reaction with rainwater and the formation of acid rains, detergent industry and its 40% phosphor salts products as well as different other wastes, which decompose releasing nitrogen and phosphor in the upper water layers.

The main eutrophication consequence is the high development rate of plankton algae, which modify water properties, mostly noticed color and smell. In time, biodiversity declines and species rates change.

Chemical composition of rain water, although related to human activities, is connected to the chemical composition of natural lakes, especially in urban areas, where emissions and waste water result in the pollution level.

The main atmospheric pollutants, such as gas and particulate matter, prove danger for both human health and natural lake water quality. The mechanism of pluvial precipitation removes undesirable compounds from the atmosphere and deposits them in the lake. Rainwater's chemical composition is different depending on season, degree and character of the territory urbanization, relevance of pollution sources. As a result, many chemical species are presents into the rainwater.

It was shown [2] that most of excess of sulfate could derive from biogenic sulfur compounds, arising from lake water, which is in a hypereutrophic stage. The ammonium ion can be due to the vicinity of agricultural lands, and chlorine is due to marine influence [3]. So the influence of rain's chemical composition and the connection to the chemical composition of natural lake water must be analyzed, in order to establish its influence on water quality and the natural reversibility of the lake's trophic stage.

For this study *pH*, the chemical oxygen demand, color, turbidity and nutrients were measured on the lake water collected from Soveja Boulevard location [4], [5]. Also, *pH*, acidity/alkalinity, chlorine, ammonium, sulfate, and conductivity were determined for the rain water collected in the same location [6] - [10]. All the samples, although measured in triplicate to confirm the reproducibility and accuracy of results, were confronted to the ones collected by the local administration department.

The primary goal was to determine the variation in time of these characters and the impact of precipitation on Tăbăcărie Lake water quality. The secondary goal was to establish common trends of such characteristics.

The variance analysis was used to analyze the annual and monthly variation of all the determined indicators. Then, mathematical models for the correlation between them were built.

II. EXPERIMENTAL

Rainwater and lake water samples were collected regularly from January 2000 to June 2008. The same time, the samples collected during the past eight years from the same sampling site were centralized.

Rainwater samples were collected in bulk precipitation collector, mounted 2 m above ground level and filling a 2 liter polyethylene bottle. The bottles were collected each time after the precipitation falling. The *pH*, ammonium, sulphate, chloride, alkalinity and conductivity were determined.

The lake's water samples were also collected in 2 liter polyethylene bottles each time after precipitation and analyzed simultaneously with the rainwater samples in order to identify connections between the studied values.

All the recipes were well washed and dried before sample collection and kept closed, clean, and in the absence of light inside a cupboard.

All the samples were filtrated in order to separate solid and suspended matter with a filter paper. The recovered particulate matter was analyzed with a scanner electron microscope.

The *pH* measurements were carried out both at the sampling site and in the laboratory as soon as the samples were collected, with Merck, Baker – *pH* - Fix and Macherey - Nagel *pH* - Fix paper.

The concentrations of the SO_4^{2-} , NH_4^+ , Cl^- ions were determined by titration, accordingly to Romanian standards.

The conductivity was measured with an electric conductivimeter.

III. MATHEMATICAL BACKGROUND

In our study, the generalized linear models (GLM) and the variance analysis (ANOVA) were used [11].

Univariate GLM is the general linear model and is often used to implement long-established statistical procedures as regression and members of the ANOVA family. It is "general" in the sense that one may implement both regression and ANOVA models. One may also have fixed factors, random factors, and covariates as predictors. Also, in GLM one may have multiple dependent variables and one may have linear transformations and/or linear combinations of dependent variables.

Moreover, one can apply multivariate tests of significance when modelling correlated dependent variables, not relying on individual univariate tests as in multiple regressions.

GLM also handles repeated measures designs.

Finally, because GLM uses a generalized inverse of the matrix of independent variables' correlations with each other, it can handle redundant independents which would prevent solution in ordinary regression models.

Analysis of variance (ANOVA) is used to uncover the main and interaction effects of categorical independent variables (called "factors") on an interval dependent variable. A "main effect" is the direct effect of an independent variable on the dependent variable. An "interaction effect" is the joint effect of two or more independent variables on the dependent variable.

Whereas regression models cannot handle interaction unless explicit crossproduct interaction terms are added, ANOVA uncovers interaction effects on a built-in basis.

The key statistic in ANOVA is the F-test of difference of group means, testing if the means of the groups formed by values of the independent variable (or combinations of values for multiple independent variables) are different enough not to have occurred by chance. If the group means do not differ significantly then it is inferred that the independent variable(s) did not have an effect on the dependent variable. If the F test shows that overall the independent variable(s) is (are) related to the dependent variable, then multiple comparison tests of significance are used to explore just which values of the independent(s) have the most to do with the relationship [11].

Let us consider the linear model, written as:

$$y = Ax + \varepsilon,$$

where:

$$- y = \begin{pmatrix} y_1 \\ y_2 \\ \vdots \\ y_n \end{pmatrix} \text{ is the vector of dependent variable,}$$

- x – the vector of independent variables,
- A – the matrix of coefficients,
- ε – the error vector.

We remember the general conditions that must be satisfied, in order to perform a parameterized linear regression [12]:

- The model is linear in the dependent variable;
- The values of dependent variable are observed without errors;
- The model's mean error is zero;
- The errors' variance is constant;
- The errors are not correlated;
- The errors don't depend on the explicative variables.

Student test is used to verify if the explicative variables have significant contributions to the explanation of the dependent variable. F – test is performed to test the hypothesis of the global significance of the model, e.g. if the set of the explicative variables has an influence on the variable y .

The variance of y explained by the regression of y on x is measured using the determination coefficient:

$$R^2 = 1 - \frac{ee'}{\sum_{i=1}^n (y_i - \bar{y})^2}$$

and the modified determination coefficient:

$$\bar{R}^2 = 1 - \frac{n-1}{n-k-1} \cdot (1 - R^2),$$

where:

- n is the number of observations,
- k - the number of explicative variables,
- e - the vector that contains the residuals, $e_i = y_i - \hat{y}_i$,
- e' - the transposed of the vector e ,

$$- \bar{y} = \frac{\sum_{i=1}^n y_i}{n} - \text{the mean,}$$

- \hat{y}_i - the value calculated for y_i , using the regression model.

When R^2 (\bar{R}^2) is close to 1, the model fitting quality is good.

Remarks. 1. It must distinguish between the specification error of the model, ε_i , which is and remains unknown and the residual, e_i , which is known.

2. The following tools were used to verify the errors properties:

- the autocorrelation function – for the correlation,
- the Kolmogorov - Smirnov and Shapiro – Wilk tests – for the normality hypothesis,
- the Levene test - for homoscedasticity.

IV. RESULTS AND DISCUSSIONS

A. Rainwater analysis

In Constanta, especially during cold seasons, the rainwater was slightly acid, as result of vehicles emissions, nearby petrochemical complex and coal/fuel oil power plant. All the high values of ions were due to anthropogenic sources, including urban transport and the loss of green plants (Tăbăcărie Park itself lost an important surface area because of recent construction), and organic sources, such as the soil and sea water. Since our sample area was strictly punctual, we could determine the sources of anthropogenic pollutants.

The samples tended to have high concentrations of Cl^- because of the sea vicinity. So, we could easily conclude that Cl^- is arising from the sea salts. The SO_4^{2-} and the NH_4^+ were found in all the samples.

There is a clear pattern with respect to the places where we found large concentrations of Cl^- because the lake is near the coast, so the rainwater acquires its Cl^- content from large bodies of salt water. When the sea water evaporates, some anions travel with the water vapor. The rain generated by the

evaporation of coastal lakes has small quantities of Cl^- because they contain fresh water from underground rivers.

The results of sulfate and even chloride concentrations had big variations.

The comparative analysis of our samples gave us conflicting information how valuable sampling was, because they were temporal and strictly local, without taking into account the variation with atmospheric conditions. That's why we also made use of the "official data" provided by the local administration regarding environmental protection, on legal base of public use data.

The small rainwater amount, low rainfall and low wind speed and some other meteorological conditions such as local winds and sea breeze might caused abnormally values. We could not take into account the effect of physical factors in the chemistry of rainwater or lake water (wind speed and direction, which affect Cl^- and SO_4^{2-} ; rainfall amounts and intensity, which determine Cl^- , SO_4^{2-} , NH_4^+ and pH ; washout and rainout process, correlated with Cl^- , SO_4^{2-} and pH).

The analysis of correlation coefficient of the samples suggested that low pH of rainwater determined the vapor salts to decompose in ions. Our model showed the active role of the analyzed ions and the pH dependence of their concentration.

The statistical analysis also revealed their sources: anthropogenic emissions (industrial plants, transport, and use of fossil fuels), sea salt component (especially Cl^- , SO_4^{2-} , and NH_4^+), construction component (particulate matter, solid building wastes), acidifying species.

The study couldn't show the importance of rainfall intensity and cloud scavenging in changing indicators' value.

The degradation of air quality, arising in the deterioration of rainwater and, by consequence, of lake water and soil, resulted from the fuels' high sulfur content. The combustion phenomenon occurring in motor engines also generates NO_x , so both SO_x and NO_x determine acidic rain and unsatisfactory values of studied indicators. Combined with a massive loss of green areas and intense constructions they gave an odd correlation between factors.

B. The variation of rainwater characteristics

In Figs. 3 – 5 the charts of annual characteristics studied (pH , alkalinity and the concentrations of Cl^- , SO_4^{2-} , NH_4^+ ions of rainwater) are represented, for the period 2000 - 2007.

In Figs. 6 - 8 the charts of monthly variation of the same characteristics are presented, for the period January 2006 - April 2008.

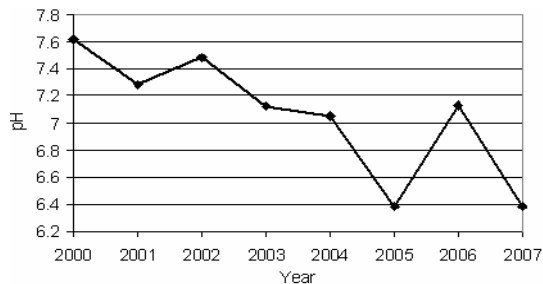


Fig.3. Annual pH variation

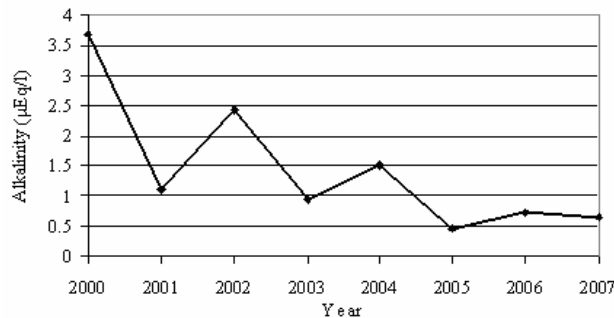


Fig.4. Annual alkalinity variation

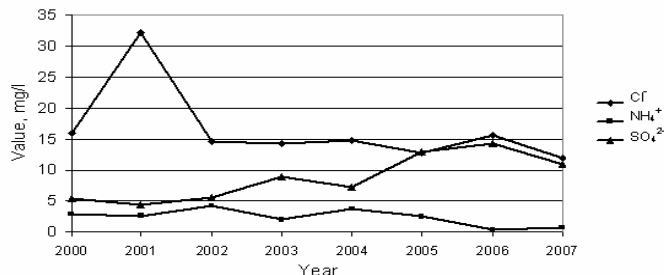


Fig.5. Annual variation of ions' concentration

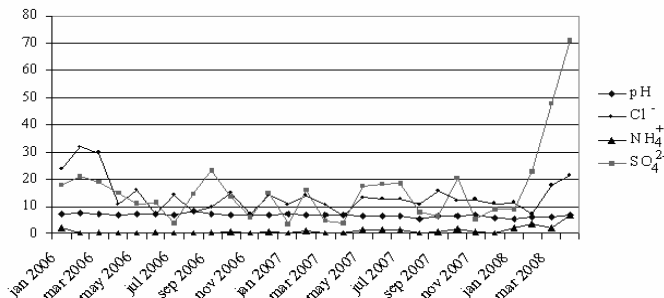


Fig.6. Monthly variation of data

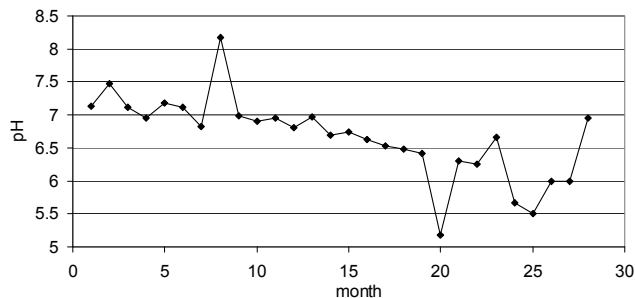


Fig.7. pH monthly variation January 2006 - April 2008

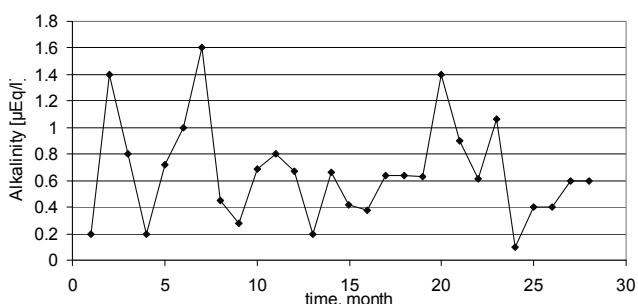


Fig.8. Monthly rainwater alkalinity between January 2006 and April 2008

B₁. Annual data analysis

The interaction *pH* – alkalinity was studied. The results of the variance analysis of dependent variable (*pH* annual rainwater) function of the influence of the annual rainwater alkalinity are presented in Table I, where the significances of data are the following:

- column 2: the degree of freedom of the independent variable (in this case alkalinity) and residual;
- column 3: the sum of squares of deviations of the dependent variable (*pH*) due to the regression model and residual;
- column 4: the estimation of variances due to the two sources of variation (regression and residual);
- column 5: the value of F - statistic, calculated as the ratio between the values of MS (for alkalinity and residual, in this case);
- column 6: the *p* - value, which represents the probability of making a Type I error, or rejecting the null hypothesis when it is actually true. The smaller the *p* - value, the smaller the probability is that you would be making a mistake by rejecting the null hypothesis.

A commonly used cut - off value for the *p* - value is 0.05. If the calculated *p* - value of a test statistic is less than 0.05, the null hypothesis that there is no relation between the variables is rejected.

Table I. Dependence of annual *pH* rainwater on annual rainwater alkalinity

	df	SS	MS	F	<i>p</i> - value
Alkalinity	1	0.875	0.875	8.801	0.025
Residual	6	0.597	0.099		
Total	7	1.472			

F = 8.801 was compared to $F_{1,6} = 5.99$, the value found in the table of Fisher test, with 6 and 1 degrees of freedom, at the significance level $\alpha = 0.05$.

Since $8.801 > 5.99$ and $p = 0.025 < 0.05$, the hypothesis that there is no relation between the *pH* of rainwater and its alkalinity is rejected. So, with a probability of 95% the *pH* significantly depends on the alkalinity.

The determination coefficient is $R^2 = 69.5\%$ and the

modified determination coefficient, $\bar{R}^2 = 62.79\%$, confirming that the biggest part in the variance in the model is due to alkalinity, fact that is in concordance with the chemical knowledge.

As consequence, the following model was proposed:

$$y_i = 6.594 + 0.321 \cdot x_i + \varepsilon_i \quad (1)$$

where:

- y_i is the *pH* at the moment *i*,
- x_i - the alkalinity,
- ε_i - the error.

The results of the *t*-tests (Table II) prove that the coefficients of the model are significantly different from zero.

Table II. Test of significance for the coefficients of model (1)

Model	unstandardized coefficients		standardized coefficients	t	<i>p</i> - value
	B	std.err	Beta		
constant	6.594	0.191		34.506	0.000
alkalinity	0.321	0.108	0.771		0.025

In order to validate the model, the studies of normality (Table III) and autocorrelation function (Fig.9) of residuals [13] were performed.

Table III. Tests of normality

Kolmogorov - Smirnov			Shapiro - Wilk		
Statistic	df	<i>p</i> - value	Statistic	df	<i>p</i> - value
0.284	8	0.058	0.843	8	0.081

Since the *p* - values corresponding to both Kolmogorov – Smirnov and Shapiro – Wilk are higher than 0.05, we accept the normality hypothesis, at the significance level of 5%.

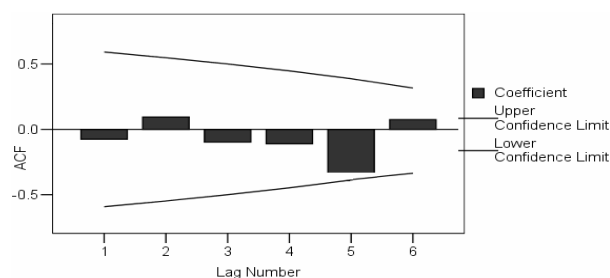


Fig.9. The autocorrelation function of residuals

The values of the autocorrelation function of the residuals are inside the limits of the confidence limits at the confidence level of 95%, so we accept the hypothesis that the series is independent. The result of Levene test leads us to the acceptance of homoscedasticity hypothesis.

So, the model (1) is a good one.

The results of the analysis of dependence of annual rainwater *pH* on the annual concentrations of Cl^- , SO_4^{2-} ,

NH_4^+ are displayed in Table IV, where df, F, p - value have the same significance as in Table I.

Table IV. The dependence of annual rainwater pH on the concentration of Cl^- , SO_4^{2-} , NH_4^+ ions

	df	Adj SS	F	p - value
NH_4^+	1	0.09337	68.71	0.076
SO_4^{2-}	1	0.00445	3.27	0.321
Cl^-	1	0.06147	45.23	0.094
$NH_4^+ \cdot SO_4^{2-}$	1	0.05389	39.65	0.100
$NH_4^+ \cdot Cl^-$	1	0.09435	69.43	0.076
$Cl^- \cdot SO_4^{2-}$	1	0.01190	8.76	0.207
Residual	1	0.00136		
Total	7			

The adjusted sums of squares provided in column 3 of Table IV do not depend on the order the factors entered into the model. It is the unique part of SS regression explained by a factor, given all other factors in the model, regardless of the order they were entered into the model.

Analyzing the p - values, it appears that in a model of type:

$$pH = \alpha_1 NH_4^+ + \alpha_2 SO_4^{2-} + \alpha_3 Cl^- + \beta_1 NH_4^+ \cdot SO_4^{2-} + \beta_2 Cl^- \cdot SO_4^{2-} + \beta_3 NH_4^+ \cdot Cl^- \quad (2)$$

none of the factor or interaction between them have a influence on the rainwater pH .

A model of the type:

$$pH = \alpha NH_4^+ + \beta SO_4^{2-} + \gamma Cl^- + \varepsilon \quad (3)$$

was also analyzed and the tests on coefficients lead us to accept the hypothesis that $\gamma = 0$. Therefore, the following model was proposed:

$$pH = \alpha NH_4^+ + \beta SO_4^{2-} + \varepsilon. \quad (4)$$

The result of variance analysis and the parameters' estimations ($\alpha = 0.417$, $\beta = 1.341$) are presented in Tables V and VI.

Table V. Variance analysis - model (4)

	SS	df	MS	F	p - value
Model	384.748	2	192.374	77.425	0.000
SO_4^{2-}	61.414	1	61.414	24.718	0.003
NH_4^+	52.389	1	52.389	21.085	0.004
Residual	14.908	6	2.485		
Total	399.656	8			

The regression coefficients are significant since the value 0 in not inside the confidence interval and the probability values for the t - test are less than 0.05.

Table VI. Parameter estimation - model (4)

parameter	coeff.	std. error	t	p - value	95% confidence interval	
					lower bound	upper bound
SO_4^{2-}	0.417	0.084	4.972	0.003	0.212	0.622
NH_4^+	1.341	0.292	4.592	0.004	0.626	2.056

Also, the hypotheses that the errors are not correlated and are normally distributed were accepted.

The determination and the modified determination coefficients were respectively $R^2 = 96.3\%$ and $\bar{R}^2 = 95\%$, proving a high correlation between the variables in the model (4).

During our analysis it was remarked that the influence of NH_4^+ on pH is higher than that of SO_4^{2-} .

We have to remember the neutralization ability of ammonia gas on acidic sulfur and nitrogen oxides from the atmosphere; so, the precipitation acidity was partially neutralized by NH_4^+ in this area. On the other hand, the decrease of pH corresponded to the decrease of alkaline ions during the precipitation events.

The acidity appeared to be lower than expected in the presence of NH_4^+ only. So, it was proved that NH_4^+ and SO_4^{2-} ions were sources of acid precipitations.

B₂. Monthly data analysis

The same analyses were performed for the monthly data. The result of ANOVA is presented in Table VII. As expected there is a clear dependence between the pH of monthly rainwater and its alkalinity. It is also confirmed by the determination coefficients, which have respectively the values: $R^2 = 97.3\%$ and $\bar{R}^2 = 97.25\%$.

Table VII. Dependence of monthly pH rainwater on annual rainwater alkalinity

	df	SS	MS	F	p -value
Alkalinity	1	504.96	504.96	1942.6	0.000
Residual	54	14.037	0.260		
Total	55	518.997			

A model analogous to (4) was also determined for monthly data (Tables VIII and IX). It is given by the equation:

$$pH = -1.68 \cdot NH_4^+ + 0.362 \cdot SO_4^{2-} + \varepsilon. \quad (5)$$

The tests on the coefficients, as well on the errors lead us to accept the model (5).

The values of determination and modified determination coefficients, respectively $R^2 = 86.2\%$ and $\bar{R}^2 = 85.09\%$, come to confirm the influence of NH_4^+ and SO_4^{2-} ions on the pH of monthly precipitation.

Table VIII. Variance analysis – model for monthly data

	SS	df	MS	F	p-value
Model	784.906	2	392.453	21.754	0.000
SO_4^{2-}	386.262	1	386.262	21.411	0.000
NH_4^+	52.389	1	57.609	3.193	0.006
Residual	57.609	26	18.040		
Total	1253.95	28			

Table IX. Parameter estimation – monthly data

parameter	coeff.	std. error	t	p-value	95% confidence interval	
					lower bound	upper bound
SO_4^{2-}	0.362	0.94	4.627	0.000	0.201	0.523
NH_4^+	-1.680	0.078	-1.787	0.036	0.126	0.256

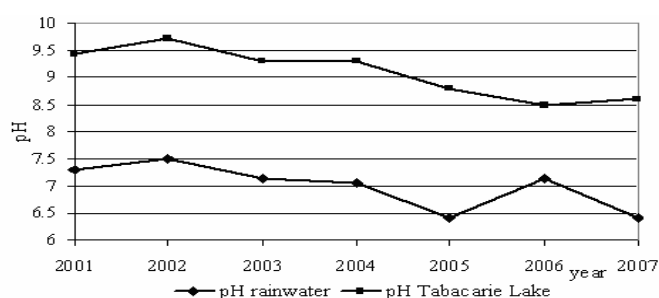
C. The analysis of rainwater influence on Tăbăcărie Lake water quality

C₁. Annual data analysis

Tăbăcărie Lake has been classified as eutrophic and hypereutrophic in the past years. We tried to determine its quality indicators, as clarity level and turbidity, but no variation was registered. Therefore, total nitrogen, total phosphorus, phytoplankton biomass, *pH*, dissolved oxygen, oxygen demand were analyzed, considering them as directly responsible for trophic stage characterization.

The evolutions of mean annual *pH* of rainwater and of the Tăbăcărie Lake water are represented in Fig. 10.

The results of the variance analysis are given in Table X.

Fig.10. *pH* variation in time for rainwater and lake waterTable X. Results of variance analysis of Tăbăcărie Lake *pH* function of rainwater *pH*

	df	SS	MS	F	p-value
<i>pH</i> of rainwater	5	1.2529	0.2506	12.53	0.211
residual	1	0.0200	0.0200		
Total	6	1.2729			

The value $F = 12.53$ of the F - statistic is compared to the value given in the table of Fisher distribution, with 5 and 1 degrees of freedom, at the confidence level of 95%,

$F_{5,1} = 230$. Since $F = 12.53 < 230 = F_{5,1}$ and $0.211 > 0.05$, the null hypothesis that there is no relation between the *pH* of rainwater and the *pH* of Tăbăcărie Lake is accepted.

Thus, we can not conclude that the *pH* of rainwater has a significant influence on the *pH* of Tăbăcărie Lake.

C₂. Monthly data analysis

The same analysis was carried out for the monthly data between December 2006 and April 2008, with the same results as for annual data.

V. CONCLUSIONS

As it is known, in chemistry, *pH* (short for potential for hydrogen ion concentration) is a measure of the acidity or basicity of a solution. It approximates but is not equal to the negative logarithm (base 10) of the molar concentration of dissolved hydrogen ions (H^+). Crudely, this matches the number of places behind the decimal point, so for example 0.1 molar hydrochloric acid should be near *pH* 1 and 0.0001 molar *HCl* should be near *pH* 4. [14]

In the studied case, the values of annual rainwater *pH* were between 6.38 and 7.62, the acidity decreasing from 2001 to 2008, those of monthly rainwater becoming more and more basic, from April 2007.

Although chlorine had the highest concentration between all the analyzed ions in the rainwater (correlate with proximity to the Black Sea, which is very salty), its influence on the *pH* water was not significant.

The presence of NH_4^+ and SO_4^{2-} ions in water is due especially to anthropogenic influence. Models describing the influence of these ions on the *pH* of precipitation water were determined in this article. Also, it was proved that there is no correlation between the rainwater *pH* and Tăbăcărie Lake water *pH*, even if precipitation is one the main effective factor for the atmospheric pollutants removal.

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