# STUDIES REGARDING NITROGEN POLLUTANTS IN WELL WATERS FROM ROMANIA

## MARIA PELE, GINA VASILE, MIHAELA ARTIMON

University of Agronomic Sciences and Veterinary Medicine of Bucharest

**Keywords:** nitrate, nitrite, water, health, methemoglobinemia

#### **Abstract**

The nitrate contamination of ground water is a serious threat to public health and high nitrate levels can cause. The aim of our research was to evaluate nitrate and nitrite concentrations in well water from Matca (Galaţi), Săhăteni (Buzău), Brăneşti (Ilfov) and Clinceni (Ilfov) localities. The lowest nitrate level was recorded in Clinceni. Nitrite levels were generally low, except one water sample from Matca (1.13 mg/l).

## INTRODUCTION

Water quality has become an increasing, environmental and social constraint for modern society. Contamination of drinking water by nitrate is usually associated with the pollution resulting from human activities, especially from agriculture. Over time, due to great solubility, nitrates can accumulate in groundwater that may then be used as a drinking water supply.

The nitrate in itself is not very toxic. Inside the human body, nitrates are converted to nitrites, due to the action of specific enzymes and, in the end, converted to nitrosamines that generate cancer. The hazardous effect of nitrite is its ability to react with haemoglobin (oxyHb) to form methaemoglobin (metHb) and nitrate [10], according to reaction:  $NO_2^- + \text{oxyHb} (Fe^{2+}) \rightarrow \text{metHb} (Fe^{3+}) + NO_3^-$ .

Methemoglobinemy is also known as "blue baby syndrome" because its first manifestation is a bluish colour of the infant's skin. For example, in the counties where the villages from where we collected the samples there were, in 2007, 11 baby blue syndrome cases in Buzău County, 2 in Galați County and 2 in Bucharest.

There are also reported other negative effects produced by large quantities of nitrates, as follows: gastric cancer [8], central nervous system defects and some other cancers [1, 7]. A Danish research group has shown that nitrate can interfere with iodine retention by thyroid, resulting in the hypertrophy of the thyroid [11]. There is a positive association between nitrates in drinking water and non-Hodgkin lymphoma and colorectal cancer [5].

Nowadays, nitrate concentrations in water are close to levels which are unacceptable under current legislation of the European Union such as Nitrate Directive [3] and Drinking Water Directive [2].

Toxicity and physiological effects of excess of nitrates and nitrites in water are well known and have been reported in many publications [4, 6, 9].

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 [12].

We chose to analyze the water from a village with intensive agricultural practices (Matca), a viticulture area (Săhăteni), an industrial area (Brăneşti) and a village with no intensive agriculture (Clinceni).

# MATERIAL AND METHODS

The well water collected from different sources from Matca, Săhăteni, Brăneşti and Clinceni villages were analyzed. The samples analyzed of well water collected from a depth of 5-60 m. All samples were collected in polyethylene bottles and carried to the laboratory where were stored at 4°C.

The nitrate content in water samples was determined through two analytic methods: spectrophotometric (phenoldisulphonic method) and ionometric, using nitrate-selective electrode. The obtained results using these methods were similar so we used as the final results the media of results obtained by the two methods. All chemicals used were of analytical reagent grade. The calibration curves for nitrate and nitrite were linear for studied concentration ranges. The nitrite levels were determined spectrofotometrically using Griess reagent.

Spectrophotometric measurements were carried out using Metertek SP830 Plus apparatus, meanwhile ionometric measurements were performed with a Metler Tolledo ionometer with a nitrate selective electrode.

# RESULTS AND DISCUSSION

For experiments we have selected four villages with different main activities and located in the south - east of the country, namely Clinceni (Ilfov County), Brăneşti (Ilfov County), Săhăteni (Buzău County) and Matca (Galați County).

The localities Clinceni and Brăneşti are situated in the Romanian Plain to one side, and another of the capital Bucharest, Clinceni 16 km west and Brăneşti 18.9 km the east. The localities are situated as folows: Săhăteni at 107.1 km north and Matca on 240.9 km north-east from Bucharest. Matca is located in the Galați County and is famous for the vegetables (especially tomatoes) grown especially in protected area. It is quite sure that farmers use fertilizers and, as consequence, it is important to determine the levels of nitrate and nitrite contaminants in well water that is used by inhabitants for drinking and cooking.

Table 1
Analytic results for analyzed well water samples from Clinceni

No.	рН	Nitrate, ppm (MAL=50 ppm)	Nitrite, ppm
1	7.02	52.08	< LD
2	7.00	50.03	< LD
3	7.15	44.70	< LD
4	7.16	66.58	0.17
5	7.02	45.42	0.13
6	6.90	45.79	0.02
7	7.03	45.06	< LD
8	7.02	48.64	0.17
Average	7.03	49.78	-

Table 2
Analytic results for analyzed well water samples from Brănești

No.	pН	Nitrate, ppm (MAL=50 ppm)	Nitrite, ppm
1	7.92	<ld< td=""><td>0.28</td></ld<>	0.28
2	7.97	<ld< td=""><td>0.16</td></ld<>	0.16
3	7.98	<ld< td=""><td>0.20</td></ld<>	0.20
4	8.32	29	0.11
5	6.98	314	0.01
6	6.97	272	0.03
7	6.92	288	0.16
8	6.79	493	0.01
9	6.92	449	0.03
10	7.30	< LD	0.01

The main activities in the four communes are quite different. Taking into account these activities, we can presume that the smallest pollution with nitrates and nitrites has to be in the two villages nearest Bucharest: Clinceni and Brăneşti. Nevertheless Brăneşti had a non-ferrous industry represented by Neferal enterprise even if this factory is practically not working today.

Water samples were taken from 7-10 wells distributed in every village so that they can cover relatively the entire area. Results are presented in Tables 1-4.

Table 3
Analytic results for analyzed well water samples from Săhăteni

No.	рН	pH Nitrate, ppm (MAL=50 ppm) Nitrite, ppm	
1	7.44	403.1	<ld< td=""></ld<>
2	7.25	270.4	<ld< td=""></ld<>
3	7.40	101.6	<ld< td=""></ld<>
4	7.22	222.9	0.07
5	7.53	82.0	<ld< td=""></ld<>
6	7.07	48.2	<ld< td=""></ld<>
7	7.55	322.2	<ld< td=""></ld<>
8	7.70	540.8	<ld< td=""></ld<>

Table 4
Analytic results for analyzed well water samples from Matca

No.	рН	Nitrate, ppm (MAL=50 ppm)	Nitrite, ppm
1	7.54	149	0.01
2	7.04	182	1.13
3	7.40	153	0.51
4	7.34	452	0.02
5	7.66	311	0.33
6	7.46	358	0.08
7	7.23	352	0.31

Analysing the results (Tables 1-4), it can be concluded that the water samples from Clinceni contain the lowest levels of nitrate and nitrite. However, to visualize clearer the nitrate levels we represented these results graphically against the MAL in the Figure 1.

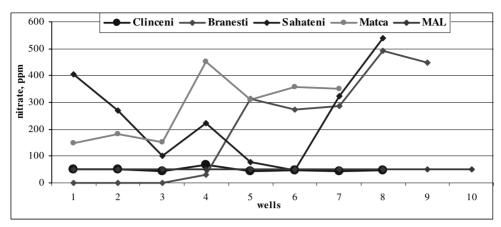


Fig. 1. Comparative data regarding nitrate contents in wells of the four villages

The data show us that, although nitrate pollution from agriculture has received a lot of attention, many private wells have been polluted with nitrates due to misuse of fertilizer on lawns that were close to shallow water wells.

From the graphic presentation, we can see clearly that in the villages near Bucharest, there are fountains with a low content of nitrate near the maximum permitted (MAL) - in Clinceni 100% and 40% in Brănești. At the same time, in the two localities, Săhăteni and Matca, with mainly agricultural activities, the pollution with nitrates is practically 100% above MAL.

Also, as we assumed, because of intensive cultivation of vegetables, in fields, solariums and greenhouses, in the village Matca pollution with nitrates is greater. In addition, if in communes Săhăteni and Brăneşti pollution is range from fountain to fountain with extreme values, the content near the maximum value admitted up to 10 times higher in the wells of Săhăteni, in Matca the smallest value was found 3 times MAL. Thus, if we consider that a people of 60 kg drink 2 liters of water per day, only in this way, in Matca, the consumer should exceed the maximum admitted for human consumption. Regarding the content of nitrites, we can say that for the wells in Săhăteni values obtained are not conclusive, they could only be errors of analysis.

For wells in other villages, taking into account the fact that legitimate nitrites should miss in drinking water, the values obtained may be worrisome to the wells from Matca village and to limit for other villages.

Water contamination by nitrates is one of the problems associated with vegetable growing and agriculture, generally. That is due, among other things, to the fact that nitrates are highly soluble and migrate easily into ground water through soil. It is nonetheless difficult to establish a link between nitrogen supply and water pollution. The leaching of nitrates also depends on geological, climatic and

biological factors. Nitrates can be de-nitrified by microbes, however. Despite these phenomena, over-use of fertilizers always increases the nitrate level of water.

This could be the explanation of the high levels of nitrates in the water well tested in Săhăteni and Matca in particular. In addition the high levels of nitrites raise a lot of problems because these levels together nitrates ones classifies analyzed water between the most dangerous ones.

Regarding the village Brăneşti, likely pollution by nitrates is due mainly of nonmetals industry, even if this production is today practically zero. Only farming household does not explain the high pollution in some wells.

### CONCLUSIONS

- 1. Analyzing the results, it can be concluded that, excepting samples from Clinceni village, almost all water samples exceed the maximum admitted level (MAL = 50 ppm) and endanger human health.
- 2. Farmers apply nitrogen fertilizers to increase plant yield, but too often fertilizers are applied in excess quantities and in inefficient ways. So, they have to use controlled quantities of nitrogen fertilizers.
- 3. The analysis of water samples from the sources of Săhăteni, Matca, Brăneşti and Clinceni villages that were investigated were alarming, from the point of view of nitrate concentrations.
- 4. The graphic representation of the nitrate levels in water (Figure 1) shows that all water samples have exceeded the MAL, 50 ppm. Also, nitrite is present in well water from the villages with agriculture as main activity but however in small quantities.
- 5. Because the level of nitrates in drinking water exceeds the safe limits for many wells, the people have two basic choices: to obtain an alternate water supply or to use some type of treatment to remove the nitrate-nitrogen.

#### REFERENCES

- Dourson M., B. Stern, S. Griffin, K. Baily, 1990. Impact of risk-related concerns on U.S. Environmental Protection Agency programs. Nitrate Contamination. NATO ASI Series, Vol. G30, Eds. I. Bogardi and R.D. Kuzelka, Springer Verlag, Berlin Heidelberg (pp. 477-487).
- 2. EEC Council Directive on the quality of water for human consumption. (80/778/EEC). Official J. European Communities L, 229, 11, 1980.
- 3. EEC Council Directive Concerning the Protection of the water against pollution caused by nitrates from agricultural sources. (96/676/EEC). Official J. European Communities L., 375, 1/5, 1991.

- 4. El-Garawany M.A., F.N. Assubaie, 2005. *Determination of nitrate and nitrite levels in soil and groundwater in Al Hassa, Saudi Arabia*. Scientific Journal of Kin Faisal University, 6(2) (pp. 87-97).
- 5. Gulis G., G. Czompolyova, J.R. Cerhan, 2002. An ecologic study of nitrate in municipal drinking water and cancer incidence in Trnava District. Slovakia. Environmental Research, 88(3) (pp. 182-187).
- 6. Jussara A. de M.Gondim, Rina L.da S. Medeiros, Zacheu L. Santos and Robson F. de Farias, 2005. *Is there, indeed, a correlation between nitrite and nitrate levels in drinking water and methemoglobinema cases? (a study in Brasil)*. Bulletin of Chemists and Technologists of Macedonia, 24(1) (pp. 35-40).
- 7. Mirvish S.S., 1991. *The significance for human health of nitrate, nitrate and N-nitroso compounds. Nitrate Contamination.* NATO ASI Series Vol. G30, Eds. I. Bogardi and R.D. Kuzelka, Springer Verlag, Berlin Heidelberg (pp. 253-265).
- 8. Prakasa R. and K. Puttanna, 2000. *Nitrates, agriculture and environment*. Curr. Sci., 79 (pp. 1163-1168).
- 9. Sadeghi A., J. Nouri, F.M. Mohammadian, A.A. Babaie and F. Mohsenzadeh, 2006. *Nitrite and nitrate in the municipal drinking water distribution system.* International Journal of Agriculture and Biology, 8(5) (pp. 706-707).
- 10. Santamaria P., 2006. *Nitrate in vegetables-toxicity, content, intake and EC regulation*. J. Sci. Food Agric. 86 (pp. 10-17).
- 11. Vermeer I.T.M., D.M.F.A. Pachen, J.W. Dallinga, J.C.S. Kleinjans, 1998. *Volatile N-Nitrosamine formation after intake of nitrate at the ADI level in combination with an amine-rich diet.* Environ. Health Perspect, 106 (pp. 459-463).
- 12. WHO, Guidelines for drinking water quality, Geneva, 2004, vol. 1 (pp. 191).