PRELIMINARY STUDY ON GROUNDWATER POLLUTION WITH NITRITES AND NITRATES IN GĂTAIA (TIMIȘ COUNTY)

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ABSTRACT
Nitrate pollution of water is a widespread issue. This study analyses the pollution with nitrites and nitrates in wells from Gătaia. We collected water samples from 17 wells. The nitrites and nitrates content was determined by the photometric method, using the Spectroquant NOVA60 photometer. We analysed following factors impacting pollution: manure deposits, latrines, livestock farms, slope and depth of the groundwater level in wells. The distances between wells and the analysed pollution sources as well as the slope were determined in ArcGIS 9.3. Software. The statistical analysis has been performed in Excel and GraphPad InStat. The maximum admissible concentration of nitrates has been exceeded in 41.17% of the water samples, and the maximum admissible concentration of nitrites in 11.76% of the water samples. Both simple and multiple regressions (with 2 to 5 independent variables) have been performed in order to analyse the relationship between nitrates concentration, respectively nitrites concentration in water and the factors impacting pollution. The simple linear regression could explain to a very small extent this relationship but it was explained to a greater extent by multiple regression. As more factors impacting pollution have been taken into consideration as independent variables, the correlation coefficient between the nitrites content, respectively nitrates, in water and these factors increased. The greatest correlation coefficient (0.6079) with p significant (0.0419) was obtained in case of multiple regression with all 5 independent variables, the dependent variable being the nitrite concentration.

KEY WORDS: nitrite, nitrate, pollution, groundwater

INTRODUCTION
Groundwater is the main source of drinking water for a great part of world population, especially in the rural areas (Nas & Berktay, 2006). The quality of groundwater, one of the most important natural resource, is subject to hydrological, physical, chemical and biological factors. A slow deterioration of the groundwater quality occurs everywhere, most of the issues being difficult to detect and remedy (Yadav et al, 2002). Of all types of pollution which degrade the environment, probably the least recognized and understood is the hidden deterioration of the groundwater quality. A particular aspect of this pollution lies in the fact that after having penetrated into the groundwater system, the pollutants are no longer accessible, and may rarely be
detected by random monitoring methods, their presence becoming evident upon their re-emergence in wells, fountains and other points of surface discharge (Zaporozec, 1981).

Nitrates are the most common aquifer chemical contaminant on global level and the contamination is currently increasing (Spalding & Exner, 1993). Moderate nitrate concentrations in groundwater can be found in many environments, but they can increase to a level which exceeds the acceptable limit, as a result of various anthropic activities (Reddy et al., 2011) Natural concentrations of nitrates in groundwater depend upon the type of soil and geology (Fewtrell, 2004). Given the fact that geological sources of nitrogen are rare, the occurrence of nitrates in the groundwater is mainly a consequence of anthropic activities (Brindha et al., 2010). Pollution may be caused directly by nitrates, as in the case of agricultural or industrial pollution, or by organic substances which form nitrates by their decomposition (Mănescu et al., 1996). Ammonia is the initial decomposition product of organic matter, and is found in water as ammonium ion. The nitrite ion occurs as an intermediate stage in the nitrogen oxidation process, while the nitrate ion is the most oxidated form of nitrogen (Postolache & Postolache, 2000). The nitrate pollution increased following the systematic use of nitrogen-based chemical fertilizers (Ghidra, 2002), while the excessive use of manure in agriculture may have also contributed to the nitrate pollution of groundwater (Reddy et al., 2011). The growing use of chemical fertilizers, waste disposal from animal farms and changing land use are the main factors responsible for the increased level of nitrates in groundwater in the recent 20 years (World Health Organization, 2011). The rural area, where the sanitary conditions are not always appropriate, and where the waste disposal sites may be randomly disposed, contributes in a significant manner to the nitrate contamination of groundwater (Reddy et al., 2011). Excessive nitrates in drinking water causes severe health problems, and the most exposed age group is artificially fed nursing infants up to 4 months, who may develop methemoglobinemia (Fewtrell, 2004). Nitrites and nitrates ingestion also plays a potential role in the development of cancer at the level of digestive tract, by leading to the formation of nitrosamines (Camargo & Alonso, 2006).

Several Eastern European countries, including Romania, reported increased nitrates levels in a large number of private wells (Ward et al., 2005). Several studies have been conducted in Romania regarding the nitrates and nitrites levels of groundwater. The results of one such study shows increased levels of nitrates and a lower level of nitrites in wells from localities in Galați, Buzău, Ilfov counties (Pele et al., 2010). Also, a study conducted in several localities from western Romania shows increased levels of ammonium, nitrites and nitrates in groundwater (Brînzei et al., 2005). In 1988, 36% of the wells from Romania contained nitrates concentrations exceeding 45 mg/l (Proca et al., 2009).
This study analyses the pollution with nitrites and nitrates in wells from Gătaia. The town of Gătaia is located in western Romania, on the fertile, alluvial soil of Gătaia Plain. Agriculture and animal breeding are the main economic activities carried out in this area.

**MATERIALS AND METHODS**

Water samples have been extracted from 17 private wells in the autumn of 2009. The water samples have been collected in plastic containers and brought to the laboratory under 5-6 degree Celsius conditions. The nitrites and nitrates content has been determined by the photometric method, using the Spectroquant NOVA60 photometer.

The distances between sampling points and the analyzed pollution sources were determined in ArcGIS 9.3. software. Distance maps to the pollution sources have been prepared, based on which the distances to each well were automatically extracted. The slope, a key morphometric factor both for surface and groundwater flow, has been derived from a digital elevation model (DEM) with a spatial resolution of 5 m. The value of the slope has been automatically extracted for each well in ArcGIS 9.3.

The statistical analysis has been performed in Excel and GraphPadInStat. For statistical tests, the following interpretation of p values was used: p < 0.05 = significant, p < 0.01 = highly significant, p < 0.001 = extremely significant, p > 0.05 = not significant (Marzillier, 1990).

**RESULT AND DISCUSSION**

We analyzed first the nitrite and nitrate content from the 17 water samples (fig. 1). In compliance with law no. 458/2002 on the quality of drinking water, completed by law no. 311/2004, the maximum admissible concentration of nitrates is 50 mg/l, and of nitrites is 0.5 mg/l.

In 41.17% of water samples analysed for nitrate content (fig. 2) the admissible limits were exceeded. The cases where nitrites exceeded the admissible limit are less frequent (fig. 3), only 11.76%. The average value of nitrate concentration in the analysed samples is 59.73 mg/l, with a standard deviation of 67.535. The minimum value of nitrate concentration in the analysed samples is 1 mg/l and the maximum value is 188.10 mg/l. The average value of nitrite concentration is 0.23 mg/l, with a standard deviation of 0.407, the minimum value is 0.02 mg/l and the maximum value is 1.48 mg/l. The water in these wells is not currently used for drinking, as the town of Gătaia is connected to the public water supply network, but it is used occasionally for cooking.

We analyzed further the relationship between the content of these pollutants in water and some factors impacting pollution (table 1). The sources of nitrites and nitrates in water that have been analysed are manure storage sites, latrines, livestock farms, cemeteries.
Given the fact that a decrease of slope gradient implies an increase of infiltrations (Li et al., 2006), the slope was also taken into account as a determining factor for the penetration of nitrites in groundwater, as well as the depth of the groundwater level in wells. High concentrations of nitrates are often reported in private wells, less than 15 m deep, in areas with permeable soil (Fewtrell, 2004). Considering the current situation, the wells are bored at a small depth, the biggest depth being 4.5 m. These wells are fed from the groundwater, and according to the hydrogeological map 1:25.000 scale (Romanian Waters National Administration – Banat Branche, unpublished data) its level lies between 2 and 5 m in this area.

Several regression analysis have been performed to determine the extent in which such sources of nitrates and the factors influencing their accumulation affect the quality of water. The regressions performed have been both simple, with one independent variable, and multiple with 2, 3, 4 and 5 independent variables, respectively. The independent variables were the distance to the manure storage sites, distance to latrines, distance to livestock farms and cemeteries, slope and the depth of groundwater level in wells. The dependent variables were the nitrate, respectively the nitrite content in water.
Following the simple linear regressions between nitrates and nitrites respectively, as dependent variables and one factor impacting the pollution as independent variable, we have obtained correlation coefficients with very small values (between 0.0387 and 0.0039 for nitrates and between 0.0039 and 0.3758 for nitrites) and a not significant p value from a statistical perspective (p>0.05).

In cases of multiple regression between nitrites, respectively nitrates, as dependent variables, and two of the factors mentioned above as independent variables in different combinations, the correlation coefficient had bigger values (between
0.0670 and 0.1836 for nitrates and between 0.0920 and 0.4137 for nitrites), the p value being also not significant from a statistical perspective.

Table 1. Nitrate and nitrite concentrations, depth of groundwater level in wells, slope and distance from sampling points to pollution sources

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nitrate (mg/l)</th>
<th>Nitrite (mg/l)</th>
<th>Depth of groundwater level in wells (m)</th>
<th>Slope (degrees)</th>
<th>Distance (m) to: Latrine Livestock farms/cemeteries Manure storage sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.80</td>
<td>1.48</td>
<td>4.50</td>
<td>5.83</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>170.40</td>
<td>0.04</td>
<td>3.50</td>
<td>0.41</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>22.60</td>
<td>0.32</td>
<td>2.40</td>
<td>0.48</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>1.10</td>
<td>0.04</td>
<td>3.50</td>
<td>0.18</td>
<td>34</td>
</tr>
<tr>
<td>5</td>
<td>3.70</td>
<td>0.03</td>
<td>3.70</td>
<td>0.18</td>
<td>34</td>
</tr>
<tr>
<td>6</td>
<td>10.80</td>
<td>1.01</td>
<td>3.40</td>
<td>0.11</td>
<td>89</td>
</tr>
<tr>
<td>7</td>
<td>86.80</td>
<td>0.37</td>
<td>3.50</td>
<td>0.22</td>
<td>12</td>
</tr>
<tr>
<td>8</td>
<td>188.10</td>
<td>0.04</td>
<td>3.20</td>
<td>0.10</td>
<td>30</td>
</tr>
<tr>
<td>9</td>
<td>2.70</td>
<td>0.03</td>
<td>4.50</td>
<td>3.19</td>
<td>25</td>
</tr>
<tr>
<td>10</td>
<td>128.20</td>
<td>0.03</td>
<td>3.50</td>
<td>1.55</td>
<td>25</td>
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<tr>
<td>11</td>
<td>115.40</td>
<td>0.37</td>
<td>3.00</td>
<td>0.27</td>
<td>20</td>
</tr>
<tr>
<td>12</td>
<td>144.00</td>
<td>0.05</td>
<td>2.10</td>
<td>0.08</td>
<td>11</td>
</tr>
<tr>
<td>13</td>
<td>95.80</td>
<td>0.06</td>
<td>3.50</td>
<td>0.33</td>
<td>13</td>
</tr>
<tr>
<td>14</td>
<td>1.50</td>
<td>0.02</td>
<td>3.20</td>
<td>0.26</td>
<td>90</td>
</tr>
<tr>
<td>15</td>
<td>3.10</td>
<td>0.02</td>
<td>3.40</td>
<td>0.18</td>
<td>87</td>
</tr>
<tr>
<td>16</td>
<td>1.00</td>
<td>0.07</td>
<td>3.00</td>
<td>0.48</td>
<td>15</td>
</tr>
<tr>
<td>17</td>
<td>36.30</td>
<td>0.04</td>
<td>3.80</td>
<td>0.26</td>
<td>94</td>
</tr>
</tbody>
</table>

In cases of multiple regression with three independent variables in different combinations, the correlation coefficient recorded values between 0.1729 and 0.3998 for nitrates and between 0.1144 and 0.4863 for nitrites. The correlation coefficient of 0.4863 has been recorded in cases where the independent variables were the distance to latrine, the slope and the distance to livestock farms. The p value recorded in this situation was significant (0.0298). In cases where the independent variables were represented by slope, distance to livestock farms and distance to manure storage sites, and the dependent variable was the nitrite content, the p value was also significant (0.0467), and the correlation coefficient was 0.4468.

In cases of multiple regression with four independent variables in different combinations, where the dependent variable was the nitrate content, the biggest value of the correlation coefficient was 0.4214, and the p value was 0.1324. For the similar analysis on nitrites, the biggest value of the correlation coefficient obtained was 0.5961, with a significant p (0.0199). In this situation, the four independent variables have been represented by the distance to latrine, distance to the manure storage site, distance to livestock farms.

When all five independent variables were included in the analysis, in relation to nitrate content as dependent variable, the correlation coefficient increased slightly
(0.4264) compared to the case with four independent variables, but increased more compared to the cases with two or three independent variables. For the same analysis, with all five independent variables, performed on nitrites, the correlation coefficient reached 0.6079, with a significant p value (0.0419).

The relationship between the factors under analysis and the nitrite concentration is more obvious than in the case of nitrates, regardless of the number of factors taken under consideration, as demonstrated by the higher values of the correlation coefficient. The content of nitrites and nitrates in water can be explained by multiple factors, as shown by the correlation coefficient, which increases with the number of independent variables taken into consideration. This fact shows the complex character of pollution. Given that the increase of nitrites and nitrates concentration in water may also be influenced by other factors, such as the use of fertilizers in agriculture, an essential factor, a future study which includes an analysis on the fertilizer use could contribute to a better understanding of pollution development in that respective area.

**CONCLUSION**

The maximum admissible concentration of nitrates has been exceeded in 41.17% of the water samples, and the maximum admissible concentration of nitrites in 11.76% of the water samples.

The simple linear regression could explain to a very small extent the relationship between nitrites concentration, respectively nitrates concentration in water and the factors under analysis (distance to manure storage sites, distance to latrine, distance to livestock farms, cemeteries, land slope and well depth). This relationship is explained to a greater extent by multiple regression, when, as more factors impacting pollution have been taken into consideration, the correlation coefficient between the nitrites content, respectively nitrates, in water and these factors increased. The greatest correlation coefficient (0.6079) with p significant (0.0419) was obtained in case of multiple regression with all 5 independent variables, the dependent variable being nitrite concentration.

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**REFERENCES**

TÖRÖK-OANCE et al: Preliminary study on groundwater pollution with nitrites and nitrates in Gătaia (Timiș County)