STATISTICAL STUDIES ON WATER QUALITY PARAMETERS FROM TWO UNDERGROUND SOURCES FROM SUCEAVA COUNTY

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Abstract

The main objective of this paper is to study two individual sources of water, analysing the chemical parameters - ammonium, nitrite, nitrate and permanganate index, during two years 2011 and 2012. Samples of water were collected from two wells located in the plateau region of Suceava county. The results of water quality parameters were statistically analysed. The parameters studied for the year 2011 were higher than those of 2012, this fact leading to the conclusion that the first year analysed was wetter. Higher values of parameters were registered in the first sample source (Dumbrăveni well) than in the second one (Vornicenii Mici).

Key words: *water quality, ammonium, nitrite, nitrate, permanganate index (oxidability)*

INTRODUCTION

Water is a good medium of transport for chemical compounds and microorganisms, its importance for public health issues is related to its level of chemical or microbiological pollution. Chemical compounds have a great influence on the health of the population and therefore seeks to eliminate them by periodical analyses and water disinfection (Foppen J.W.A., 2002). Periodic monitoring of water quality is a constant concern of the water supplier and for holders of individual water sources (Jahangir M. et al, 2013).

The wells are local facilities for water supply. Wells reconditioning is performed to correct major weaknesses within its producing water contamination (Mănescu S., 1984).

The most common types of pollution that occur on the surface of the well are due to construction deficiencies, further deterioration or accidental pollution. Contamination and pollution away from the water layer due to presenting different infiltration, from warehouses, stables, etc. (Bonton A. et al., 2010).

Romanian legislation admits maximum limits for the parameters mentioned above: ammonium - 0.50 mg/l, nitrite - 0.50 mg l nitrate - 50 mg/l and permanganate index (oxidability) - 5 mg O_2/l. Maximum limits are in accordance with Law 458/2002, republished in 2011. These parameters (ammonium, nitrites, nitrates and oxidability) are chemical indicators of pollution (Lockhart K.M. et al., 2013; Malaguerra F. et al., 2013).

If the analysis of a sample of the source water is high in ammonium then this means that it has recently pollution (hours or days). This parameter is the initial indicator of pollution (Molinari V, et al., 2012; Zhang X. et al., 2013). When nitrites are present and are of high value, water pollution is average and if nitrates and water pollution presents a constant and old.

Another indicator of pollution is the permanganate index or oxidability, on a scale of contamination of water is after the nitrite (Mrazovac S. & Vojinović-Miloradovm., 2011; Mrazovac S. & Vojinović-Miloradovm., 2011).

Water contamination can be caused by ground (especially those rich in nitrogen or those that have been heavily fertilized with nitrogen fertilizers) by involving these compounds in soil when rainfall and thus into the water (Wang C. & P.F. Wang, 2008; Pastén-Zapata E. et al., 2014).

Several studies shown that high levels of nitrogen may be unsafe for health people if they drink directly from groundwater wells (Ibendahl G. & R. A. Fleming, 2007, Ju X.T. et al., 2006).

Nitrogen can be found in fertilizers or farm animal wastes and, in some cases (Burkart M.R. & J.D. Stoner, 2008; Jahangir M. et al., 2013).

MATERIALS AND METHODS

The analysed waters were from two wells (underground water sources) - one located in Dumbrăveni and the other in Vornicenii Mici from the region of Suceava (during two years 2011 and 2012), following chemical parameters - ammonium, nitrite, nitrate and permanganate index.

Determination of ammonium content (SR ISO 7150-1)

The method used is manual spectrophotometric method for the determination of ammonium in water directly applicable drinking water and most raw and waste waters. It can cause an ammoniumcal nitrogen concentration of up to ρ = 1 mg / l (1.288 mg / l NH 4) using the sample not exceeding 40 ml. The reaction of chloramine with sodium salicylate takes place at pH 12.6 in the presence of sodium nitroprusside. Chloramines present in the sample are determined quantitatively. Sodium citrate is added to mask interfering time cations, particularly calcium and magnesium.

Determination of nitrite content (SR EN 26777:2002)

The method used is molecular absorption spectrometric method for the determination of nitrite in drinking water, raw water and wastewater. The method is applicable to content of up to 0.25 mg / l N (0.8285 mg / l NO2) using a sample volume of no more than 40 ml. The detection limit of the method using cells having path length of 40 mm and a 40 ml sample volume is in the range from 0.001 to 0.002 mg / l N (0.0033 to 0.0066 mg / l NO2). For cells with 10 mm optical path, and a sample volume of 40 ml detection limit is in the range from 0.0132 to 0.0264 mg / l NO2) (1mg / l N = 3.29 mg / l NO2). Nitrite ions in the strongly acidic medium pH = 1.9 is reacted with the reagent 4-amino benzene sulfonamides in the presence of orthophosphoric acid to form a diazonium salt that forms a red complex of N-(1-naphthyl) ethylenediamine dihydrochloride. It measures the absorbance at 540 nm.

Determination of nitrate content (SR ISO 7890-3: 2000)

The method for determination of nitrate ion in water is applicable to analyzing samples of raw water. The method is applicable to a nitrogen content of up to 0.2 mg / l N (0.88 mg / l NO3) using the sample volume max. 25 ml. The method consists in measuring the spectrophotometric absorbance of the yellow compound formed by the reaction of sulfosalicylic acid (formed by the addition of sodium salicylate in the sample and sulfuric acid) to nitrate, followed by treatment with alkaline solution. Ethylenediaminetetraacetic acid disodium salt is added to the alkaline solution to prevent precipitation of calcium and magnesium salts.

Determination of permanganate index (SR EN ISO 8467:2001)

The method is used to determine the parameter "oxidability". It applies water to a concentration of chloride ions of less than 300 mg / l Permanganate index is a conventional measure of contamination of water samples with organic and oxidizable inorganic materials, mainly used to characterize the quality of both drinking water and water of crude. Heating a sample of water in a boiling water bath in the presence of a quantity of potassium permanganate and sulfuric acid over a period of time (10 min). Permanganate index is the maximum recommended 10 mg / l, corresponding to a consumption of about 60% of the permanganate added to the undiluted sample.

RESULTS AND DISCUSSION

Statistical studies presented in the following are based on the data collected in the years 2011 and 2012, for two wells located in the plateau region of Suceava county, about 10 km from Suceava River: the well 1 (denoted by W1) in Dumbrăveni (situated at 17 km from Suceava town) and the well 2 (denoted by W2) in the area Vornicenii Mici - Moara (situated at 8 km from Suceava town). These wells have a depth of about 10 m and are used for domestic water supply to households in their adjacent area.

In this study we made an analysis of the monthly variation of parameters ammonium, nitrite, nitrate and oxidability. Compared variations for the parameters measured in the years 2011 and 2012 (for W1 and W2) are shown in Figures 1 - 4.

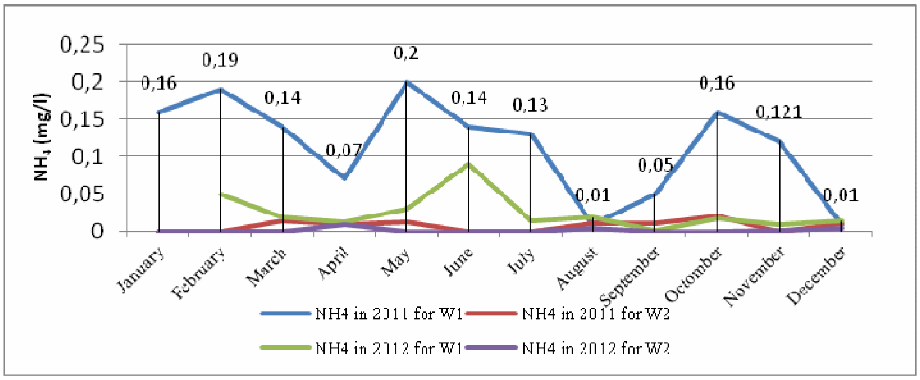


Figure 1. Variation of the ammonium content (NH4 mg / l) resulted in W1 and W2 water

From Figure 1 it is noted that the higher values of ammonium (NH4, mg / l) of water were recorded in W1 in February, May and October of 2011, due to abundant rainfall in 2011 compared to 2012. Values of ammonium (NH4, mg / l) of water recorded at W2 were significantly lower than in W1.

All of ammonium values were within the limits allowed by law (Law 458/2002, republished in 2011), being smaller than the maximum of 0.50 mg / l (NH4).

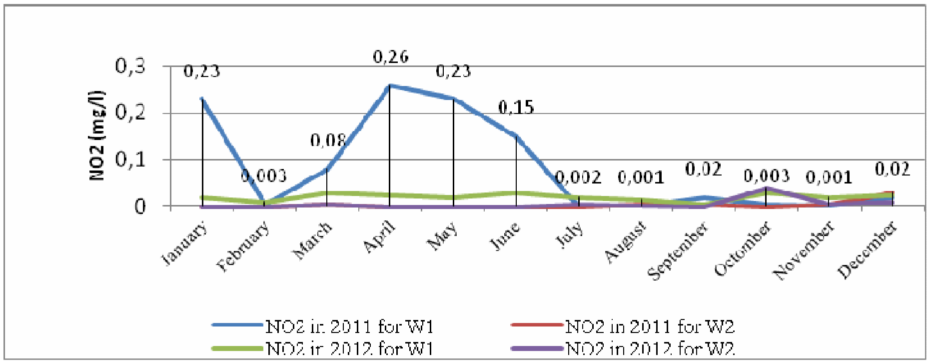


Figure 2. Variation of the nitrite content (NO$_2$ mg / l) resulted in W1 and W2 water

From Figure 2 it is observed that the highest values of nitrite content (NO2, mg / l) of water were also recorded at W1 in January, April and May of 2011. In 2012 these values were much lower. Nitrite content of the water values recorded was significantly lower for W2 than W1. All nitrite content values were within the limits allowed by law (Law 458/2002, republished in 2011), being smaller than the maximum of 0.50 mg / l (NO2).

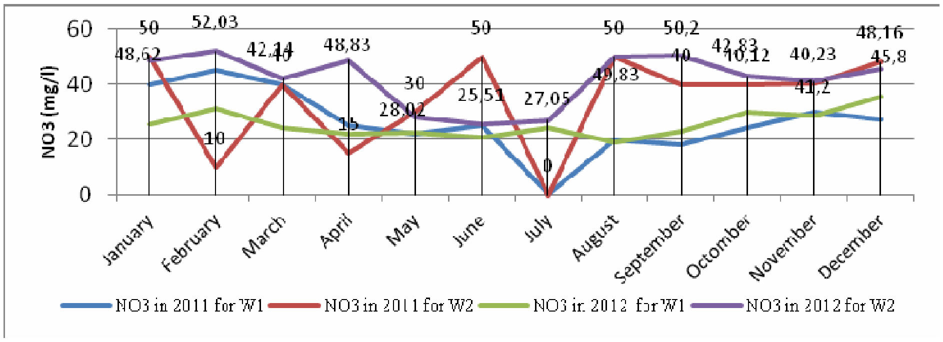


Figure 3. Variation of the nitrate content (NO_3 mg / l) resulted in W1 and W2 water

From Figure 3 it is noted that the higher values for nitrate (NO_3, mg/l) of water were recorded for W2 in February, April, August and September of 2012 and June and August of 2011, being of the limit or exceeding the very least limits allowed by law of 50 mg / l (NO_3), because these months are the heavy rainfall.

It is known that the waters Dumbrăveni have a high content of nitrates through the soil - is an agricultural area. Lower values for nitrate in water were recorded for W1 than W2 in 2012, complying with the limits allowed by law (Law 458/2002, republished in 2011).

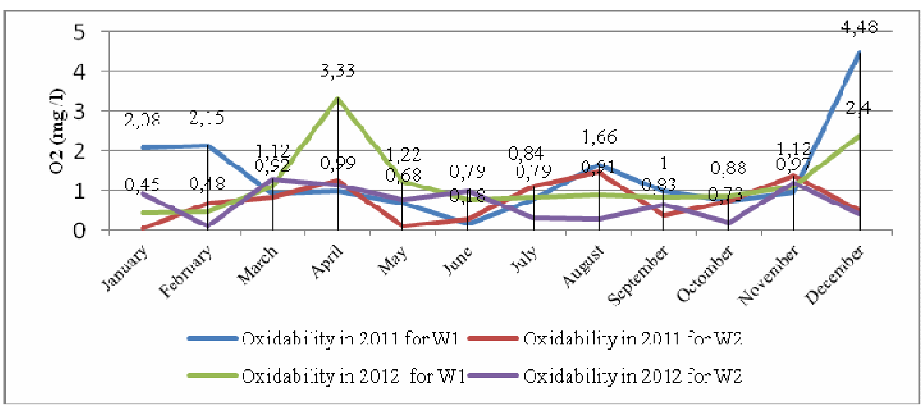


Figure 4. Variation of the oxidability (O_2 mg / l) resulted in W1 and W2 water

From Figure 4 it is observed that the values in the analyzed oxidability within the limits prescribed by law (5 mg O2 / l). The index of oxidability in 2011 for W1 has values close to the maximum permitted by law. For W1 it was registered the maximum value of 4.48 mg O2 / l in December 2011 and 3.33 mg O2 / l in April 2012. Similar variations of the index are obtained for W2 oxidability, without exceeding the value of 1 mg O2 / l.

In the Table 1 we present means ± standard deviations for water quality parameters (ammonium, nitrites, nitrates and oxidability, respectively) for the two wells for Dumbraveni (W1) and Vornicenii Mici (W2) wells and we looked at whether there are significant differences between the two wells during the two years (2011 and 2012), using the statistical t test.

Table 1.

Mean values for water quality parameters registered for W1 and W2 wells

Parameters of water quality	2011		2012	
	W1	W2	W1	W2
Ammonium (NH4, mg/l)	0.115^{a} ± 0.065	0.008^{b} ± 0.007	0.030^{c} ± 0.172	0.002^{d} ± 0.040
nitrite (NO_2, mg/l)	0.314^{a} ± 0.850	0.004^{b} ± 0.008	0.021^{c} ± 0.143	0.005^{b} ± 0.072
nitrate (NO_3, mg/l)	$26.46^{a,b}$ ± 11.81	$34.45^{a,c}$ ± 17.11	25.55^{b} ± 5.055	41.58^{c} ± 6.468
oxidability (O2, mg / l)	1.385^{a} ± 1.877	$0.734^{a,b}$ ± 0.856	1.197^{a} ± 0.836	0.692^{b} ± 0.423

Mean values ± standard deviation ($n = 3$); Means with the same superscript letter from the same line are not significantly different from one another ($p < 0.05$)

From the table 1 we observe that there are significantly differences between ammonium values in years 2011 and 2012, for any studied samples of water from these two wells (W1 and W2). Values of nitrite have significantly differences for W1, but does not have significantly differences for W2 in years 2011 and 2012. The samples of water from W1 are no significantly differences between the nitrate values in the years 2011 and 2012. The same situation was recorded for the samples of water from W2. Also, there are no significantly differences between the oxidation index values for W1 and W2 in the years 2011 and 2012.

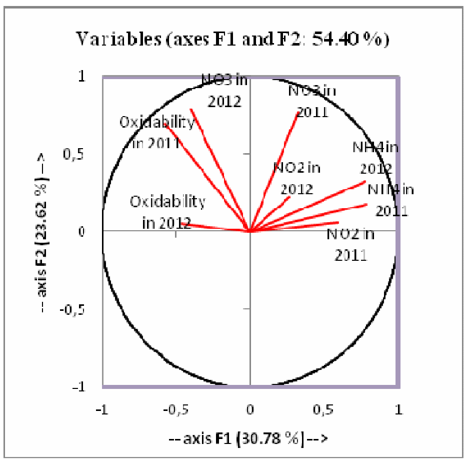
Principal component analysis (PCA) was used to test for the correlation between variables (ammonium, nitrite, nitrate and oxidability) and their evolution in all months of the years 2011 and 2012.

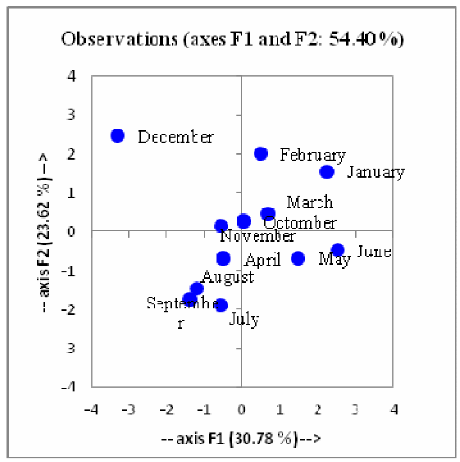
The variation of the water quality parameters studied for the two wells from Dumbraveni and Vornicenii Mici implies 8 factors of variability. A great importance for the significance of variability is given by the factors which have eigenvalues more than the value 1. The principal components for Dumbraveni well samples that have eigenvalue more than 1 are, as follows: F1 (2.462), F2 (1.890) and F3 (1.552). For F4 to F8, the eigenvalue are less than 1 thus, we cannot consider them in our study. The percentage of variability represented by the first two factors is not very high (54.4%).

Using the third factor F3 together with F1 and F2, these explain over 73.8% of the total variability in the data.

Some categories of factors loading can be consider: strong factors (which are greater than 0.75), moderate factors (which varies between 0.75 and 0.50) and weak factors (which varies between 0.49 and 0.30). Only strong or moderate factor loadings are selected for the principal components interpretation of water quality parameters.

Principal component analysis (PCA) for the most important factors (F1 and F2) is illustrated in the figure 5. PCA is used for verify the correlation among ammonium, nitrite, nitrate and oxidability (figure 5 .a) and their evolution in all month of the years 2011 and 2012 (figure 5. b).





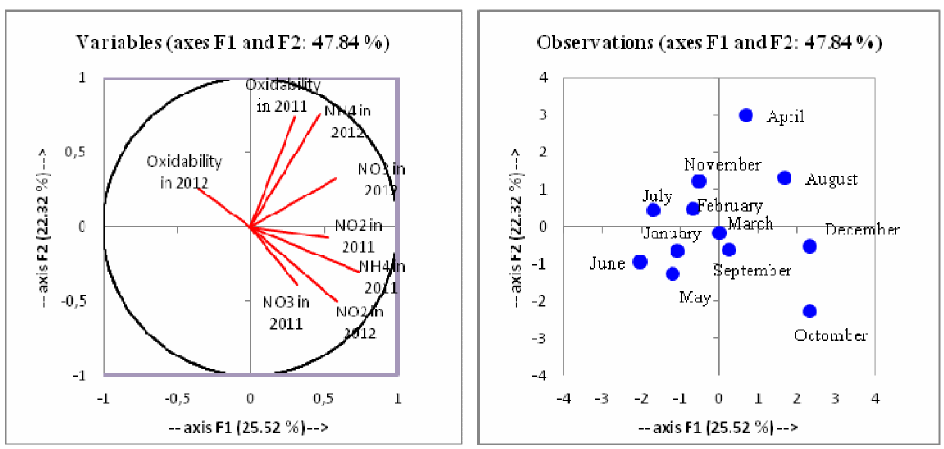
a. b.

Figure 5. Principal component analysis for water quality parameters from Dumbrăveni well (W1). a. The importance of water quality parameters. b. Contributions of the observations - the importance of months in the variation of water quality parameters

The first factor (F1) explains 30.78 % of the total variance, with the significant parameter NH_4 in 2011 and in 2012 (figure 5.a.). Values of ammonium (NH4, mg/l) show a strong positive loading, having the values of factor loading 0.785 in the year 2011 and 0.780 in the year 2012. Important contributions of the observations (%) for the factor F1 (figure 5.b.) are given by the following months: December (36.79 %), June (21.7 %) and January (17.6%). The second factor (F2) explains 23.624 % of the total variance with a significant parameter which is NO_3 in 2011 and 2012. Values of nitrate (NO_3, mg/l) show strong positive loading, having the values of factor loading 0.769 in the year 2011 and 0.786 in the year 2012. Important contributions of the observations (%) for the factor F2 (figure

5.b.) are given by the months: December (26.85%), February (17.79 %) and July (15.65 %). Also, the third factor has an important influence (19.4%) with one significant parameter, oxidability in 2012, having the value of factor loading 0.827 in the year 2012.

For Vornicenii Mici well samples, principal components of the parameters which have eigenvalue more than 1 are: F1 (2.041), F2 (1.786) and F3 (1.454). As in the case of Dumbraveni well samples, factors F4 to F8 have the eigenvalue less than 1 and it cannot consider them in our study. The percentage of variability represented by the first two factors is not very high (47.83%). Using the percentage of variability represented by the third factor F3 (18.18%), together with F1 and F2, these explain over 66% of the total variability in the data. Principal component analysis (PCA) for the most important factors (F1 and F2) of water quality parameters from Vornicenii Mici well samples is illustrated in the figure 6. PCA is used for verifying correlations among ammonium, nitrite, nitrate and oxidability (figure 6 .a) and their evolution in all month of the years 2011 and 2012 (figure 6. b).



a. b.

Figure 6. Principal component analysis for water quality parameters from Vornicenii Mici well (W2). a. The importance of water quality parameters. b. Contributions of the observations - the importance of months in the variation of water quality parameters

The first factor (F1) explains 25.52 % of the total variance, having significant parameters: NH_4 in 2011 and NO_3 in 2012 (figure 6.a.). The values of ammonium (NH_4, mg/l), nitrite (NO_2, mg/l) and nitrate (NO_3, mg/l) show strong positive loading, having the value of factor loading: 0.734 for ammonium in the year 2011, 0.585 for nitrite and 0.583 for nitrate in the year 2012. Important contributions of the observations (%) for the factor F1 (figure 6.b.) are given by the following months: December (22.17%), October (22.12 %) and June (16.73 %).

The second factor (F2) explains 22.32 % of the total variance with significant parameters: oxidability in the year 2011 and ammonium in 2012. These values show strong positive loading, having the value of factor loading: 0.731 for oxidability in the year 2011 and 0.760 for ammonium in 2012. Important contributions of the observations (%) for the factor F2 (figure 6.b.) are given by the following months: April (41.78 %) and October (23.93%). Also, the third factor has an important influence (18.18%), having significant parameters: nitrate in 2011 and oxidability in 2012. These parameters have the factor loading: 0.725 for nitrate in the year 2011 and 0.651 for oxidability in 2012.

CONCLUSION

Statistical analyzes of water quality parameters (ammonium, nitrite, nitrate and permanganate index (oxidability)), analyzed for the two wells (W1 from Dumbrăveni and W2 from Vornicenii Mici) during the years 2011 and 2012 highlighted the following conclusions: ammonium was an important factor in water pollution of wells. Values of ammonium (NH4, mg / l) of water recorded at W2 were significantly lower than in W1. There are significantly differences between the ammonium values in years 2011 and 2012, for any studied water from the two wells; the values of nitrite have significantly differences for W1, but does not have significantly differences for W2 in years 2011 and 2012. Nitrite content of the water values recorded was significantly lower for W2 than W1; nitrate was another important factor in water pollution of wells, being of the limit or exceeding the very least limits allowed by law of 50 mg / l (NO3), in the months with the heavy rainfall. There are no significantly differences between the nitrate values for W1 in the years 2011 and 2012 and for W2 in 2011 and 2012; there are no significantly differences between the oxidability values for W1 and W2 in the years 2011 and 2012, without exceeding the value of 1 mg O2 / l. All the values of the water quality parameters studied above (excepting nitrate values) were within the limits allowed by law.

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