Modeling Precipitation Influence on Tăbăcărie Lake Water Quality

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Abstract: - It is well – known that the human activity has a major impact on the environment. In order to identify the effects of air pollutants on the water, in this paper we present the results of an analysis of annual and monthly indicators of the rainwater quality, in Constantza, Romania. A correlation study between the rainwater indicators and the Tăbăcărie Lake quality indicators is also performed and mathematical models are built.

Key-Words: - water quality, indicators, precipitation, variation, impact.

1 Introduction

The 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 level of pollution. The main atmosphere 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 [4] that most of the excess of sulfate could derive from biogenic sulfur compounds, arising from lake water, which is in a hypereutrophic state. The ammonium ion can be due to the vicinity of agricultural lands, and chlorine is due to marine influence [10]. 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 state.

Constantza city (Fig.1), 303,712 habitants, is the oldest populated location in Romania, with the biggest harbor on the Black Sea, having high development potential. It has a moderate continental climate, strongly influenced by both the Black Sea and Mediterranean Sea. Constantza recently experienced changes in temperature and precipitation, but also an increase of pollution.

Fig.1. Constantza region and its coastal lakes

Tăbăcărie Lake 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 cannot be used for drinking, but is satisfactory for recreation. At the present time, the lake needs urgent attention. Its location is determined by 44.12^0N latitude and 28.38^0E longitude. 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 without appropriate treatment, so water quality has been decreasing in the past years to the hypereutrophic stage.

The enrichment of coastal water with nutrients leads to the lakes eutrophisation. The main eutrophisation causes, in this case, are the discharge of waste water from Constantza 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 eutrophisation 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.

For this study pH, the chemical oxygen demand, color and turbidity and nutrients were measured on the lake water collected from Boulevard location [1], [2]. Also, *pH*, acidity/alkalinity, chlorine, ammonium, sulfate, and conductivity were determined for rain water collected in the same location [3], [5] - [7], [11]. 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 so the impact of rain on Tăbăcărie Lake quality. The secondary goal was to establish common trends of such characteristics. The analysis of variance was used to test the annual and monthly variation of all the determined indicators. Then, a mathematical correlation between them was proved.

2 Experimental

Rainwater and lake water samples were collected regularly from January to June 2008. In 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 2m above ground level and filling a 2l polyethylene bottle. The bottles were collected each time after the precipitation fall. The samples were analyzed for pH, ammonium, sulfate, chloride, alkalinity and conductivity.

The lake's water samples were also collected in 2 l polyethylene bottles each time after precipitation and analyzed simultaneously with the rainwater samples in order to identify any connection 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. SO_4^{2-}, NH_4^+, Cl^- were determined by titration, according to our national standards. The conductivity was measured with an electric conductivimeter.

3. Results and discussions

3.1 Rainwater analysis

In Constantza, especially during cold seasons, the rainwater was slightly acid, 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 aria 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^{2-}_4 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 may have 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, use of fossil fuels), sea salt component (especially Cl^-, SO_4^{2-}, 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 so both 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.

3.2. The variation of rainwater characteristics between 2000 and 2007

In Figs. 2 – 5 we present the charts of annual and monthly characteristics studied: *pH*, alkalinity, Cl^-, SO_4^{2-}, NH_4^+.

In what follows we focus on the annual data analysis.

The interaction *pH* – alkalinity was studied. The results of the variance analysis [8] of dependent variable (*pH* annual rainwater) function of the influence of the annual rainwater alkalinity are presented in Table 1, where the significances of data are 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.

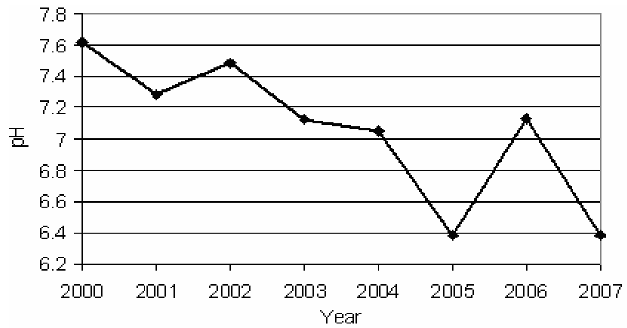

Fig.2. Annual *pH* variation

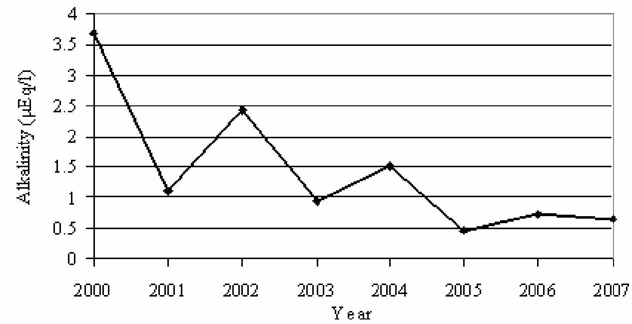

Fig.3. Annual alkalinity variation

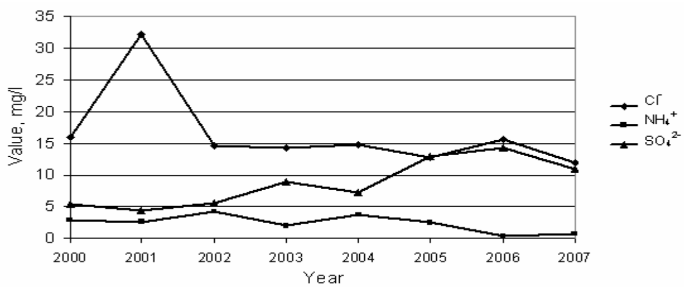

Fig.4. Annual variation of ions' concentration

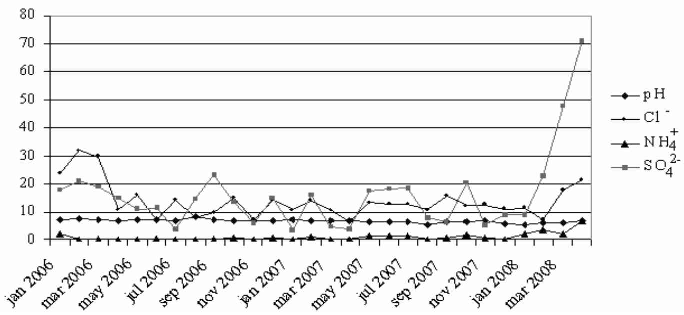

Fig.5. Monthly variation of data

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 1. Dependence of annual *pH* rainwater on annual rainwater alkalinity

	df	SS	MS	F	p-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 with $F_{1,6}$ = 5.99, 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, is $\overline{R}^2 = 62.79\%$, 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:

$$y_i = 6.594 + 0.3221 \cdot x_i + \varepsilon_i \qquad (1)$$

where y_i is the alkalinity, and ε_i – the residual.

In order to validate the model, the studies of normality (Table 2) and autocorrelation function (Fig.6) of residuals [9] were performed.

Table 2. Tests of normality

Kolmogorov – Smirnov			Shapiro – Wilk		
Statistic	df	Sig.	Statistic	df	Sig.
0.284	8	0.058	0.843	8	0.081

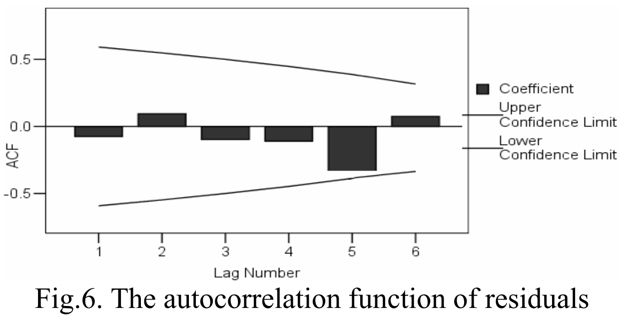

Fig.6. The autocorrelation function of residuals

Since the value Sig. for both Kolmogorov – Smirnov and Shapiro – Wilk is higher than 0.05, we accept the normality hypothesis, at the significance level 5%.

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. 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 3, where df, F, p have the same significance as in Table 1.

Table 3. Annual rainfall dependence on Cl^-, SO_4^{2-}, NH_4^+

	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
$NH_4^+ * SO_4^{2-}$	1	0.05389	39.65	0.100
$NH_4^+ * Cl^-$	1	0.09435	69.43	0.076
$SO_4^{2-} * Cl^-$	1	0.01190	8.76	0.207
Residual	1	0.00136		
Total	7			

The adjusted sums of squares provided in column 3 of Table 3 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:

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

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

A model of the type:

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

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

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

The result of variance analysis and the parameters' estimations ($\alpha = 0.417$, $\beta = 1.341$) are presented in Tables 4 and 5.

Table 4. Variance analysis - model (4)

	SS	df	MS	F	p-value
Model	384.748	2	192.374	77.425	.000
SO_4^{2-}	61.414	1	61.414	24.718	.003
NH_4^+	52.389	1	52.389	21.085	.004
Residual	14.908	6	2.485		
Total	399.656	8			

Table 5. Parameter estimates - model (4)

parameter	coeff.	std. error	t	Sig.	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

The determination and the modified determination coefficients were respectively $\overline{R}^2 = 95\%$, proving a high correlation between the variables in the model (4). The regression coefficients are significant since the value 0 in not inside the confidence interval and the probability values (Sig) for the t - test are less than 0.05. Also, the residuals were normally distributed and independent.

During our analysis it was remarked that the influence of NH_4^+ on *pH* is bigger 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, which is far from agricultural lands. On the other hand, the decrease of pH corresponded to the decrease of alkaline ions during the rain events. The acidity appeared to be lower in the presence of NH_4^+ than expected only from SO_4^{2-}. So, NH_4^+ and SO_4^{2-} were proved to be sources of acid rainwater.

3.3. The analysis of rainwater on Tăbăcărie Lake water

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 they had no variation at all. 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.7. The results of the variance analysis are given in Table 6.

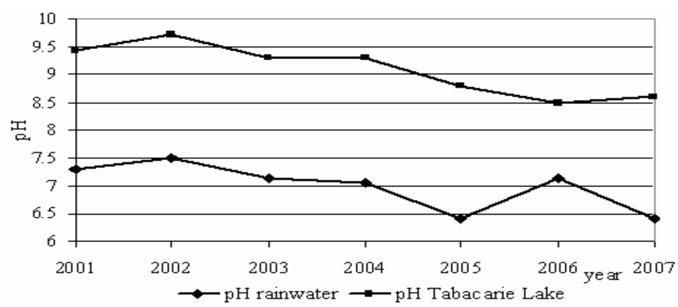

Fig.7. *pH* variation in time for rainwater and lake water

Table 6. Results of variance analysis of Tăbăcărie Lake *pH* function of rainwater *pH*

	df	SS	MS	F	p-value
rainwater pH	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 with 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.

The same analysis carried out for the monthly data between December 2006 and April 2008, didn't give us new information.

4 Conclusion

Although chloride concentrations correlate with proximity to the Black Sea, which is very rich in salt, and NH_4^+ and SO_4^{2-} are due to anthropogenic influence, they could all have been correlated with the pH values in a mathematical model and then related to the lake water values.

From the present study we have to conclude that we should be precautious when choosing to build near lake waters and affect parks' areas and we should pay attention to our water sources and preserve them because nature itself cannot improve them significantly.

Precipitation remains the most effective scavenging factor for the removal of atmospheric pollutants and also for the improvement of Tăbăcărie Lake water quality.

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