Risk assessment of population exposure to nitrates/nitrites in groundwater: a case study approach

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Abstract. Drinking water is a necessary element for vital activity of population and the presence of nitrates/nitrites in excess may lead to severe health problems. Nitrates/nitrites can reach groundwater as a consequence of agricultural activity (including excess application of inorganic nitrogenous fertilizers and manures) and from oxidation of nitrogenous waste products in human and animal excreta. This study is focused on the evaluation of water quality within a rural area from Romania - i.e. Branesti - which is included on the authorities list of vulnerable areas to nitrate pollution. The aim of the paper was to establish the exposure of population in a more accurate way by the correlation between the content of pollutants in water, characteristics of the population group at risk (e.g. body weight) and the reference dose established in available toxicological research studies. The results indicated frequent concentrations exceeding the limit for nitrates imposed by current regulations concerning the water quality for human consumption, as well as some cases when other chemical and/or bacteriological indicators exceeded the maximum allowable limit. According to the European Drinking Water Directive (Directive 98/83/EC), a need for further monitoring emerged in this rural area together with the need of increasing the awareness of the population towards the health risk posed by nitrate/nitrite contamination.
Key Words: hazard index, nitrates/nitrites, rural area, well water.

Introduction. The environment plays a significant role in people's health and well-being. The improvement of environmental quality and the reduction of effects on human health are of a paramount importance for the modern society and progress has been made in this sense, however many threats still remain (Deák et al 2015). In Romania, the physical, chemical and biological parameters of groundwater quality were altered as a result of pollution. Most of hydrological basins were altered due to nitrate contamination. The consequences of pollution are largely different, thus in some area the levels of nitrate are significantly higher than the allowable limit (National Environmental Protection Agency 2015).

The factors that affect the contamination of groundwater with nitrates are multiple and often additive, however, the major source is agriculture. Excessive application of fertilizers may cause severe damages as a result of nutrient leaching to the groundwater (Mateo-Sagasta & Burke 2012). There are also other agricultural sources of nitrates. Among these, one may mention manure, effluents from the silos and untreated or insufficiently treated wastewater resulting from farms, which have a significant nutrient content and their leakage may have severe consequences on water quality (Fleșeriu & Oroian 2010).

One example of areas vulnerable to nitrate contamination is Brănești – Muntenia Country. This area is located in the Southern part of Romania, on a relatively plain space, with low fragmentation, specific for this area. The characteristics of this area are influenced by the hydro-geographic factors and vegetation and in a less extent by the relief.

Taking into account the characteristics of the area, the main economic activity within the Brănești area was agriculture. However, over the last years, the agricultural surface decreased, as a result of construction projects.

Within the Brănești area, livestock was not the primary activity. Usually, the manure was used as fertilizer in agriculture. Brănești is located close to an important urban area - Bucharest, thus livestock is not the principal activity within the area.

The Brănești area was included by the national authority for the environment on the list of areas vulnerable to nitrate contamination by means of agriculture sources (EU Directive 91/676/CEE). The decision was made based on soil and land conditions, climate and hydrogeological conditions regarding the transfer of the nitrates to the groundwater, as well as on nitrogen balance (nitrogen from the manure – nitrogen from crops) (MO 1552/743/2008).

The effects of nitrates/nitrites on human health. Nitrates are soluble compounds that permeate from agricultural lands to groundwater. The groundwater remains contaminated for a long period of time even when the nitrate load decreases. Nitrate is the dominant compound in groundwater, while nitrite is usually present in low concentrations and is readily oxidised to nitrate (Popescu et al 2014; WHO 2011).

Nitrates (NO_3^-) are not considered to be toxic for humans, however nitrites (NO_2^-) resulting through the reduction of nitrates in human body and abiotic environments (wells, reservoirs, pipes) are toxic for humans, thus providing a secondary toxicity to nitrates (Mensinga et al 2013; Pele et al 2010).

As to the effects of nitrates on human health, two aspects must be taken into account, namely the occurrence of methemoglobinemia and cancer risk.

In the human body, nitrates are converted to nitrites through the activity of specific enzymes and they are further converted to carcinogenic nitrosamines. The main biological effect of nitrites is related to their role in oxidation of haemoglobin (oxyHb) to methaemoglobin (MetHb), which is unable to supply the tissues with oxygen. The effects of methemoglobinemia vary from cyanosis and cardiac arrhythmia to circulatory failure and effects on the central nervous system. When the methaemoglobin level is above 10%, methaemoglobinemia (blue baby syndrome) occurs, which leads to cyanosis and asphyxia. In this case, new born babies are highly at risk, as the oxidation of haemoglobin is rapid (Mensinga et al 2013; Renseigne et al 2007; Smical et al 2014; WHO 2011).

Nitrate contamination leads also to gastro-intestinal diseases, injuries of the digestive tract, indigestion, gastroenteritis, abdominal pains and diarrhoea. Moreover, the exposure to low concentrations of nitrate over a long period of time may lead to the occurrence of some cancers, such as cancer of the digestive system, stomach, oesophagus, lung, colon, bladder and ovaries cancer and non-Hodgkins lymphoma (Jamaludin et al 2013).

The most important route of exposure to nitrates/nitrites through diet is drinking water consumption. Threshold values were established for nitrates and nitrites. Within the European Union, the maximum allowable limit for nitrates is 50 mg/L, while for nitrites the limit is 0.5 mg/L (Figure 1) (Directive 98/83/EEC).

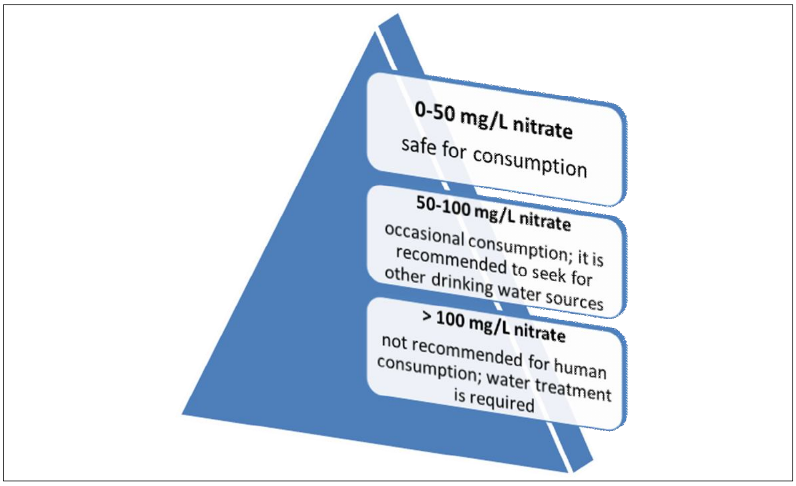

Figure 1. Nitrate levels in water and their safety to human consumption (Scăeteanu & Pele 2014).

Material and Method. In order to assess the exposure to nitrates/nitrites of the population from the Brănești area, a sampling and analysis program was established. 22 samples were taken from wells with depth up to 150 m, most part (68.2%) being taken from wells with depths of 10-20 m.

Standard sampling and analysis methods have been employed to determine the main quality parameters of the groundwater, namely the determination of the nitrates

(SR ISO 7890-3:2000), nitrites (SR ISO 6777-2002), oxidability (SR EN ISO 8467-2001) and pH (SR ISO 10523-2009).

Results and Discussion. The experimental results show frequent exceeding of the maximum allowable concentration (MAC) for nitrates, as shown in Figure 2. This is the case of 14 out of 22 wells, with exceeding amplitudes of 34.6-946.4%. However, as to other water quality assessment, they are within the regulated quality criteria (oxidability = 0.20-1.04 mgO_2/L compared to MAC = 5 mgO_2/L and respectively nitrites = 0.031 mgO_2/L compared to MAC = 0.5 mgO_2/L).

Significant levels of nitrates were recorded on every depth (0-50 m), except for two samples R1 and R2 (considered to be reference samples) taken from a depth of 100 and respectively 150 m. Table 1 shows the variation of nitrate concentrations in relation to the well depth. The results were analysed using simple statistical indicators of data variation, namely the mean value and the standard deviation.

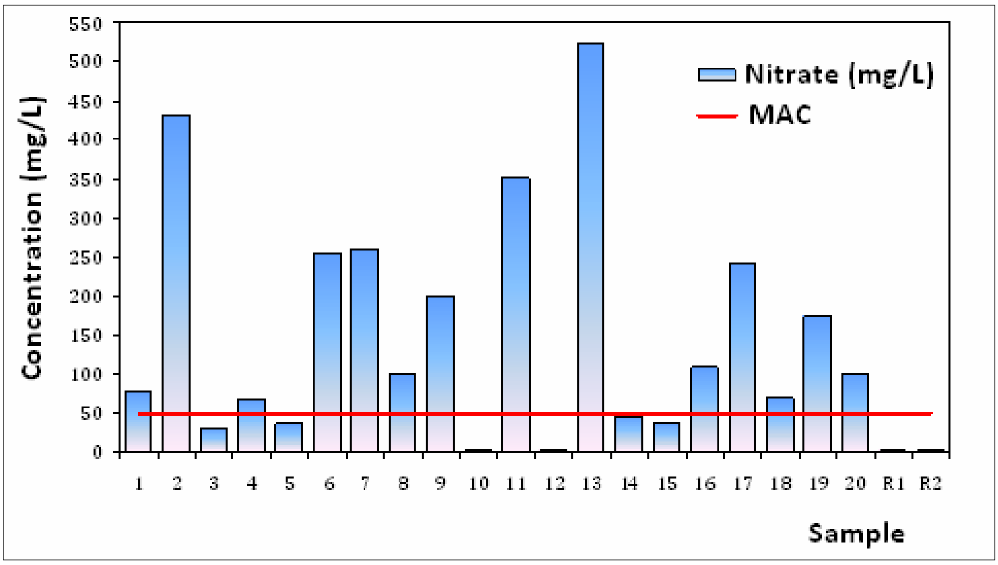

Figure 2. The variation of nitrates in the wells from the Brănești area.

Table 1

Distribution of nitrate concentrations in well water depending on the well depth

Well depth (m)	*Sample code*	*Nitrate (mg/L)*			
		Minimum value	*Mean value*	*Maximum value*	*Standard deviation*
< 10	2, 11	350.71	391.24	431.78	57.32
10 - 20	10, 13, 15, 16, 17	1.99	182.45	523.19	75.02
20 - 30	3, 4, 5, 6, 7, 8, 9, 14, 18, 19, 20	29.90	121.43	259.30	26.43
40 - 50	1, 12	2.16	39.89	77.62	53.36
100 - 150	R1, R2	1.06	1.26	1.46	0.28

As one may see, the mean values of nitrate concentrations decrease with well depth, indicating the existence of contamination from surface sources (e.g. the use of nitrogen-based fertilizers, improper septic tanks etc.).

The fluctuations of nitrate concentrations vary around the mean value between 14.6-41.7% for well depths of up to 50 m, indicating a very high variability of nitrate load.

As to the evaluation of groundwater quality in relation to their use (Figure 3), only 36.4% of the wells have nitrate concentrations below the limit of 50 mg/L, with water safe to be used for consumption by the entire population, including children and people having health problems. 22.7% of the wells have nitrate concentrations between 50-100 mg/L, with water to be used only in small quantities and only by the healthy population, while 40.9% of wells have nitrate concentrations above the limit that makes the water improper to be used for human consumption, with high risk for the population.

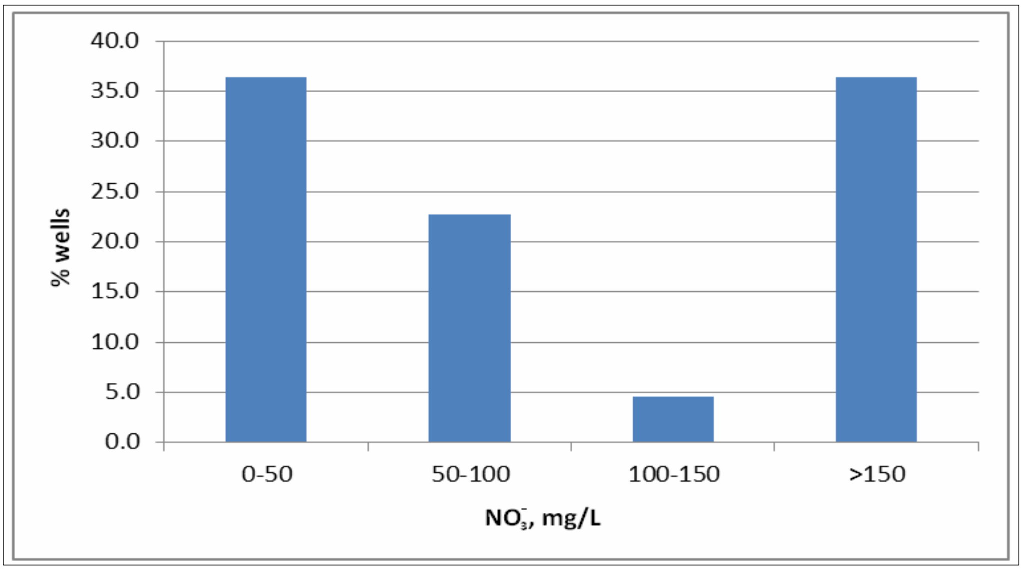

Figure 3. Wells distribution depending on the measured nitrate concentration.

As nitrates and nitrites may be present simultaneously in drinking water, World Health Organisation provides that a ratio (R) between the concentration of nitrates/nitrites and the maximum allowable limit needs to be computed. The relation between the nitrates and nitrites present in water must be described by R values below 1 (WHO 2011).

$$R = \frac{C_{NO_3^-}}{MAC_{NO_3^-}} + \frac{C_{NO_2^-}}{MAC_{NO_2^-}} \leq 1 \quad (1)$$

Starting from the experimental data, this ratio was computed for each sampling point. The values are shown in Table 2. The distribution of the R ratio in relation to monitored wells is depicted in Figure 4. The results show that 63.6% of the wells have R values above 1. Among them, more than 50% (57.1%) have R values above 3, indicating a high risk of exposure of human population to nitrates/nitrites.

Figure 4. The distribution of the R values depending on the monitored wells.

These results are confirmed also by the values of the hazard index (HI) (Table 2), which is used to assess the effects of substances that do not have carcinogenic effects. The index is computed as described by Jamaludin et al (2013) and it takes into account the quantity ingested daily by the human population that drinks nitrate-containing water directly. The daily ingested quantity (DIQ) is calculated using the expression (Jamaludin et al 2013):

$$DIQ = \frac{C \times IQ}{BW} \tag{2}$$

where:
C – nitrate concentration in water (mg/L);
IQ – water quantity ingested daily by a person (L/day);
BW – body weight (kg).

The hazard index (HI) is the ratio between the daily ingested quantity (DIQ) and the reference dose (RfD) (Jamaludin et al 2013):

$$HI = \frac{DIQ}{RfD} \tag{3}$$

For computing this index, a mean water consumption of 2 L/day and a mean body weight of 70 kg were considered. The reference dose for nitrates is 1.6 mg/(kg bw·day) (cfpub.epa.gov).

Results show that 63.6% of the wells have hazard index values above 1, proving there is the risk of negative effects to occur on human health following the ingestion of nitrate-containing water.

Table 2

Values of R and hazard index (HI) for all sampling points

Sampling point	*R*	*HI*
1	1.55	1.39
2	8.64	7.71
3	0.60	0.53
4	1.35	1.20
5	0.73	0.65
6	5.10	4.55
7	5.19	4.63
8	2.03	1.76
9	4.02	3.58
10	0.05	0.04
11	7.02	6.26
12	0.05	0.04
13	10.48	9.34
14	0.91	0.81
15	0.74	0.65
16	2.17	1.93
17	4.87	4.33
18	1.37	1.22
19	3.50	3.12
20	2.02	1.80
R1	0.03	0.02
R2	0.05	0.03

Conclusions. The major concerns about the health related to the environment are our common goal and the increase of life quality represents the concept which stands for the progress of the modern mankind.

The effects of nitrates/nitrites on human health and the high per cent of population that use untreated drinking water, directly from groundwater sources imposed the necessity to assess the risk of exposure of human population to nitrates/nitrites.

This paper focused on highlighting the risk associated to nitrate contamination of groundwater by applying an assessment system on a particular case – the Brănești area – Muntenia Country (Romania), included as a vulnerable area to nitrate contamination from agricultural sources, according to EU Nitrates Directive Nitrates are easy to be analysed and high contents of nitrates are an indicator of agriculture's impact on groundwater quality. However, high levels of nitrates may also be due to livestock and sanitation systems.

The approach suggested by this paper takes into consideration the key elements of exposure to nitrites/nitrates, namely: mean groundwater consumption for drinking purposes, the load of contaminants, body weight, all in relation to the reference dose at which some toxic effects may occur in humans.

The risk assessment of population exposure to nitrates/nitrites in the agricultural areas was achieved by means of an index (R), by addition of the ratio between the concentration of each contaminant (nitrates and nitrites) and the maximum allowable concentration and comparing with 1. Also, a hazard index (HI) was computed as the ratio between the daily intake of nitrates and the reference dose.

The results of this study have revealed a high risk of exposure to nitrates/nitrites as 63.6% of wells had R index and hazard index values above 1. Taking into account the fact that most of drinking water used by the population from the Brănești area is provided from wells with low depths (up to 20 m), their location in the vicinity of the agricultural land and the high per cent of bacteriological contamination (approximately 60%), one may consider that the local population is exposed to the risk of waterborne diseases.

The suggested approach regarding the risk of exposure to nitrites/nitrates based on a hazard index may be extrapolated to large human agglomerations.

This approach may be used by the local and national authorities as a tool for the sustainable management of water resources in their attempts for reducing direct and indirect contamination of water resources with nitrates originating from agriculture, for protecting human health and aquatic ecosystems and for ensuring an efficient use of water resources.

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