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NITRATE MONITORING IN PRIVATE WELLS FROM PRAHOVA DISTRICT

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Abstract

As water quality has become an increasing, environmental and social constraint for modern society, we found it suitable to evaluate the nitrate levels in drinking water collected from private wells from Fantanele, Prahova County. The present study conducted during November 2012 and April 2013 describes the nitrate levels of drinking water from four private wells (F1-F4). Nitrate species were assessed using spectrophotometric method and the analytic results allowed us to draw up the following variation of nitrate concentrations: F4<F3<F2<F1. In the case of well F1 nitrate levels were greater than 50 mg/L at all three collection moments and these results are associated with nitrogen fertilisation techniques adopted by well owner, a local vegetable producer. Nitrate concentrations for F3 and F4 were below maximum admitted level (50 mg/L), meanwhile in the case of F2 water collected at M3 (25.04.2013) reached the value 50.14 mg/L.

***Key words**: nitrate, well-water, pollution, methemoglobinemy.*

INTRODUCTION

Nowadays, protecting the quality of groundwater is a major challenge considering that it represents an important water source used intensively for domestic purposes and for drinking, as well. Undesirable pollutants in groundwater may be unacceptable due to their health effects and decrease of water quality (bad taste, unpleasant odour, aesthetic reasons). Among the contaminants of water, nitrate occupies an important place and is a common problem in many parts of the world and it is generated by agriculture (fertilizers and manure), domestic activities, municipal wastewater and sludge, septic systems. Nevertheless, the intensive use of nitrogenous fertilizers in agriculture is the main contributor to nitrate in water worldwide.
According to current legislation of the European Union such as Nitrate Directive (96/676/EEC), Drinking Water Directive (98/83/EC) and Romanian legislation (Law 458/2002), nitrate concentrations in water used for drinking purposes must not exceed the threshold of 50 mg/L. The WHO report of 2004 maintains that extensive epidemiological data support limiting the value of nitrate-nitrogen to 10 mg/L or as nitrate to 50 mg/L for human consumption (WHO, 2004).
Despite the European Community Directives there still exist regions in EU countries (Karavoltsos et al., 2008; Pele et al., 2010) and in other different parts of the world (Suthar et al., 2009) where nitrate concentrations exceed the value of 50 mg/L threshold.
Nitrates by themselves are not very toxic, but in human body are converted to nitrites due to the action of specific enzymes and, finally lead to carcinogenic products like nitrosamines and nitrosamides. The hazardous effect of nitrite is its ability to react with haemoglobin (oxyHb) to form methaemoglobin (metHb), according to reaction: $NO_2^- + oxyHb\ (Fe^{2+}) \rightarrow metHb\ (Fe^{3+}) + NO_3^-$ (Santamaria, 2006). Ferrous haemoglobin iron (II) is oxidized to ferric iron (III) which is not able to participate in oxygen transport (Bradberry, 2011). This manifestation is known as methemoglobinemy (blue baby syndrome) and is characterized by cyanosis which is the earliest clinical feature that occurs when approximately 15% of total haemoglobin is replaced by methaemoglobin (Bradberry, 2011). Methemoglobin levels between 35-40% cause headache, fatigue, dizziness and dyspnea,

meanwhile levels greater than 70% may be lethal (El-Husseini, 2010).
The link between nitrate-contaminated water and blue baby syndrome was firstly described by Hunter Comly who identified two infants that were fed with formulas prepared with nitrate rich well water (90 mg/L and 150 mg/L, respectively) (Knobeloch et al., 2000). There are studies that support the idea that the maximum contaminant level of 45 mg/L nitrate or 10 mg/L nitrate-nitrogen protects the babies from nitrate induced toxicity (Fan et al., 1987).
A national study developed in Romania during 2009 (Tudor et al., 2009) revealed that 58% from reported cases of infant methemoglobinemy appeared when consumed well water was 101-500 mg /L nitrate-contaminated. When nitrate levels were between 0-50 mg/L, it were reported 20% cases, meanwhile levels between 51-100 mg/L led to 10% cases.
In Romania, Bacau County during 2000-2005 period it were reported a number of 161 cases of methemoglobinemy (Popescu et al., 2008).
In Romania, during 1997-2004 were reported 2160 cases of methemoglobinemy at infants, the highest number of cases (453) being encountered in 2000. During 2005-2009, infantile methemoglobinemy cases decreased to 807, the highest number (243) being reported in 2006 and the smaller (89) in 2009 (Tudor et al., 2009).
Beside methemoglobinemy, there are reported many other negative effects produced by large quantities of nitrates: gastric cancer (Prakasa et al., 2000), central nervous system defects and some other cancers (Dourson et al., 1990; Gondim et al., 2005). Also, it has been demonstrated that nitrate can interfere with iodine retention by thyroid, resulting in hypertrophy of the thyroid (Vermeer et al., 1998).
Given that the presence of nitrates in groundwater is mainly perceived as a pollution problem and are harmful for human health, we have developed a monitoring study for six months (during 2012-2013) of nitrate contents from wells located in Fantanele, Prahova County. Other reason that sustained our research was that literature survey reveals lack of information regarding this subject related to Fantanele area.

MATERIALS AND METHODS

Studied area

Fantanele (Prahova) is geographically located at latitude (45.0075 degrees) 45°0'27.18" North of the Equator and longitude (26.3793 degrees) 26°22'45.74" East of the Prime Meridian on the Map of the world. It is located in the east of the county Prahova, in the contact area between of Mizil plain and Dealu Mare, wine-region. The position of Fantanele on Prahova district map is presented in Figure 1 and sampling points are detailed in Figure 2.

Figure 1. Position of Fantanele on Prahova map

Figure 2. Sampling points (F1, F2, F3, F4) located on Fantanele map

Sample collection
Water samples collected from four wells (labelled F1, F2, F3, F4) located in Fantanele, Prahova were analyzed. The samples were collected from a depth of 10-15 m at three moments: M1 (07.11.2012), M2 (18.02.2013) and M3 (25.04.2013). Selected wells represent sources of drinking water and are used also for domestic usage as cooking, washing, etc. From each well at every sampling moment were taken four samples. It were analyzed in totally 48 water samples in duplicates and the results are average of the determinations. All samples were collected in polyethylene bottles rinsed with sample water before collection and were carried to the laboratory where were stored at 4°C to avoid possible degradation of chemical species that are present in water. Chemical analyses were conducted within 48 hours of collection. The samples were allowed to stay until they reached room temperature before analysis.

Reagents
Analytical grade chemicals were used throughout the study without any further purification. Standard stock solution containing 1000 mg/L NO_3^- was prepared by dissolving 0.1631 g of KNO_3 in 100 mL distilled water, after drying in oven at 105°C for 6 hours. Working standards were prepared by diluting the stock solution.

Analytical method
Nitrate content in water samples was determined by spectrophotometric method. This was based on reaction between phenol-2,4-disulphonic acid and nitrate ions in basic medium. It was obtained yellow nitroderivatives that have absorption maxima at 420 nm. The calibration curve for nitrate was linear for studied concentration ranges (R^2=0.9987).

RESULTS AND DISCUSSIONS

Water collected at three different sampling moments from four wells distributed in the area of Fantanele village from Prahova County have been subject of analysis in order to determine nitrate levels. It has been analyzed 48 water samples in duplicates and the results presented in table 1 are average of the determinations.

Table 1. Nitrate concentrations for all analysed water samples

Well	Parameters	Sampling moment		
		M1 07.11.2012	**M2** 18.02.2013	**M3** 25.04.2013
F1	NO_3^-, mg/L	87.97	76.44	58.45
		85.44	77.42	62.23
		88.73	77.84	61.33
		86.22	74.54	59.79
	Av.± SD	87.09±1.52	76.56±1.46	60.45±1.67
	CV, %	1.74	1.91	2.76
F2	NO_3^-, mg/L	49.19	43.28	48.42
		47.23	44.28	51.29
		47.93	44.94	51.78
		50.06	45.30	49.08
	Av.± SD	48.60±1.26	44.45±0.88	50.14±1.64
	CV, %	2.60	1.99	3.27
F3	NO_3^-, mg/L	38.30	35.46	37.80
		38.88	36.48	38.38
		40.42	34.96	36.58
		39.97	35.20	37.39
	Av.± SD	39.39±0.97	35.52±0.66	37.53±0.75
	CV, %	2.47	1.88	2.01
F4	NO_3^-, mg/L	19.86	23.96	25.43
		21.56	25.09	25.20
		20.34	24.26	24.87
		19.56	25.29	25.93
	Av.± SD	20.33±0.88	24.65±0.64	25.35±0.44
	CV, %	4.33	2.60	1.75

Av.= average; SD= standard deviation; CV= coefficient of variation, %

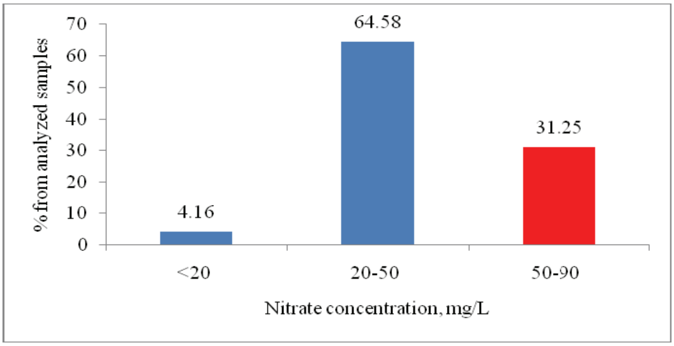

Figure 3. Quantification of nitrate levels

Analyses indicated that 31.25% from all water samples contain nitrate over admitted level imposed by EU and Romanian legislation (Figure 3) and it is recommended to find another water sources for drinking and further monitoring and surveillance of water from these points need to be enhanced. A small number of water samples (4.16%) contain nitrates close to 20 mg/L and there are no concerns regarding environmental or health issues.

The influence of well locations and sampling moments on the nitrate found levels were investigated (Table 2) and the conclusions are withdrawn below.

The average of the nitrate concentrations in different wells located in Fantanele village indicate significant differences, with concentrations that are over limit set by European (96/676/EEC; 98/83/EC) and Romanian (Law 458/2002) legislation, in the case of F1 (74.40 mg/L) and close to the threshold in the case of F2 (47.73 mg/L). The influence of the sampling moment on the recorded nitrate levels present significant differences with values that are exceeding the value 40 mg/L, but below the maximum admitted level.

The highest concentration (48.85 mg/L) was found in the water sample collected at moment M1 (07.11.2012).

The variance analysis indicates at the same sampling moment very significant differences determined by the location of the wells from which the samples were collected. The highest nitrate concentration (87.09 mg/L) was found in F1 sampling point at M1 sampling moment. Well F1 is situated in an area where are grown vegetables in intensive system. In the case of the same well (sampling point), the variance analysis shows for F1 and F3 significant differences between sampling moments, that suggesting variations of nitrate levels during evaluation period.

Even if for F1 are recorded decreasing values of nitrates (87.09 > 76.56 > 60.45 mg NO_3^-/L), all of them are over maximum admitted level at all sampling moments, this well representing the highest polluted point and the most dangerous drinking water source. This situation appeared as consequence of intensive agriculture practices and is associated with nitrogen fertilisation techniques adopted by well owner, a local vegetable producer. It is widely known that high nitrate levels are often associated with poorly constructed or improperly located wells (near septic fosses, greenhouses, etc). In addition, literature studies related to nitrate levels in water and methemoglobinemy (Fan et al., 1987; Tudor et al., 2009) must be considered a serious warning, it is recommended to suspend the consumption of water from this point. Also, nitrate levels must be monitored strictly and environmental risk produced by these species is mandatory to be estimated.

In the case of F2 and F4 wells there are not observed significant differences at moments M1 and M3, M2 and M3, respectively.

Nitrate concentrations for sampling point F2 are very close to the limit value (50 mg/L) and at M3 moment exceed very slightly this value (50.14 mg/L).

The lowest values for nitrate are encountered in F4 location, at M1 sampling moment the value was 20.33 mg NO_3^-/L.

Table 2. The influence of location (A factor) and sampling moment (B factor) on nitrate concentrations (mg/L) from water samples collected from Fantanele, Prahova County

B / A	M1 07.11.2012	M2 18.02.2013	M3 25.04.2013	Average A
F1	a87.09a	a76.56b	a60.45c	a74.70
F2	b48.60a	b44.45b	b50.14a	b47.73
F3	c39.39a	c35.53c	c37.54b	c37.49
F4	d20.33b	d24.65a	d25.35a	d23.44
Average B	48.85a	45.30b	43.37c	
Average A: DL 5%= 0.98* mg/L; DL 1%=1.41 mg/L; DL 0.1%=2.08 mg/L. Average B: DL 5%= 0.84* mg/L ; DL 1%=1.13 mg/L; DL 0.1%=1.52 mg/L. B ct. A var.: DL 5%= 1.55* mg/L; DL 1%=2.14 mg/L; DL 0.1%=2.97 mg/L. A ct. B var.: DL 5%= 1.68* mg/L; DL 1%=2.27 mg/L; DL 0.1%=3.05 mg/L.				

*Interpretation of the results were made according to DL 5%

CONCLUSIONS

Nowadays, in many regions nitrate concentrations in drinking water are close to levels which are unacceptable under current legislation of the European Union and this is due mainly to the intensive use of nitrogenous fertilizers in agriculture. The increasing interest has been observed essentially on account of environmental and human health concerns.

The aim of present survey was to evaluate nitrate levels in wells located in Fantanele village, Prahova County after six months monitoring. The results allowed us to withdrawn the conclusions that are discussed below.

Violations of the parametric value (50 mg/L) imposed by European and Romanian legislation were detected for a large number of water samples (31.25% from total).

A percent of 4.16% water samples contain nitrates close to 20 mg/L and there are no concerns regarding environmental or health issues.

Even if for F1 are recorded decreasing values of nitrates (87.09 > 76.56 > 60.45 mg NO_3^-/L), all of them are over maximum admitted level at all sampling moments and greater than any water sample analyzed in this study.

Well F1 represent the highest polluted sampling point and the most risky drinking water source, this situation occurring because of the nitrogen fertilisation techniques adopted by well owner, a local vegetable producer.

In the case of F2 sampling point, nitrate levels were close to maximum admitted level at M1 and M2 moments, meanwhile in the case of M3 the found value was slightly above limit value (50.14 mg/L).

Water samples collected from wells F3 and F4 contain nitrate species below 50 mg/L, the latter containing lower concentrations.

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