Seasonal Statistical Analysis on the Quality of Underwater Supplies in South-Eastern Romania

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In this paper are presented preliminary results of seasonal statistical approach on monitoring of a series of drilled water well corresponding on a surface of about a quarter of Galati County which has a total area of 4,466 square km. In order to offer an adequate picture of the status of this natural resource we started a monthly monitoring program that cover approximately 20 monitoring points for two years. The study is an extension of previous research, with a total of 21 sampling points.

Keywords: monitoring, water quality, drilled water well, Principal Components Analysis

In 2014, at the Cornell University was designed and is in developing stage a water quality monitoring program that includes both groundwater monitoring and surface water monitoring. The data from this periodic monitoring can be used to identify issues that may need corrective actions [1]. In addition, water quality monitoring of irrigation sources (particularly water supply wells and storage lakes) provides valuable agronomic information that can inform nutrient and liming programs. A water quality monitoring plan should identify appropriate sampling locations, frequency, and monitoring parameters (Florescu et al., 2011, Timofti et al., 2016, Popa et al., 2018).

In this paper are presented preliminary results of an ambitious plan of monitoring a series of drilled water well corresponding on a surface of about a quarter of Galati County which has a total area of 4,466 square km. The started program covers about 20 monitoring points for a series of two years, in order to succeed in reaching a fine representation of the well water quality in this area.

This study will be submitted to the local authorities and to the county institutions in order to offer an adequate picture of the status of this natural resource.

Experimental part

The sampling of water probe that were used in this study was made on a route with a length of 56 km located in Galati County [3]. The starting point was the Serbanesti village followed by: Hanu Conachi, Tudor Vladimirescu, Vânes, Piscu, Independenta, Braniste, Sendreni, Movileni, the end point being located in Filesti and Barboși, districts of Galati. All settlements are located on county road DN 25. In table 1 we presented the GPS coordinates references of sampling points.

In figure 1 is presented a conventional map of Galati County and the sampling points for studied water. In table 1 the GPS coordinates references of sampling points are presented.

It should be mentioned that in each locality two sampling points have been settled with minimum distance of 500 m

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All the authors have equal contributions to this article.

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Table 1

| Crt. No. | Sampling Point | Latitude  | Longitude |
|----------|----------------|-----------|-----------|
| 1        | Șerbanesti     | 45.615189 | 27.336738 |
| 2        | Șerbanesti 1   | 45.600174 | 27.335923 |
| 3        | Hanu Conachi   | 45.597765 | 27.331027 |
| 4        | Hanu Conachi 1 | 45.586481 | 27.601551 |
| 5        | Ț Vladimirescu | 45.779478 | 27.857989 |
| 6        | Ț Vladimirescu 1 | 45.350143 | 27.854753 |
| 7        | Vânes         | 45.343615 | 27.706846 |
| 8        | Vânes 1       | 45.531966 | 27.706189 |
| 9        | Piscu         | 45.514474 | 27.71091 |
| 10       | Piscu 1       | 45.500527 | 27.728763 |
| 11       | Independenta 1 | 45.475233 | 27.754726 |
| 12       | Independenta 1 | 45.473705 | 27.762237 |
| 13       | Braniste      | 45.439937 | 27.854433 |
| 14       | Braniste 1    | 45.453868 | 27.852386 |
| 15       | Sendreni      | 45.472189 | 27.921098 |
| 16       | Sendreni 1    | 45.441357 | 27.928253 |
| 17       | Movileni      | 45.404823 | 27.967254 |
| 18       | Movileni 1    | 45.406561 | 27.966858 |
| 19       | Galău - Barboși | 45.399934 | 27.987714 |
| 20       | Galău - Filești | 45.444116 | 28.006033 |

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Fig. 1. Sampling points of water probes
apart from each other. Exception was made for Movileni which lies at a distance of only 400 m between them. For the Galati City were chosen a well drilled in Barbod district and a fountain from Filesti district. It should also be noted that the towns of Movileni, Sendreni, Branistea, Independence, Piscu and Vamases have centralised source of drinking water supply.

The water sample was representative and the composition of the water probe wasn’t altered through improper use of sampling techniques. All water probes were done manually, according to standardized methods [3].

Parameters method

The methods of analysis that were used are both chemicals (complexonometry) and instrumentals (electrochemical with specialized sensors) and there are standardized methods [4-7]. The quality indicators that were analyzed, the methods of analysis and the equipment that were used are presented in table 2.

Temperature - t (°C), pH (u pH), potential - ε (mV), electrical conductivities - C (µS/cm), total dissolved solids - TDS (mg/L), salinity - SAL (mg/L), dissolved oxygen - DO (mg/L), oxygen saturation - Sat O₂ (%), and gas pressure (mbarr) was determined with instrumental standardized methods [4]. Total hardness, and calcium (Ca²⁺) was determined with titrimetric methods [5, 6] and magnesium (Mg²⁺) was determined by mathematical equation [7].

Experimental determination of total water hardness principle is based on the ability of Ca²⁺ and Mg²⁺ ions to form chelate complexes with EDTA sodium salt, at pH=10, in the presence of a specific indicator: Erlo - Black T.

Determination of calcium in the water principle is based on the ability of Ca²⁺ ions to form stable complexes with EDTA sodium salt, at pH=12-13 in the presence of a specific indicator: murexide [6].

| Water Quality Indicators | Methods of analysis (STAS, SR sau SR ISO) | Type of analysis |
|--------------------------|------------------------------------------|-----------------|
| Temperature (°C)         | SR EN 1622/2000. Water quality. Determination of temperature in water | Instrumental    |
| pH (u pH), t (mV)        | SR ISO 10523/1997. Water quality. Determination of pH in water |                |
| Electrical conductivities - C (µS/cm) | SR EN 27886/1997. Water quality. Determination of electrical conductivities in water |                |
| Total Dissolved Solids - TDS (mg/L) | - |                |
| Salinity - SAL (mg/L)    | - |                |
| Dissolved oxygen - DO (mg/L) | SR ISO 5814/1990. Water quality. Determination of dissolved oxygen in water |                |
| Gas pressure (mbarr)     | - |                |
| Total hardness (°d)      | SR ISO 6059/2008. Water quality. Determination of total hardness in water | Titrimetric    |
| Calcium (mg/L)           | SR ISO 6059/2008. Water quality. Determination of calcium content in waters (drinking, surface, underground mineral supply) |                |
| Magnesium (mg/L)         | Mathematical equation | Mathematical    |

Table 2 QUALITY INDICATORS AND USED METHODS

Determination of magnesium in the water principle used mathematical calculation and it’s based on difference between the amount of reagent used for titration of the amount of cations Ca²⁺ and Mg²⁺ and the amount of reagent used for titration of the Ca²⁺ [7].

Results and discussions

In order to succeed in reaching a fine representation of the quality of well water in Galati County it was performed sampling of water probes for about 20 well water that represent monitoring points. The water samples were taken and analyzed monthly during a two years’ period.

In figure 2 are presented the pH seasonal variation box-plot for the monitoring points. It could be noted that in all locations, values of higher pH value are registered in the rainy seasons (spring and autumn) compared to other seasons where rainfall is lower. The variations are in the range of 7.4-8 units and for some locations one can notice a remarkable established throughout the year, being the fountain in Serbanesti. On another hand, during the annual interval there are significant differences between the measured pH from the same village as the Independena water wells case.

In figure 3 are presented the DO seasonal variation box-plot for the monitoring points. There are registered significant differences between the seasons. The lowest values are recorded during the summer due to the fact that the solubility of oxygen decreases as water temperature increases [3-5]. There are significant differences between the seasons for all sampling points, measured values showing increases of about 10 times during the cold periods (such as the water fountains in ’erbâne’ti or Tudor Vladimirescu).

Figure 4 shows the salinity seasonal variation box-plot for the monitoring points. For ’erbâne’ti and Tudor Vladimirescu monitoring point there are major differences between seasons and between sampling points. This is an aspect that results primarily from the realistic depth of the studied wells.

The TDS seasonal variation box-plot for the monitoring points is showed in figure 5. During the annual interval there are significant differences between all monitoring points for the measured values of TDS. Also, significant differences can be easily noticed during a seasonal analysis of the recorded data.

The conductivity seasonal variation box-plot for the monitoring points is presented in figure 6. During the annual interval there are significant differences between all monitoring points for the measured conductivity at Serbanesti and from a season to another. For Tudor Vladimirescu monitoring points there are differences between the water conductivity sampled from the two sampling points for autumn and spring seasons.
In figure 7 is presented the total hardness seasonal variation box-plot for the monitoring points. During the annual interval there are differences between seasons for the determined total hardness at Hanu Conachi monitoring points and in spring season between monitoring points. In winter season there are differences between monitoring points at Tudor Vladimirescu.

In figure 8 is presented the calcium seasonal variation box-plot for the monitoring points and in figure 9 are presented the magnesium seasonal variation box-plot. During the annual interval there are differences between seasons for the determined calcium for all monitoring points. In summer and spring season there are differences between monitoring points at Hanu Conachi. In winter season there are differences between monitoring points at Tudor Vladimirescu.

**PCA method approach for specific correlations**

In order to identify the factors that affect the water quality, besides seasonal variation box-plot for each quality indicators, it was made PCA for each monitoring points [8, 9]. Entire statistical analysis was performed using StatSoft STATISTICA 10 (StatSoft, Inc., USA).

For the monitoring points, results of PCA statistical analysis will be presented for the particular case of dependence between pH, calcium concentration and TDS.
Fig. 4. Salinity seasonal variation box-plot for the monitoring points.

Fig. 5. TDS seasonal variation box-plot for the monitoring points.
Fig. 6. Conductivity seasonal variation box-plot for the monitoring points.

Fig. 7. Water hardness seasonal variation box-plot for the monitoring points.
respectively. The results that had been obtained are presented in figure 10 to figure 12.

As it is known, TDS correlates positively with conductivity and affects pH [7]. The higher TDS and conductivity and lower the pH towards the acidity [3, 6, 7]. Worldwide, there are no agencies having scientific data to support that drinking water with low TDS will have adverse health effects [7]. Due to the reason, we considered for each monitoring point the dependence between pH, calcium concentration and TDS [6, 7].

As it can be seen, fountains that show significant seasonal variations for pH (such as Hanu Conachi or Tudor Vladimirescu fountains) show unstable dynamic equilibrium response surfaces with the positioning of representative points in peak areas. For monitoring points showing pH stability, there are some forms of the stable dynamic balance chart, with the positioning of representative points in minimum areas (for instance the Serbanesti 1 or Vames fountains). Future numerical analysis of chemical equilibrium states will allow the deepening of the internal mechanisms that determine these configurations. A number of important works in this regard have been published [9-12] and our research is under way.

There is a recommendation regarding high TDS, which is to drink water with less than 500mg/L [1, 8-10]. Our
Fig. 10. Surface plot for pH dependence by calcium concentration and TDS variation for Serbanesti, Serbanesti 1, Hanu Conachi, Hanu Conachi 1, Tudor Vladimirescu, and Tudor Vladimirescu 1 monitoring points.

Fig. 11. Surface plot for pH dependence by calcium concentration and TDS variation, for the second series of monitoring points.
The results showed that 1 of 20 annual samples set contained <500mg/L, 5 of 20 annual samples set contained <1000mg/L, 1 of 20 annual samples set contained <1500mg/L and 3 of 20 annual samples contained >1500mg/L.

Conclusions

A plan of monitoring of a series of drilled water wells corresponding on a surface of about a quarter of Galati County was started two years ago. The monitoring program was made monthly and covered about 20 monitoring points in order to show a fine representation of the well water quality in this area.

We used both chemicals (complexometry) and instrumentals (electrochemical with specialized sensors) standardized methods to studies 12 quality indicators for all of 20 monitoring points. Only 10% of a total of 20 analyzed wells in Galati County over a period of two years proved to have drinkable water. This percentage suggests an alarming urge to inform and educate the public on how to construct and use wells, monitoring water quality from private wells and implement the measures recommended by the World Health Organization [11, 12].

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