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SEASONAL VARIATION OF PHYSICO-CHEMICAL PARAMETERS IN THE DRINKING WATER SUPPLY NETWORK OF SATU MARE CITY, NW ROMANIA

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Abstract

We assessed the variability of the main physico-chemical parameters of drinking water: oxidability, turbidity, conductivity, water hardness, free chlorine concentration, chlorides and nitrates across the four seasons (Spring, Summer, Autumn of 2013 and Winter of 2014). We collected data from several points in the supply network of Satu Mare city, NW of Romania, where the source of drinking water is groundwater.
The results revealed significant higher average values in spring for some of the considered parameters such as oxidability, turbidity, water hardness, free chlorine, chlorides. The lowest average values of these parameters were registered in winter for oxidability, turbidity, chlorides and water hardness while the lowest values of free chlorine were in summer.
At the entrance of the distribution network the average values of the considered parameters were: oxidability 0.257 mg O_2/L in spring while in winter was 0.157 mg O_2/L, turbidity in nephelometric turbidity units (NTU) was 0.42 in spring and 0.08 in winter, water hardness in German degree was 9.92 in spring and 8.165 in winter, the content of chlorides was 5.98 mg/L in spring and 4.96 mg/L in winter. Free chlorine showed the highest value of 0.4 mg/L in spring and the lowest in summer (0.2 mg/L).
Our study contributes to adding new data about the seasonal variability of the parameters of drinking water from groundwater in a temperate region. In addition, we built mathematical models to capture this seasonal variability through nonlinear functions. We hope these models will be useful in predicting seasonal variability of the parameters of drinking water.

Key words: groundwater, mathematical modeling, residual chlorine, seasonal variability, turbidity

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1. Introduction

Water is an essential environmental factor. Drinking water with adequate qualitative parameters and chemical composition is essential to human life, health and well-being (Gentry-Shields and Bartram, 2014). Surface water and also ground water are commonly used as drinking water sources (Clark, 2011). Groundwater is considered the most reliable source of freshwater, with nearly 80% of global inhabitants relying on it as a source of drinking water

(Hanrahan, 2012). Usually, ground water quality is excellent, superior to that of surface water and it requires little or no treatment (WHO, 1996).

The drinking water quality is affected by the quality of raw water (groundwater or surface water), which in turn depends on natural processes as well as anthropogenic activities (Dippong et al., 2018; Singh et al., 2014). The variation of the chemical composition of the groundwater depends on the physical and chemical processes that occur during the migration from the aquifer to water table: the

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interaction with the soil or the rock of the aquifer, the solvation of different ionic substances or gases, the composition of the infiltrating water, the load of precipitation, biochemical reactions etc. (Hanrahan, 2012; Nemtinov et al., 2014). Groundwater quality can be altered by pollution sources of industrial or agricultural nature (Dippong et al., 2019; Preda et al, 2018; Romocea et al., 2018).

Water seasonality was investigated in some studies, but they were mainly focused on specific undesirable substances such as arsenic (Ayotte et al., 2015), geosmin (Dzialowski et al., 2009) or chlorine disinfection by-products (Baytak et al., 2008; Mercier Shanks et al., 2013; Serano et al., 2015). Other studies treated the water seasonality in connection with microbiological parameters (Henne et al., 2013; Burnett et al., 2014). Some studies explored the groundwater seasonality in the sub-tropical monsoonal climate with dry and wet seasons (Deng et al., 2014; Yu et al., 2016; Thomas et al., 2011). A recent study investigated aspects of the temporal/spatial variations in water quality of a recent created water reservoir in Europe after the dam construction (Amanatidou et al., 2018). We studied the variation of the physico-chemical parameters as a function of seasonality and type of water treatment in a city in NW of Romania, with temperate climate.

Groundwater composition varies during the year depending on meteorological factors (temperature, precipitations). The anthropic factors also influence the composition of ground water: the fertilization practices with nitrogen compounds that are sources of nitrates in groundwater, the mixing between the phreatic water and the runoff. In addition, chloride as sodium or calcium chloride is used during the winter in the urban transport to melt the ice formed on the streets and roads impacting ground water by growing the chlorine content (Perera et al., 2013). Of further concern was that water quality could be diminished in the distribution network system. Issues such corrosion, reactions with the pipes material, biofilm formation, occlusion of water could arise in the water distribution network diminishing the quality of drinking water (Peng et al., 2010; Tong et al., 2015; Zhu et al., 2014; Yang et al., 2012). Thus, we emphasize here the importance of a thorough characterization of the physico-chemical parameters at several points across the water distribution system.

In Satu Mare city, located in NW of Romania, groundwater is used as drinking water source. The treatment scheme of groundwater comprises the following operations: the collection of raw water from deep wells (110-120 m), the oxidation of iron and manganese with the atmospheric air, the quartz sand filtration, chlorine disinfection and distribution in the water supply network. The water supply network ensures potable water for the residents of Satu Mare (about 100000 residents) and for the surrounding villages.

Our study investigated the variation of the main physicochemical characteristics of water such as oxidability (named also chemical oxygen demand),

turbidity, water hardness, conductivity, chlorine, chloride, nitrates and pH across a year (March 2013-February 2014). We characterized the seasonal variations of the finished drinking water at the entrance in the water supply network and assessed the extent of the variation along the water distribution network in city of Satu Mare. The study also followed the variation of the water characteristics along the water supply that allows the determination of variation tendencies of water characteristics based on more sampling points.

2. Experimental

The study took place in the city of Satu Mare, the residence of Satu Mare County located in the North-West of Romania. The city is located on the Somes River meadow that is an alluvial plain on the altitude of 126 m. The prevalent soils are podsolic that are formed on a sedimentary deposits (sand, loess and gravel) by the decaying of vegetation (Bogdan and Calinescu, 1976). The climate is temperate (continental) characterized by hot dry summers and cold winters. The precipitations are registered mainly in autumn and spring (Bogdan and Calinescu, 1976).

The main water physicochemical characteristics of the drinking water in the city of Satu Mare were monitored by weekly collection of drinking water samples at 10 points of the water distribution network. The first sampling point was P1 at the entrance in the water distribution network and the others 9 points were covering the entire distribution system.

The study was carried out across the four seasons specific to a temperate climate during March 2013-February 2014 as follows: spring (March, April and May), summer (June, July and August), fall (September, October, November) and winter (December, January, February). The average values were calculated for every season and for every sampling point. Physicochemical analysis was performed within 48 hours of sampling.

pH was determined at 25°C using the electrometric method according to the EN ISO10523 - 2012 standard method using a digital pH-meter (Hanna HI 253 model) equipped with a combination pH electrode. Water turbidity was analysed with a WTW digital turbidimeter according to the SR ISO 10523: 2009 standard. Water turbidity is expressed in NTU (Nephelometric Turbidity Units). The electric conductivities of water samples were determined using a WTW digital electrical conductivity meter equipped with a conductivity cell according to the STAS 7722/84 standard. The water oxidability, known also as chemical oxygen demand, was measured by the determination of permanganate index according to the SR EN ISO 8467:2001 standard method. Total hardness of water consisted in the joint determination of Ca^{2+} and Mg^{2+} cations by their complexometric titration with the sodium salt of ethylenediamine tetraacetic acid (Na_2EDTA) in the presence of the metallochrome indicator Eriochrome

Black T and of a pH buffer (to 10.1) according to the standardized method (STAS 7313 – 82). Chlorides were determined by precipitation titration method according to the ISO 9297-2001 standard. As titrating agent $AgNO_3$ was used. Free residual chlorine was analyzed by titrating the water samples in acid medium with methyl orange solution according to a standardized method (STAS 6364/78). Nitrates were determined spectrophotometrically according to the SR ISO 7890-1-1998 standard.

3. Results and discussions

The article aims to analyze the evolution of the eight physico-chemical parameters of drinking water (oxidability, turbidity, water hardness, conductivity, chlorine, chloride, nitrates and pH) across a year during the four seasons of the year March 2013-February 2014 and their effects on the nature of drinking water. The reproducibility of the results was investigated using multiple sampling points in the water supply system of the city of Satu Mare (P1-P10).

We compared our results to the maximum admissible values or range for the investigated physico-chemical parameters, established according to Romanian legislation for drinking water (Law 458/2002 subsequent amendments of Law 311/2004): oxidability: 5 mg O_2/l; turbidity: 5 NTU; total hardness 5-20 German degree; chloride: 250 mg/L, free chlorine 0.1-0.5 mg/L; nitrate: 50 mg/L and pH in the range of 6.5-9.5. Romanian legislation concerning drinking water is harmonized with European Drinking Water Directive.

The seasonal trends of the water characteristics were discussed based on the sampling point P1 at the entrance in the Satu Mare distribution network that reflect better the raw water characteristics (ground water) and also in the other 9 sampling points (using an average value for the 10 sampling points). In the other 9 points the water characteristics were influenced also by the deposition on the pipe material, thus the water quality in the distribution system could be diminished (Al-Zahrani and Moied, 2014; Tong et al., 2015). The seasonal trends of water oxidability observed in P1, also occur in the other 9 sampling points in the distribution network as is shown in Fig. 1a. The oxidability is a parameter used to express the natural organic substances present in water. These substances could be organic matter derived from the microorganisms present in natural water or formed by microbial communities.

During spring the nutrient intake in ground water is higher due to the melting of the snow and to environmental factors such as temperature and precipitation that affect the source of drinking water (Henne et al., 2013). The seasonal variations in water oxidability for the 10 sampling points are illustrated in Fig. 1a. The average values of water oxidability were different for the four seasons showing the highest value in spring (0.257 mg O_2/L at the entrance in the distribution system) and the lowest value in winter

(0.158 mg O_2/L). In summer the water oxidability showed a slight decrease (by 26 % compared with the value registered in spring), probably due to the lack of precipitations followed by an increase in autumn (by 11 % compared with the summer oxidability). The highest values recorded in spring for the water oxidability could be explained considering the increase of temperature compared to the winter temperature. The increase of the temperature determines the decrease in oxygen solubility that is associated with a higher value of oxidability. The lowest values of oxidability were registered in winter: when the temperatures were low, the microbial activity was reduced as well as the processes of fermentation and decay. Fig. 1b shows the evolution of turbidity depending on the season in the 10 sampling points of the water distribution system.

Water turbidity is mainly due to fine particles in dispersion state present in water as clays, phytoplankton and microorganisms (Cohl et al., 2014; Li and Migliaccio, 2011). The highest turbidity were registered in spring (0.404 NTU in the sampling point P1 with an average value of 0.331 NTU for the 10 sampling points), while the lowest ones were recorded in the winter (0.088 NTU the average value). In summer and autumn the average values for the turbidity were similar: 0.11 and 0.16 NTU. In the distribution network the variability of the turbidity was higher in spring, within the range of 0.15-0.5 NTU, while in winter the range of turbidity was narrow (0.02-0.16 NTU). The turbidity level can be increased by the presence of organic matter or suspended matter. In spring the snow is melting and the precipitations are more frequent and consequently a recharge of the groundwater aquifer take place accompanied by water destratification. During the destratification, the vertical circulation of groundwater favours a uniform enrichment of water with nutrient and organic matter derived from the flow of the precipitation through soil and aquifer (Hanrahan, 2012).

An increase in turbidity was noted at some sampling points of the distribution system. This was due to the entrainment of some solids from the pipe depositions or because of supersaturating of oxygen that leaves the solution to balance the system in the form of small bubbles (Roychowdhury et al., 2003). Fig.1c presents the seasonal trend of total hardness across the four seasons for sampling points P1÷P10. Calcium and magnesium are essential minerals, highly beneficial to human health (WHO, 2009).

In Romania the water hardness is expressed in German degrees: water containing an amount equivalent to 10 mg/L calcium oxide or 0.178 mmol Ca^{2+}/L have a hardness of 1 German degree (1°dH). Water containing calcium ions below 1.5 mmol/L of Ca^{2+}(corresponding to 8 German degree) is soft; in the range of 1.5-2.5 mmol/L Ca^{2+} (8-14 German degree) medium hard; and over 2.5 mmol/L of Ca^{2+} (> 14 German degree) water is hard (Abeliotis et al., 2015; McGowan, 2000).
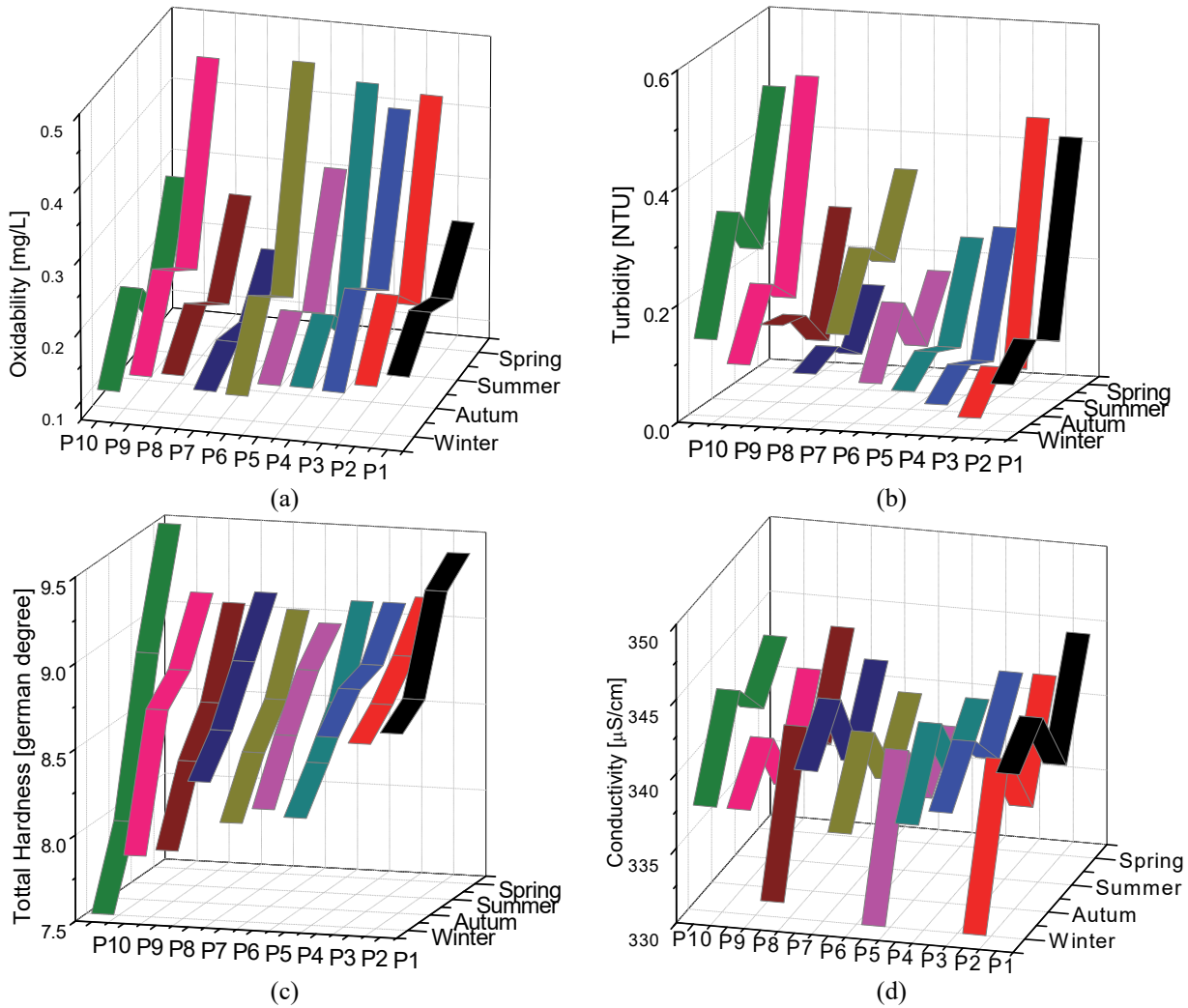
Fig. 1. The evolution of some water parameters: oxidability (a), turbidity(b), total hardness (c), conductivity (d) depending on the season in the sampling points P1-P10

Due to the calcium and magnesium content, water with a moderate hardness contributes to a good nutrition, to the development of the bone system and protection against cardio-vascular diseases (Rylander, 2008; Sengupta, 2013). Possible disadvantages of higher water hardness include: the delay of the vegetables boiling in cooking treatment, the formation of the depositions on the boiler areas, the obstruction of the pipe sections leading to danger of explosion for the boilers. Hardness in laundry water is problematic because calcium and magnesium interfere with cleaning action of soaps and detergents. When water with higher hardness is used, laundry results are not as good as when there is no hardness present (Abeliotis et al., 2015). In the water distribution supply network, hardness has bad effects developing corrosion and encrustation in pipes (Isikwue and Chikezie, 2014).

The total hardness varied in the range of 7.45 - 9.92 German degree (1.32 - 1.77 mmol Ca^{2+}/L) considering all the sampling points. The water could be classified as medium hard. In spring we recorded the highest values of water hardness: 9.42 German degree in P1 and the average value of 9.92 German

degree for the 10 sampling points in the distribution network. Across the four seasons, water hardness showed a decreasing trend with the lowest values in winter (8.64 German degree in P1 and the average value of 8.165 German degree for the 10 sampling points). In spring the precipitations are more abundant dissolving the limestone rocks they cross. The process is favored by the precipitation and by the presence of CO_2 dissolved in water (due to decomposition of the organic matter and the respiration process of the living organisms). Chemical weathering can be the prevailing source of solutes in groundwater as well as in stream water and soil water (Bestland and Steiner, 2014).

In the distribution network, water hardness was generally lower than at the entrance (sampling point P1) except P10 in spring that suggested that part of calcium and magnesium ions were deposed during the flow in the network distribution system (Peng et al, 2010; Yang et al., 2012; Zhu et al., 2014).

Water conductivity is a measure of its mineralization degree. It depends on the levels of the water table in the wells. Precipitations could influence

the conductivity of groundwater in a complex manner: a decrease could take place due to the dilution effect of the rainfall or an increase related to the dissolved mineral matter during the flow of rainwater through the aquifer. The maximum admissible level of the conductivity of water for drinking purpose is 2500 µS/cm. In the investigated water distribution network the level for the water conductivities varied in the range of 330-345 µS/cm as shown in Fig. 1d. The highest average value of water conductivity was registered in spring (341.7 µS/cm) while the lowest average seasonal value was in winter (335.7 µS/cm). Fig. 2a shows the variation of the content of chlorides in water in the four seasons along the water distribution supply.

The content of chlorides in water ranged between 4.4 and 6.1 mg/L with the highest average value in spring (5.8 mg/L). The lowest average value of 4.7 mg/L was found in winter. In spring, the content of chlorides was higher than in the other seasons due to the recharge of the aquifer both with the molten snow and precipitations usually more abundant in spring than in summer and autumn. In the groundwater a destratification can occur when at the water table are brought water layers richer in minerals including chlorides from the bottom of the column of the water in the well. Interactions among the precipitation that traveled through the soil and/or the rocks during the recharge of the aquifer occured: some inorganic or organic substances were dissolved including chloride ions. In the warmer seasons (spring and summer) the solubility is higher and as consequence more chlorides were found in groundwater and also in the treated groundwater, in P1. In winter, the predominant precipitations are the snows, and the recharge of the aquifer is reduced because the soil is frozen and the temperatures in the aquifer are lower than in the others seasons.

The content of free chlorine in drinking water network has to be maintained within regulatory limits of 0.1 and 0.5 mg/L according to the Romanian legislation and international prescriptions. A small content of chlorine in water prevents the water reinfection during the flow thorough the distribution system (Schutte, 2006). An excess of chlorine in drinking water is undesirable giving an unfavorable taste to water. In excess, chlorine has a corrosive action upon iron, especially at low temporary hardness of the water. Also chlorine in excess associated with some organic matter can give harmful disinfection by products as trihalomethanes species (Baytak et al., 2008; Mercier Shanks et al., 2013; Serrano et al., 2015). Fig. 2b shows the evolution trend of the content of free chlorine in water across the seasons. The lowest content of free chlorine in water was found in summer (with an average value of 0.2 mg/L) while the highest average values were observed in spring and in winter (0.31 mg/L).
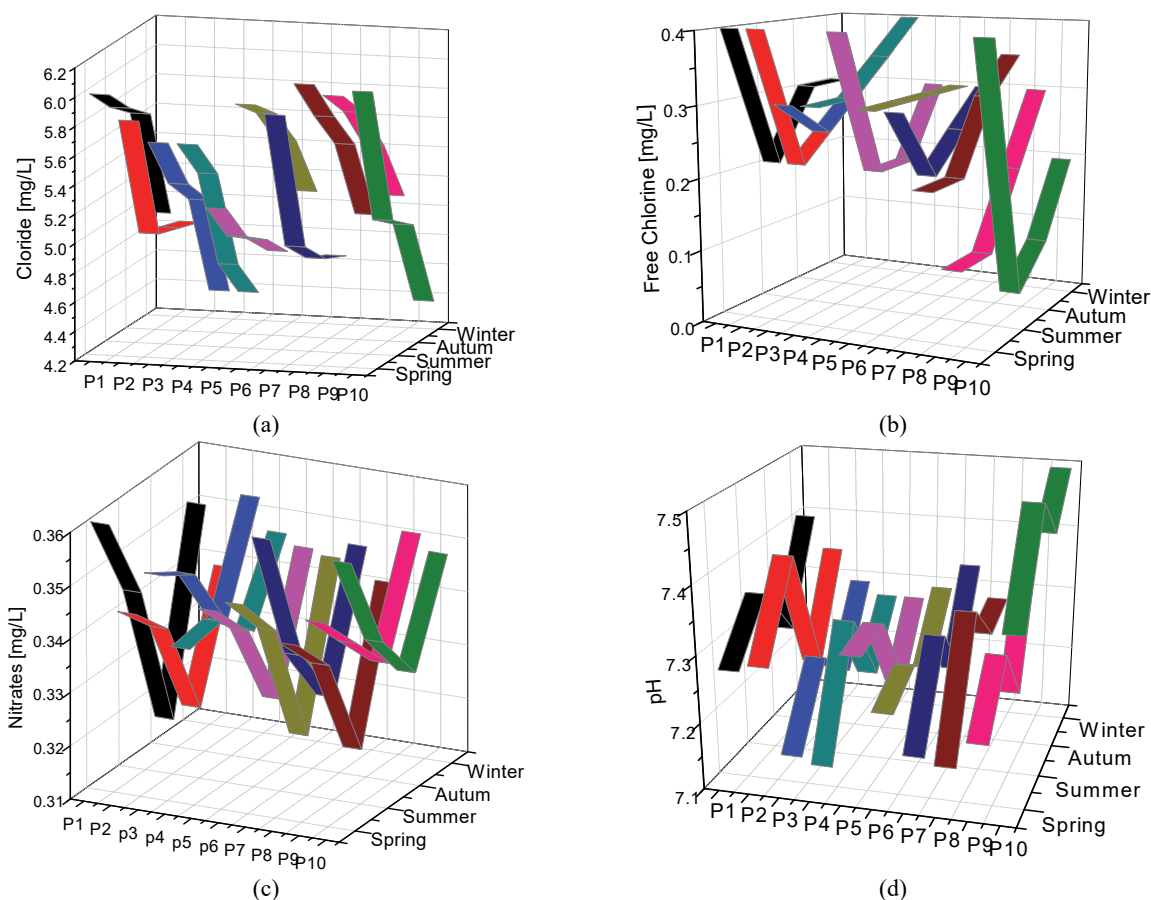

Fig. 2. The evolution of water parameters: chlorides (a), free chlorine (b), nitrates (c) and pH (d) depending on the season in the sampling points P1-P10

The lower content of free chlorine in water during the summer was due to the higher temperatures that are responsible for an increased rate of chlorine decay and also for the chlorine reactions with the organic substances or inorganic reducing agents encountered in the network (Monteiro et al., 2014). In spring, the average free residual chlorine in water was 1.55 times higher than the average value calculated for the summer samples.

Nitrates in water are usually derived from the decomposition of natural vegetation, from human and animal wastes, industrial pollutants, runoff from heavily fertilized crop areas and meadows, irrational usage of chemical fertilizers (Enea et.al., 2017) etc. Elevated nitrate concentrations have negative effects in deep waters. Their concentration in groundwater depends on the precipitation regime. In the absence of reducing conditions, nitrates in groundwater tends to acquire elevated concentrations during hot and dry periods because the dilution effect is reduced (Thomas et al., 2011; WHO, 2011; Wick et al., 2012).

Fig. 2c presents the variation of nitrates concentrations in drinking water across the seasons for the sampling points P1-P10. The higher concentrations were registered in spring and in winter (the average value of P1-P10 was around 0.35 mg/L in spring and winter).pH of drinking water is an important indicator of water quality. The standard limits for pH water of drinking water according to Romanian legislation are: 6.5 and 9.5. pH of drinking water in the distribution network of Satu Mare ranged between 7.13 and 7.5 and showed a low variability across the seasons. The lowest average pH was registered in spring (7.22) while in winter was the highest average value of pH (7.34). This range of pH is specific to a weak alkaline water (Hanrahan, 2012; WHO, 1996).

Mathematical modelling

We analyzed the seasonal variation patterns in order to find an adequate mathematical model describing them. For this purpose, Table Curve Windows program was used. Nonlinear regression method was applied in order to obtain best-fit values of the parameters. Based on the mathematical models that fit the experimental data the study attempted to predict the future trends of the considered physico-chemical characteristics of water.

The relations between some of the studied characteristics of water in the distribution system were investigated. Thus, we looked for a function that describes the relation between the oxidability and turbidity. Water oxidability, or chemical oxygen demand, indicates the organic substances dissolved in water. Between the suspensions in water (quantified by water turbidity) and the solved substances, a certain relation is expected to be observed due to the water's high capacity of solvation. Turbidity is determined by organic or inorganic substances such as humic acids or their compounds, to microorganisms, calcium

carbonate, iron containing colloidal matter. In some situations the turbidity increases in the water distribution system (Tong et al., 2015).

The mathematical models that described the oxidability variation as a function of turbidity for the four seasons consist of a set of non-linear functions obtained by regression made with Table Curve Windows program. Fig. 3 depicts the functions that described the relation between the water parameters oxidability and turbidity. The patterns of the functions were different for the four seasons.

In the case of spring season, the most relevant mathematical model was represented by the nonlinear function expressed by the Eq. (1) with the model accuracy indicator $r^2=0.9758$ (the maximum possible value is 1, in the case of functional dependence):

$$f(x)=a+bx^2+cx^4+dx^6+ex^8+fx^{10} \tag{1}$$

The values of the coefficients a-f are presented in Fig. 3a. The model accuracy indicator r^2 shows the degree in which the statistical mathematical model is significant and it is defined by the Eq. (2):

$$r^2 = 1 - \frac{SSE}{SSM} \tag{2}$$

where *SSE* is the Sum of Squares due to Error, $SSE=\sum_{i=1}^{n}(\hat{z}_i - z_i)^2$, SSM is the Sum of Squares about Mean, $SSM=\sum_{i=1}^{n}(z_i - \bar{z})^2$, *n* is the number of data points, z_i are data values, $\hat{z}_i$ are estimated values and $\bar{Z}$ is the mean of *z* data values. The mathematical model for the variation of the water oxidability with the turbidity in autumn was given by the function shown in Eq. (3) with the model accuracy indicator, $r^2=0.6053$. The pattern of the function is shown in Fig. 3c where the values of the coefficients a – d are also given.

$$f(x)=a+b/x+c/x^2+d/x^3 \tag{3}$$

In summer and winter some poorer correlations for the mathematical models were obtained. The functions that described the correlations between water oxidability and turbidity in summer and winter are given by the Eqs. (4) and (5) with the model accuracy indicator $r^2=0.5653$ and (4) cu $r^2=0.5408$

$$f(x)=a+bx+cx^2+dx^3+ex^4+fx^5 \tag{4}$$

$$f(x)=a+bx+cx^2+dx^{2.5}+ex^3 \tag{5}$$

The mathematical models describing the relation between conductivity and total hardness in the four seasons are presented in the Eqs. (6-9). The shapes of the selected nonlinear functions are shown in Fig. 4. The highest values of the model accuracy indicator were obtained for spring and summer.
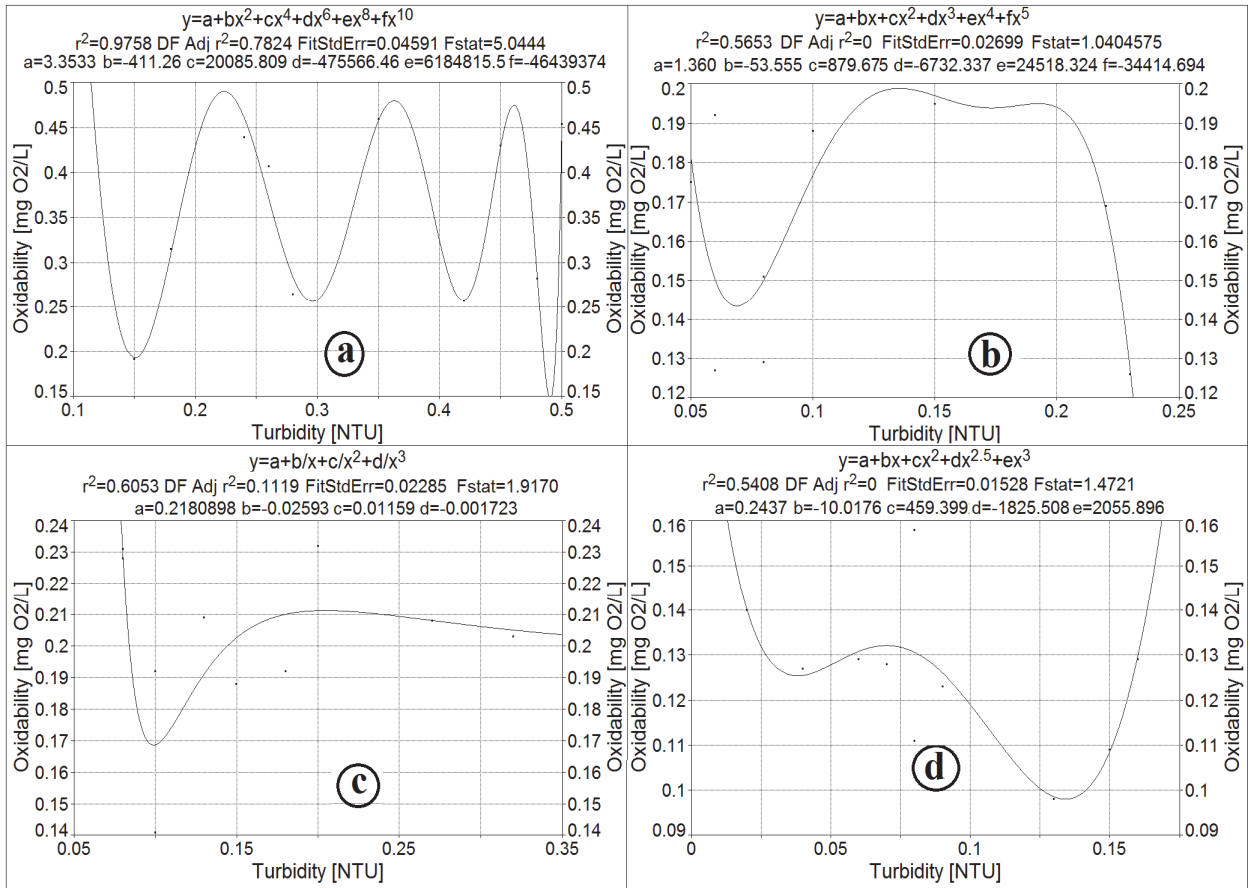
$y=a+bx^2+cx^4+dx^6+ex^8+fx^{10}$

$r^2=0.9758$ DF Adj $r^2=0.7824$ FitStdErr=0.04591 Fstat=5.0444

a=3.3533 b=-411.26 c=20085.809 d=-475566.46 e=6184815.5 f=-46439374

$y=a+bx+cx^2+dx^3+ex^4+fx^5$

$r^2=0.5653$ DF Adj $r^2=0$ FitStdErr=0.02699 Fstat=1.0404575

a=1.360 b=-53.555 c=879.675 d=-6732.337 e=24518.324 f=-34414.694

$y=a+b/x+c/x^2+d/x^3$

$r^2=0.6053$ DF Adj $r^2=0.1119$ FitStdErr=0.02285 Fstat=1.9170

a=0.2180898 b=-0.02593 c=0.01159 d=-0.001723

$y=a+bx+cx^2+dx^{2.5}+ex^3$

$r^2=0.5408$ DF Adj $r^2=0$ FitStdErr=0.01528 Fstat=1.4721

a=0.2437 b=-10.0176 c=459.399 d=-1825.508 e=2055.896

Fig. 3. The correlation of oxidability and turbidity in the four seasons: spring (a); summer(b); autumn (c) and winter (d)

$y=a+bx^{2.5}+c/lnx+d/x$

$r^2=0.6151$ DF Adj $r^2=0.3072$ FitStdErr=1.5632 Fstat=3.1968

a=1361446.5 b=-49.192073 c=-5319051.4 d=9644860.7

$y=a+bx+c(lnx)^2+dx/lnx+elnx/x^2$

$r^2=0.8610$ DF Adj $r^2=0.6874$ FitStdErr=0.8317 Fstat=7.7485

a=-7.16e+09 b=-7.55e+08 c=-9.1101e+08 d=4.5763e+09 e=-1.4012e+10

$y=a+bx^2+cx^4+dx^6+ex^8+fx^{10}$

$r^2=0.4704$ DF Adj $r^2=0$ FitStdErr=1.9526 Fstat=0.2538

a=-1.0821e+08 b=8694 c=-284015.79 d=4718.90 e=-39.2137 f=0.1032

$y=a+bx+cx^2+dx3+ex^4$

$r^2=0.4699$ DF Adj $r^2=0$ FitStdErr=4.3697 Fstat=0.7093

a=-50911340 b=31555417 c=-7818154 d=967881.18 e=-59873.0
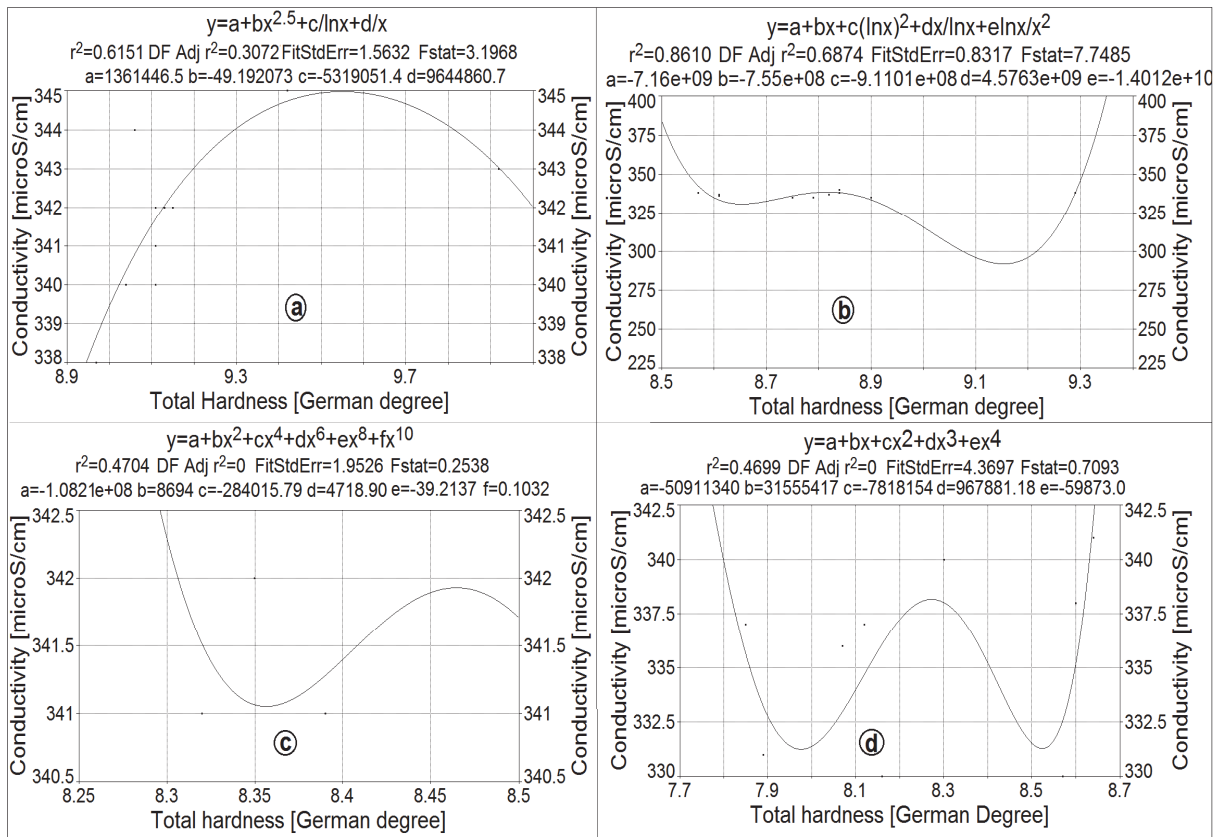
Fig. 4. The correlation of conductivity and water hardness in the four seasons: spring (a); summer (b); autumn (c) and winter (d)

In summer the nonlinear function was determined by the Eq. (6) with the value of model accuracy indicator of $r^2=0.8610$.

$$f(x)=a+bx+c(lnx)^2+dx/lnx+elnx/x^2 \tag{6}$$

For spring, the nonlinear function with the model accuracy indicator of $r^2=0.6151$ was described by the Eq. (7):

$$f(x)=a+bx^{2.5}+c/lnx+d/x \tag{7}$$

In winter was obtained also a nonlinear function given by Eq. (8) with a model accuracy indicator of $r^2=0.4704$.

$$f(x)=a+bx^2+cx^4+dx^6+ex^8+fx^{10} \tag{8}$$

Weaker correlations were obtained for data in the autumn with a model accuracy indicator of $r^2=0.4699$ and a nonlinear function describe by the Eq. (9) presented in Fig. 4d.

$$f(x)=a+bx+cx^2+dx^3+ex^4 \tag{9}$$

The functions 6-9 showed the dependence of conductivity on total hardness. When total hardness was increased, the water conductivity also was increased. The obtained functions were non-linear due to the complex processes that take place in the water supply network. Thus, the gradients of temperature or pressure were influenced by the physico-chemical equilibria in which carbon dioxide was involved such

as depositions of carbonates or resolubilisation of part of deposits of low solubility salts.

The accordance between the results generated by the mathematical models and the experimental data showed that a multivariable model can be utilized in the estimation of the correlations among the residual free chlorine, chlorides concentrations and oxidability. When oxidability was increased, the free chlorine that oxidizes the organic substances was decreased. In the oxidation process, the free chlorine was reduced to chlorides and as consequence, chlorides content was increased. In this purpose a model was utilized based on a function f(x, y, z) generated by the TableCurve3D program. Thus a set of functions was obtained. Their shapes are shown in Fig. 5(a-d).

As it could be observed in Fig. 5, the higher values for the value of model accuracy indicator were obtained in winter and in autumn: $r^2=0.6625$ and $r^2=0.6376$. The multivariable functions for winter and autumn were determined by the Eqs. (10) and (11):

$$f(x)=a+blnx+c(lnx)^2+d(lnx)^3+elny \tag{10}$$

$$f(x)=a+bx^{0.5}+c/x^{0.5}+d/x+ee^{-x} \tag{11}$$

In winter and autumn, the water consumption is reduced compared to that registered for the hot seasons (spring and summer). In spring and summer higher doses of chlorine are used to prevent the reinfection of the drinking water. So the free chlorine usually is higher and its variation more irregular than in the colder seasons autumn and winter.
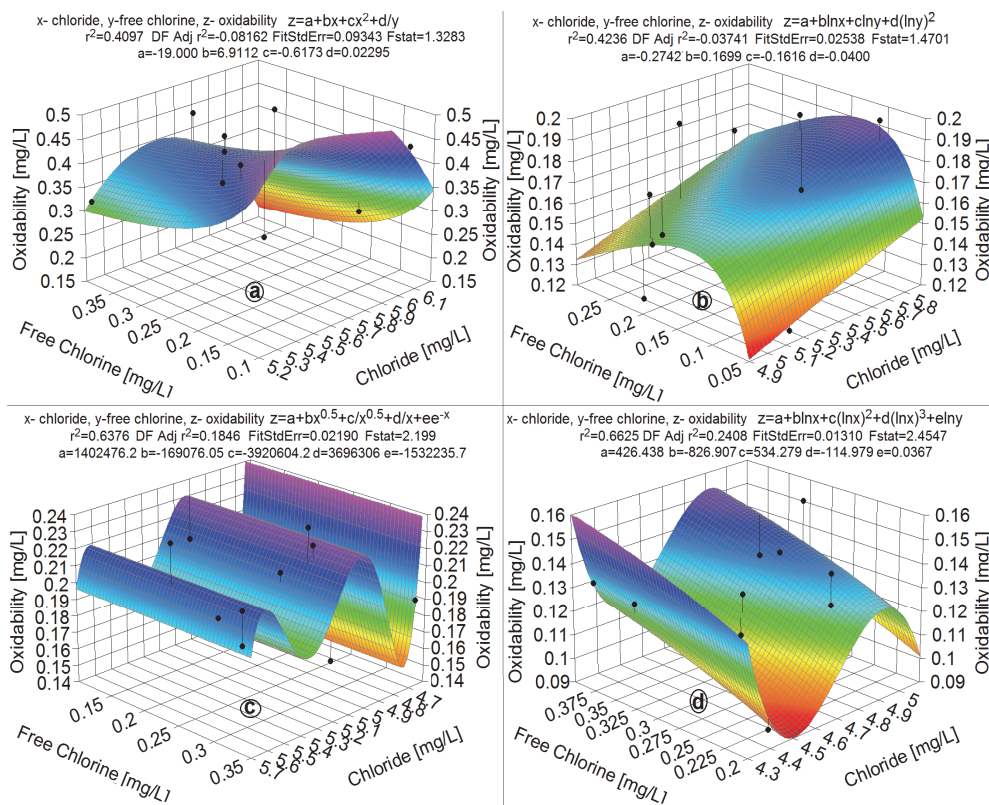

Fig. 5. The correlation of water oxidability with the residual free chlorine in water and chlorides in water for the 4 seasons: spring (a); summer (b); autumn (c) and winter (d)

In winter and autumn, the water consumption is reduced compared to that registered for the hot seasons (spring and summer). In spring and summer higher doses of chlorine are used to prevent the reinfection of the drinking water. So the free chlorine usually is higher and its variation more irregular than in the colder seasons autumn and winter.

Mathematical models with poorer correlations were obtained for summer and spring. The mathematical models were expressed by the functions determined by the Eqs. (12) and (13) with the model accuracy indicator $r^2=0.4236$ and $r^2=0.4097$:

$$f(x)=a+blnx+clny+d(lny)^2 \tag{12}$$

$$f(x)=a+bx+cx^2+d/y \tag{13}$$

The mathematical model of the variation of free residual chlorine depending on the seasons was determined by the function (14) shown in Fig. 6 with a model accuracy indicator of $r^2=0.8942$.

$$z=f(x)=a+bx+cx^2+dx^3+ex^4+f/y+g/y^2 \tag{14}$$

where: $a=1.6$, $b=-52.4666$, $c=428$, $d=-1463.3333$, $e=1800$, $f=0.675$, $g=-0.126$.
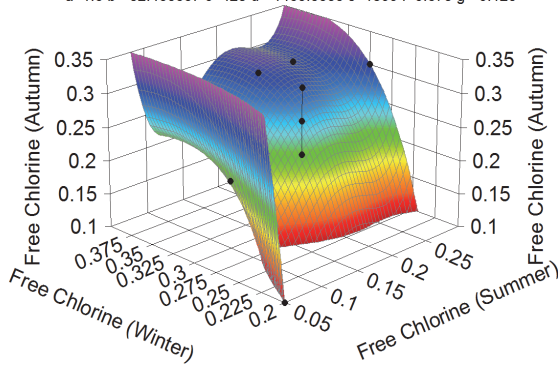

Fig. 6. The evolution of free chlorine in water depending on the season (summer, autumn and winter)

The free chlorine in autumn was related to that registered in winter and in summer. The connection between these parameters can be explained by the similarity between the water characteristics provided by the same sources and showing close range for free chlorine values. In spring, due to the high variability registered for this parameter, a similar model was not obtained.

The mathematical model for the turbidity variation depending on the season is determined by the function (15) shown in Fig. 7.

$$z=f(x,y)= a+bx^{0.5}+cy \tag{15}$$
$a=-0.07563$, $b=0.6411$, $c=0.2897$

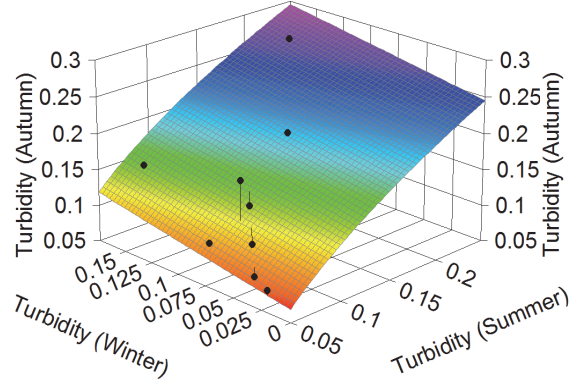In this case the value of model accuracy indicator indicates a very good correlation ($r^2=0.8741$).

Fig. 7. The evolution of water turbidity depending on the season (summer, autumn and winter)

The function shows a strong relation between the turbidities values registered in autumn, summer and winter. In these seasons, the same trend of increasing of the turbidity in the water supply network was registered. In Fig. 7 can be remarked the narrow range of the turbidities with a slight trend of increasing in autumn. For the spring a similar function was not obtained because the turbidity showed a higher variability in this season.

The mathematical model for the pH variation depending on the season is determined by the function (16) shown in Fig. 8.
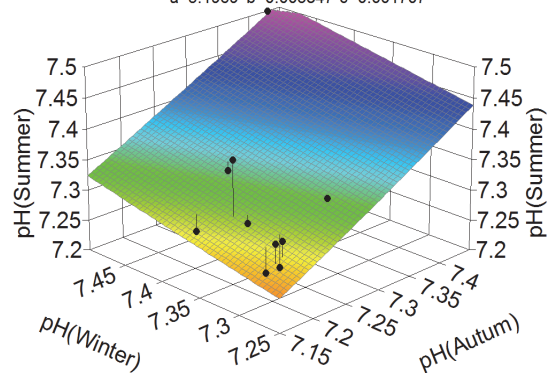

Fig. 8. The evolution of water pH depending on the season (summer, autumn and winter)

In this case a lower value for the model accuracy indicator was obtained ($r^2=0.7025$).

$$z=f(x,y)= a+bx^3+cy^3 \tag{16}$$

where $a=5.1969$, $b=0.003847$, $c=0.001707$

pH values in the summer, winter and autumn are connected by a polynomial function that reflects the seasonal interdependece of this parameter in the water supply network. The modeling of pH showed only a slight variation in a narrow range (7.2-7.5).

4. Conclusions

The seasonal variations of the water physico-chemical parameters in the drinking water supply network of Satu Mare city were investigated based on data collected weekly in Spring, Summer, Autumn of 2013 and Winter of 2014.

The study added new data about the way in which seasonality influences the physico-chemical parameters of water in temperate areas at the entrance of the drinking water distribution system (reflecting the composition of groundwater) and also along the water distribution network in other nine sampling points. A similar study about the seasonality of water physico-chemical parameters in drinking water distribution system was not performed until now.

The highest values for oxidability were observed in spring due to the intensification of fermentation processes and decay, specific to this season. These processes that occur in soil also influenced the groundwater, enriching the water with organic matter and nutrients. Turbidity, chlorides and nitrates also showed higher values in spring because of the destratification, a process specific to the spring period consisting in a vertical movement of groundwater that leads to a uniform quality of the water and to the increase of organic matter and nutrients concentration. The warm temperature specific to summer caused the increase of the reaction rates in which chlorine was involved and lower values of this indicator both at the entrance in the distribution network and in the sampling points compared to spring, autumn and winter. Water conductivity showed higher values in autumn and spring due to heavy rainfalls when the enrichment in salts of groundwater occurs. pH values ranged in a narrow interval with the highest values in winter and the lowest in spring.

The mathematical models as well as the working algorithm of data collection and modelling can be further generalized and utilized in other drinking water supply networks located in temperate areas, in other countries in order to understand, simulate and to make predictions on the water quality indicators and the factors that influence them.

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