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Dedicated to Professor Luminița Silaghi-Dumitrescu on the occasion of her 65th anniversary

MATHEMATICAL MODELING OF THE VARIATION IN WATER QUALITY ALONG THE NETWORK OF WATER SUPPLY OF SATU MARE MUNICIPALITY, ROMANIA

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ABSTRACT. Drinking water quality in the water network supply of the Satu Mare municipality was investigated, aiming to quantify the variation of some physico-chemical parameters with the distance from the water treatment plant. Usually, water quality decreases in the drinking water distribution systems due to unwanted physical, chemical and biochemical reactions occurring in the distribution systems. The variation of the main physicochemical parameters of drinking water such as turbidity, pH, oxidability, chlorides and free residual chlorine concentration, conductivity, iron content, water hardness and nitrates concentrations was studied. The drinking water samples were collected weekly during the year 2013 from 16 fixed points of the distribution network of Satu Mare. The statistical analysis of the results was accomplished and presented. Univariate and bivariate regression models of the water quality variation with the distance from the water treatment plant were proposed. The distance from the water treatment plant to the each sampling point was established by measuring the length of pipelines crossed by water until that sampling point. The sampling points were chosen on the main routes of water distribution pipes in the main districts of the city of Satu Mare. These mathematical models attempted to capture the variation of the physico-chemical parameters of drinking water along the water network supply. An increasing trend of turbidity, water conductivity, water hardness and nitrates content of water was observed while the free chlorine content showed a decreasing trend.

Keywords: *drinking water; free chlorine; supply network; oxidability; turbidity.*

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INTRODUCTION

Water is an important component of the environment and it is absolutely necessary to life, including human life. Access to safe drinking water is fundamental to human life, health and wellness. Therefore, obtaining drinking water with an adequate quality is an important objective of urban and rural communities. The assessment of water quality is an essential aspect in the case of raw water sources and also of drinking water. A water quality index (WQI) is a common tool for the quantitative assessment of water quality [1,2]. This activity needs synergetic actions and efforts from many partners such as: water resources managers, water plants, water distribution systems, communities and water consumers. To gain a proper understanding and control of water quality, the partners might bring together their different scientific backgrounds towards a comprehensive understanding of all the parameters involved [3,4].

The treatment process of raw water for obtaining drinking water includes a chemical oxidation aiming to ensure the disinfection and oxidation of undesired compounds. Through chemical oxidation the taste and odor of water are improved and micro-pollutants are removed [5]. Chlorine is one of the most used chemical oxidants in the disinfection process due to its very effective disinfectant action [6,7,8]. The chlorine dose in the water is selected depending on the chemical and microbiological characteristics of the treated water (organic substances content and microbiological load) in order to ensure a residual chlorine content after the disinfection process at the drinking water entrance in the distribution network system [9,10]. The most studied halogenated disinfection by-products are trihalomethanes and haloacetic acids. These compounds could be found in low concentrations in the water treated by chlorine if it also contains organic substances [11,12].

Water quality usually degrades with time and space in the drinking water distribution systems. The water quality decreases due to unwanted physical, chemical and biochemical reactions that occur when the residence time in the distribution systems is increased [13,14].

Water quality may decrease in the distribution system of drinking water and consequently the water quality has to be assessed also in several points of the water supply network. The network of drinking water supply is a complex installation composed of pumps, reservoirs, pipes, that contains zones of consumption and portions where water sometimes stagnates [15].

Corrosion processes could occur in the water supply network generating corrosion scale on the inner walls of the pipes in the water distribution system. The physico-chemical properties of the corrosion scale depend on the metallic material of pipes, on the water quality transported through the pipes and also on the hydraulic conditions. The water quality parameters that influence the corrosion process are: pH, natural organic matter, temperature, oxygen content etc [16,17].

Satu Mare, located in the North-West of Romania is a relative small municipality, with about 100000 residents. The water source for drinking water is groundwater extracted from wells with a depth of 110 - 120 m. The treatment process consists of filtration to reduce the iron and manganese content and chlorination for water disinfection. Residual chlorine should prevent the reinfection during the leakage of drinking water through the distribution network. Nitrates occur in groundwater related to human activities such as fertilizers application. The drinking water samples were collected weekly during a year (2013), from 16 fixed points of the distribution network of Satu Mare. 1728 physico-chemical analyses were performed in order to evaluate the variation tendency along the main distribution direction in the distribution network. The distance from the water treament plant to the sampling points was measured along the pipelines travelled by water to each sampling points. The sampling points were selected along the main distribution routes that ensures the water supply in the main districts of the city of Satu Mare.

The experimental results were statistically analyzed with the purpose of finding the best mathematical models that most accurately describe the variation of the main physico-chemical parameters of drinking water in the distribution network [18,19]. Mathematical models which describe the variation of the main physico-chemical parameters of drinking water with the distance from water treatment in the distribution network system were proposed.

RESULTS AND DISCUSSION

Samples were taken during the year 2013 from 16 sampling points from the drinking water network of Satu Mare as shown in Fig. 1.

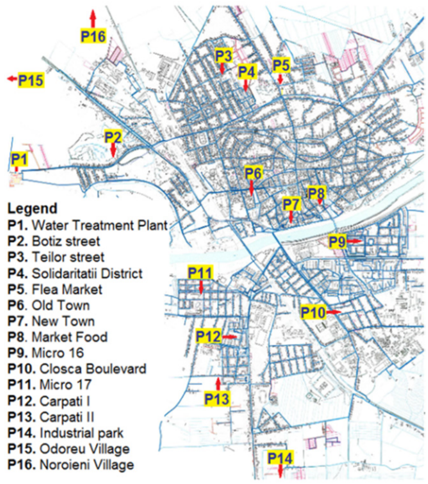

Figure 1. The locations of the sampling points in the network of drinking water supply of Satu Mare city

The average values of the physicochemical parameters were calculated and presented in Table1. The studied physicochemical parameters of the drinking water are under the maximum allowable limit according to Romanian legislation. The obtained average values presented in Table I were compared with the maximum allowable limit by law 458/2002 and 311/2004 (of Romanian legislation). Physico-chemical parameters of drinking water in the distribution system were analyzed. The extent of their changing depending on the distance from the water plant to the sampling point was investigated.

Table 1. Average values of the main physicochemical parameters from 16 sampling points in the water distribution network.

Point	Turbidity /NTU	pH	Cond./ µS/cm	Oxidab/ mgO_2/L	c_{Cl^-}/ mg/L	Total hardness /°dh [a]	$cFree_{Cl2}$/ mg/L	c_{NO3^-}/ mg/L	c_{Fe} / mg/L	*Distance/ m*
P1	0.110	7.24	323.9	0.087	4.52	8.84	0.43	0.313	0.0005	0.0000
P2	0.096	7.34	335.4	0.101	4.81	8.74	0.35	0.338	0.0029	5110.810
P3	0.081	7.34	336.8	0.132	5.05	8.60	0.28	0.343	0.0025	4010.821
P4	0.103	7.37	338.1	0.166	5.35	8.57	0.24	0.348	0.0031	4318.333
P5	0.098	7.30	339.9	0.261	5.67	8.53	0.16	0.354	0.0037	4789.037
P6	0,103	7.30	335.2	0.111	4.62	8.51	0.35	0.329	0.0038	4487.877
P7	0.116	7.31	336.8	0.123	4.84	8.48	0.29	0.336	0.0046	4583.907
P8	0.120	7.55	338.1	0.137	5.03	8.44	0.25	0.341	0.0063	6600.837
P9	0.115	7.37	338.7	0.148	5.25	8.43	0.20	0.346	0.0063	5697.981
P10	0.121	7.34	340.8	0.216	5.51	8.42	0.12	0.353	0.0063	5308.837
P11	0.120	7.30	335.2	0.123	4.96	8.64	0.33	0.335	0.0041	3341.417
P12	0.071	7.32	336.8	0.135	5.19	8.54	0.27	0.341	0.0049	3978.653
P13	0.166	7.38	339.0	0.171	5.34	8.49	0.17	0.346	0.0056	4039.944
P14	0.152	7.87	343,6	0.249	5.70	8.37	0.10	0.352	0.0157	8028.581
P15	0.188	7.41	342.2	0.177	5.40	8.55	0.11	0.348	0.0070	4878.448
P16	0.234	7.28	350.2	0.265	5.83	8.69	0.10	0.365	0.0124	11563.04
Limit[b]	**≤5**	**6.5-9.5**	**≤2500**	**≤5**	**≤250**	**Min 5**	**0.1÷0.5**	**≤50**	**0.2**	

[a] Total hardness is expressed in °dh -German degree; [b] the maximum allowable limit or range according to Romanian legislation (Law 458/2002 and 311/2004) .

Figure 2 shows the concentration of the residual free chlorine in three series of the sampling points arranged in the ascending order of the distance from the water plant. As the distance from the water plant increases, the concentration of residual free chlorine in the distribution system decreases. At lower values the regrowth of bacterial could occur. If the chlorine concentration in water distribution system falls below 0.1 mg L^{-1}, it is necessary to install chlorination systems to restore free residual chlorine in the legal range of 0.1-0.5 mg L^{-1}. At higher values, the reaction of chlorine with dissolved organic matter and bromine ions take place generating potentially harmful disinfection by-products like trihalomethanes [9]. The excess of chlorine confers the drinking water an unpleasant specific taste and odor. The decrease of chlorine concentration in the water distribution network is due both to the reaction with natural organic matter quantified by water oxidability that occurred in the bulk phase and to the reaction with iron released from pipe corrosion that took place to the boundary layer at the pipe wall [20]. Similar variations were reported by Mandel [21] after a continuous monitoring of the free chlorine concentration in the distribution network over the course of two weeks. Mandel concluded that chlorine concentration measurements are much less homogeneous, but rapid and important variations such as peaks are generally seen on all probes.

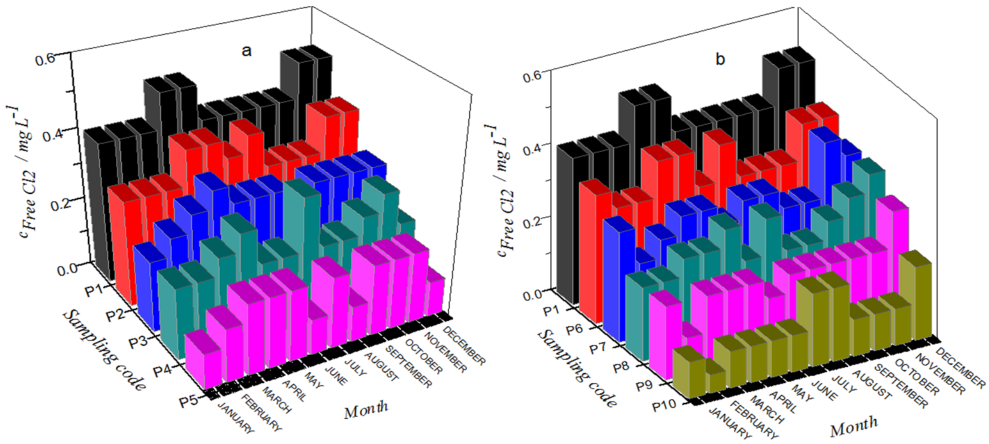

Figure 2. Evolution of free residual chlorine concentration between the sampling points P1-P2-P3-P4-P5 (a) and P1-P6-P7-P8-P9-P10 (b)

The electric conductivity of water is a measure of its content in ionic substances. In the case of two of the three series of sampling points (Fig. 3) the electric conductivity first showed a slight increase with the distance in the distribution network followed by a slight decrease. These fluctuations could be explained by the possible solubilization-deposition processes of some ionic substances contained in the corrosion scale of the pipes [16,20,21].

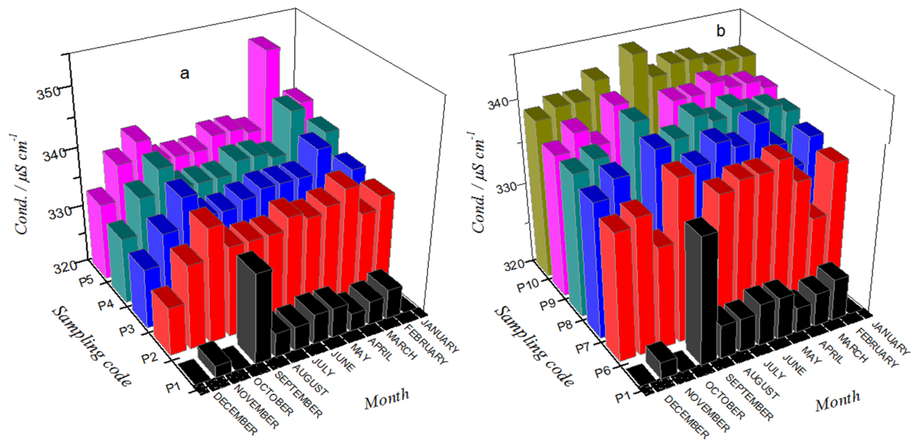

Figure 3. Evolution of the electric conductivity between the sampling points P1-P2-P3-P4-P5 (a), P1-P6-P7-P8-P9-P10 (b)

The water oxidability that is due to the remaining organic substances in the water after the chlorination step of the water treatment showed a tendency to increase along the water supply network (Fig. 4). This increasing trend was observed for the majority of the sampling points in the case of all the sequences: P1-P2-P3-P4-P5 and P1-P11-P12-P13-P14. Water oxidability varied between 0.05 and 0.3 mg $(O_2)L^{-1}$. The variation of water quality parameters such as pH, alkalinity, dissolved oxygen, natural organic matter, microorganisms, temperature, could disturb the solid-liquid equilibrium between corrosion scale and water phase, and consequently iron is released in the drinking water transported through the distribution systems [16.21].

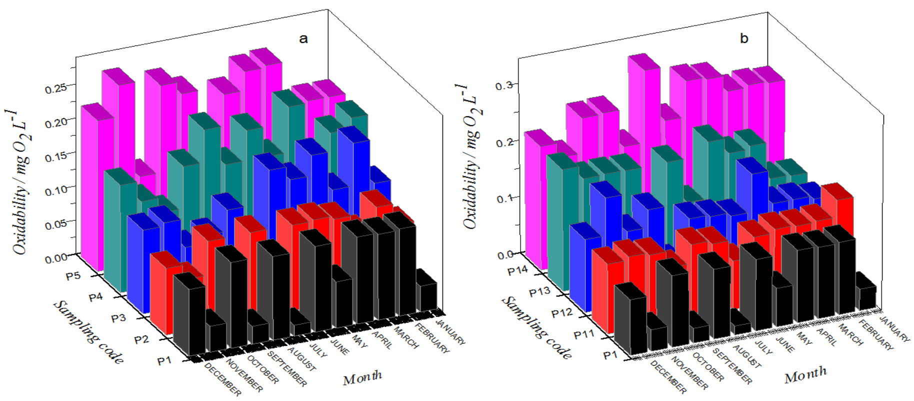

Figure 4. Evolution of oxidability between the sampling points P1-P2-P3-P4-P5 (a), P1-P11-P12-P13-P14 (b)

Mathematical models

A mathematical model is a mathematical description of a physical, chemical or biological state or process. Using a model we can design better experiments and interpret the results. When we fit a model to the data, we obtain the best-fit values that we can interpret in the context of the model that could guide further experiments. The mathematical models for the variation of the conductivity and free chlorine depending on the distance from the sampling points to the water treatment plant are given by nonlinear functions generated by the program, and the coefficients were determined.

The mathematical model for the variation of conductivity depending on the distance of sampling points P1-P11-P12-P13-P14 to the water plant (r^2=0.850, F = 106.15) is given by the equation (1):

$$f(x) = a + bx^{2.5} + cx^{3} + dx^{0.5} \quad (1)$$

where x is the distance and the coefficients are:

$$a = 323.917, \quad b = 2.196 \cdot e^{-8}, \quad c = 2.241, \quad d = 0.0955$$

The mathematical model for the variation of free chlorine concentration depending on the distance of sampling points to the water plant (r^2=0.8726, F=43.683) is given by the equation (2). The mathematical model describing the evolution of free chlorine concentration with the distance was a nonlinear function.

$$f(x) = a + bx^{0.5} + cx + dx^{1.5} + ex^{2} + fx^{2.5} \quad (2)$$

$$a = 0.433, \quad b = 9.793, \quad c = -0402 \quad d = 10.00347, \quad e = 2.478e^{-5}, \quad f = -6.429e^{-8}.$$

For the study of variation of distance to the water plant depending on free chlorine and the chloride concentrations, a two independent variables model was elaborated using *TableCurve3D* program. The graph resulted is presented in Fig. 5 and it is a nonlinear equation.

The mathematical model for variation of chloride concentration depending on the distance to the water plant and free chlorine concentration (r^2=0.6894, F=48.105) is given by the function (3):

$$z = f(x,y) = a + b\ln x + c(\ln x)^2 + e/y + f/y^2 \quad (3)$$

and the values of coefficients are:

$$a = 4.9889, \quad b = -1.112, \quad c = 0.0522, \quad e = 4.884, \quad f = -8.854$$

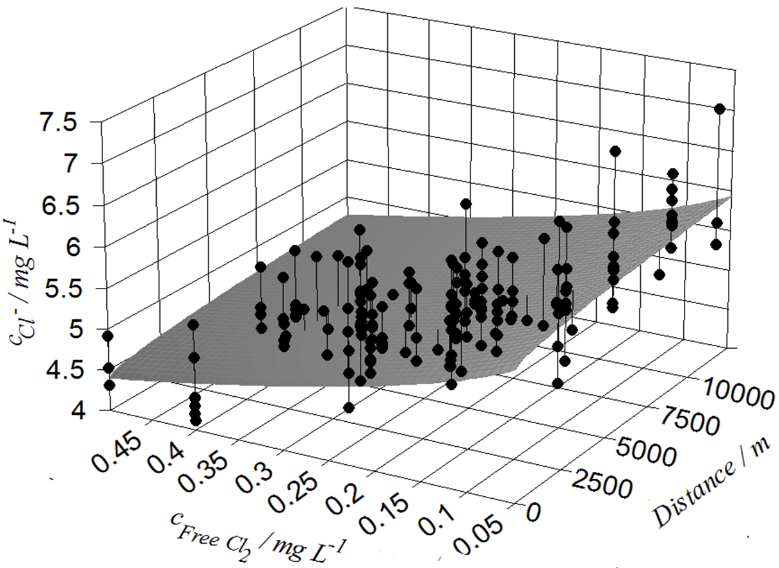

Figure 5. Variation of of chloride concentration (z) depending on the distance (x) to the water plant (P1) and free chlorine concentration (y)

The concordance between the results generated by the mathematical model and the experimental ones shows that we can use the model to approximate the value of conductivity when we know the value of water hardness and the distance to the water plant, by using the function f(x,y).

The mathematical model for variation of distance to the water plant depending on conductivity and the total hardness (r^2=0.7138, F=76.9022) is given by the function (4):

$$z = f(x,y) = a + bx + c/y + d/y^2 \tag{4}$$

The values of the coefficients are:

$$a = 201.744, \quad b = 0.00759, \quad c = 2032.142, \quad d = -8423.956.$$

The corresponding graph is presented in Fig. 6. An increase tendency could be explained by the substances dissolved form the pipes walls depositions that increased with the distance traveled by water. The increase of the conductivity is more evident for lower water hardness due to a higher power of solvation of the soft water.

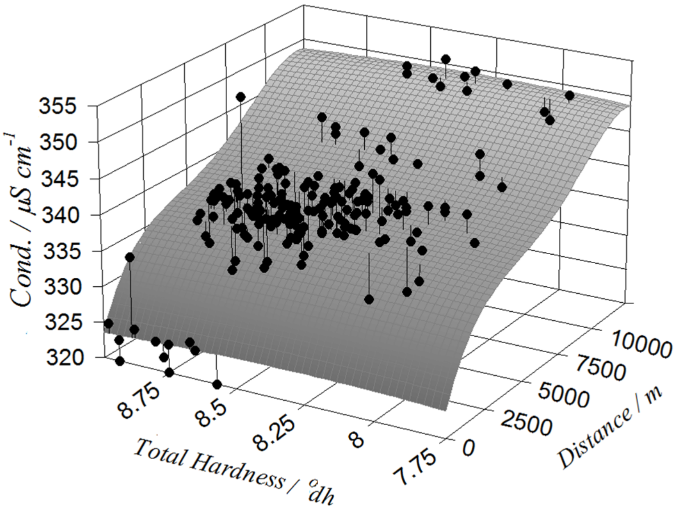

Figure 6. Variation of conductivity (z) depending on the distance (x) of the sampling points to the water plant and water total hardness (y) (°dh – german degree of hardness)

Usually, variation of the water demand occurs in the water distribution network. The variation of temperature and pressure modify the chemical equilibrium in which carbon dioxide is involved associated with carbonates depositions or solvation of previous carbonate deposits. At the end of the water distribution network, an increase of conductivity with 10-15 µS/cm was observed.

CONCLUSIONS

The paper is a comprehensive study that investigates the way in which the main pyshico-chemical parameters of water are influenced when it travels through the water supply network in Satu Mare municipality. An increase of turbidity was observed with the increase of the distance from the water treatment plant to the sampling points. Conductivity showed a slight increse along the water supply network.

The residual chlorine concentration decreased with the distance from the drinking water plant. Also the nitrates concentration registred a decrease. Other indicators of water quality such as pH, oxidability and water hardness showed slight fluctuations compared with the initial value registred at the entrance in the water distribution network.

The physico-chemical parameters showed a very good quality of water at the entrance in the distribution system as well as at its end.

Also during the water passing through the pipes, fluctuations of the parameter occurred due to the presence and action of free chlorine that oxidized a part of the easily oxidizable substances present in water

The mathematical models developed in the present work show the variation of some physicochemical parameters, and can be used to a good approximation of these parameters, for drinking water in the network of Satu Mare city.

EXPERIMENTAL SECTION

Water sampling and analysis

The water samples were collected weekly in 16 points of the distribution network of drinking water in Satu Mare municipality. The analysis of the physicochemical parameters was carried out within a maximum of 48 hours after the sampling. Turbidity was measured immediately after sampling using a portable turbidimeter. The physico-chemical parameters analysed were: turbidity, pH, electric conductivity, oxidability, chloride, free chlorine, total hardness, iron and nitrate anion.

The studied microbiological parameters were: Escherichia coli (according to STAS 3001-91), faecal streptococci (STAS 3001-91), coliforms (ISO 4831/2009 European standard) and total number of germs (TNG) according to SR EN ISO 6222/2004. These microorganisms were absent in the samples of drinking water.

pH was determined using a Hanna Instruments pH meter HI 253 equipped with a combined pH electrode according to EN ISO10523 -2012 standard. The electric conductivity was measured using a WTW INOLAB 740 conductometer according to SR EN 27888/1997.

The measurements of water samples turbidity were performed with a WTW portable turbidimeter, model 355 IR according to the Romanian standard STAS 6323/88. Turbidity was expressed in NTU units. Oxidability was determined by back titration with potassium permanganate in presence of sulfuric acid after the addition of a known amount of oxalic acid (SR EN ISO 8467:2001). Chloride concentration in drinking water was measured by precipitation titration with silver nitrate according to ISO 9297-2001 standard while free chlorine was analysed by titration with methyl orange solution in acidic medium (according to the STAS 6364/78 standard). Iron was analysed by spectrometry according to SR ISO 6332/2011 standard.

The analysis of nitrate was made by the spectrophotometric method according to the SR ISO 7890-1-1998 standard using a UV-VIS T-60 PG Instruments spectrophotometer.

Water hardness was measured by EDTA titrimetric method according to SR ISO 6059/2008 standard.

Models development

Aiming to study the variation of the different physico-chemical parameters of water in the sampling points depending on distance from the sampling points to the water treatment plant, we used TableCurve Windows program, which applies the nonlinear regression method in order to obtain best-fit values of the parameters. Regression analysis was used to develop empirical models that relate some physico-chemical parameters of water such as oxidability, conductivity, free chlorine concentration to the distance from the water treatment plant. Also some correlations among the parameters were developed.

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