DETERMINATION OF NITRATE AS A SOURCE OF RISK FOR HUMAN IN GROUNDWATERS

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ABSTRACT

We monitored the content of nitrates (NO$_3^-$) in samples taken from individual groundwater resources in the cadastral territory of the city of Nitra and Zobor (Svorad’s spring, spring Sindolka and spring Buganka), also used for human consumption in the period 2012 - 2014. NO$_3^-$ contents were assessed by Photocolorimetric method. We also evaluated the results achieved in relation to the current legislation in this area.

The results of the performed analyzes throughout the period shows that the average concentration of NO$_3^-$ represented in the samples of water from Svorad’s spring was 12.6 mg.dm$^{-3}$, spring Sindolka 38.0 mg.dm$^{-3}$ and spring Buganka 103.1 mg.dm$^{-3}$.

The nitrate concentration did not exceed the limit value in samples from spring Sindolka and spring Svorad. Spring Buganka had this value exceeded by up to 100 % of cases. We do not recommend to use water for human consumption from spring Buganka based on the measured values.

Keywords: Groundwater, quality, nitrates, city of Nitra

INTRODUCTION

The origin, evolution and physical - chemical characteristic of the water cover of Earth - hydrosphere is closely linked with the development of its other parts. Between the earth’s mantle and the earth's crust, the hydrosphere, atmosphere, lithosphere and biomass occurs constant exchange of water (Wen Ling, Saintillian, Rogers, 2009). that causes changes its chemical and isotopic composition (Harris, Hobbs, Higgs, 2006). This is called hydrological cycle, which represents a stable water cycle on Earth. An indispensable part of the hydrological cycle and a key element in maintaining wetlands and flows in rivers during dry periods is groundwater. It is the part of subsurface water, which forms a continuous level in the ground and the part that fills the cavity of water-bearing rock irrespective of whether it generates or does not generate continuous level (Bekes, Moller, 2009). According to the mineralization (total dissolved solids) and gas content are divided groundwaters to normal and mineral.

Processes determining qualitative and quantitative composition of natural waters are the nature of the physical, chemical and biochemical (Gemitz, Stefanopoulos, 2011). Furthermore, the nature of natural waters are also affected by climatic conditions, the overall landscape, density and nature of the settlement and so on. (Turnbull, Jin, Clancy, 2007).

We use groundwaters for drinks water in our area. It is representing almost 82,2 % and so on. Furthermore, the nature of natural waters are also affected by climatic conditions, the overall landscape, density and nature of the settlement and so on. (Turnbull, Jin, Clancy, 2007).

Nitrates are in the human body after oral intake rapidly and completely absorbed in the upper small intestine and rapidly distributed in the body. About 25 % is excreted into the saliva, which is partially reduced to nitrite by oral microflora. Bacterial nitrate reduction (NO$_3^-$) to nitrite (NO$_2^-$) may be configured in other parts of the digestive tract other than the stomach, where it occurs only at a reduced pH (Abern, Wise, Wright, 2004) by the equation:

NO$_3^-$ + H$_2$O → H$_2$NO$_2^-$ → NH$_2$OH → NH$_3$ + NH$_3$

MATERIAL AND METHODS

Due to the fact that there are currently no available literature and data sources with a specific analytical outputs to the population in terms of quality ground water resources in the city of Nitra, we mentioned the issues addressed in our work. Aim of this study therefore was to obtain knowledge about the long-term quality of selected groundwater resources used for human consumption and for drinking purposes in the cadastral area of the city Nitra and Zobor, in terms of nitrate levels in the period 2012 - 2014 with the evaluation of their potential risk to the population. As a source of groundwater were evaluated:

1. Svorad’s spring ($\phi = 48020'47'', \lambda = 18005'27'') located in the woods, on a hiking trail Zobor and Svorad’s cave under the hill of Zobor (586.9 m asl). It is situated at the highest altitude (305 m asl) from all sources in the cadastral area Zobor. It is a tourist places frequently visited throughout the year.

2. Spring Sindolka ($\phi = 48019'50'', \lambda = 18005'00'') is situated on Orava street in Nitra. From the assessment of groundwater resources is at the lowest altitude of 158 m above sea level This spring is a significant of power flow throughout the year. People often use this water to irrigate their crops and also for direct consumption. In the surrounding area of the spring there are several potential polluters (Secondary school for agriculture, road, proximity to agricultural use of land and gardens).

3. Spring Buganka ($\phi = 48019'50'', \lambda = 18006'04''), located on Panská dolina street close to the restaurant. It is located on private land at an altitude of 214 m above sea level, but access to it is enabled. Water quality is threatened mainly fertilization and used in the surrounding garden and transportation.
We took water samples intended for chemical analysis into polyethylene sample containers of 500 cm$^3$, which we first rinsed with water and then filled up to the cap. The total nitrate content were assessed by Photocolorimetric method using UV mini 1240 PL.

**RESULTS AND DISCUSSION**

We collected and defined the content of nitrate (NO$_3^-$) in groundwater samples from their individual sources monthly in the period 2012 - 2014. The results were processed in Table 1 which shows that:

The measured values of nitrate in Svorad’s spring were ranged from 12.0 mg dm$^{-3}$ (July) to 15.8 mg dm$^{-3}$ (January) during 2012. According to the literature, the toxic effects (particularly in children) depend mainly on the reduction of the nitrite and the subsequent reaction of nitrite with hemoglobin. Nitrate of occurrence of foodborne methemoglobinemia and oxidation of Fe$^{2+}$ to Fe$^{3+}$ in the conversion of hemoglobin (Hb) to a dark brown methemoglobin (MetHb), which is unable to transport oxygen (Savino, Maccario, Guidi, 2006).

We found the minimum content of nitrates 6.7 mg dm$^{-3}$ (March) up to a maximum of 15.8 mg dm$^{-3}$ (July) in 2013. We had the lowest value recorded in February (10.4 mg dm$^{-3}$), while the maximum in April - 16.3 mg dm$^{-3}$ NO$_3^-$ in 2014.

According to the authors (Erkekoglu, Baydar, 2009), to give the nitrate of alimentary methemoglobinemia apply particular factors, such as water with an inadmissible amount of nitrate, the pH of gastric juice, bacterial flora of the upper GIT reducing nitrates, the absorption of nitrate from the gastrointestinal tract into the blood, influence enzyme system reducing methemoglobin to hemoglobin and possible influence of fetal hemoglobin.

The average nitrate content found throughout the period 2012 amounted in water spring Svorad in 2013 and by 56.3 mg dm$^{-3}$ in 2014. If we try to show in Figure 10, it is associated with their relatively rapid liquidation of the kidney. It is known that up to 12 hours the kidneys excreted about 80 % of the nitrate in middle population and about 50 % in the elderly (Erkekoglu, Baydar, 2009). For the permissible daily doses or with prolonged intake does not cause any disturbance to health, is the FAO / WHO established a daily amount of nitrate equivalent to 5 mg NaNO$_3$ per 1 kg of body weight (FAO / WHO, 1985).

The average nitrate content found in 2012 and 2013 were in water samples from the source spring Sindolka more or less balanced by a concentration. It represented 39.1 mg dm$^{-3}$ in 2012. It was 39.9 mg dm$^{-3}$ in 2013 and a slight decrease to 34.7 mg dm$^{-3}$ during the period of 2014.

It was exceeded in samples of water from spring Buganka in 2014. If we try to show in Figure 10, it is associated with their relatively rapid liquidation of the kidney. It is known that up to 12 hours the kidneys excreted about 80 % of the nitrate in middle population and about 50 % in the elderly (Erkekoglu, Baydar, 2009). For the permissible daily doses or with prolonged intake does not cause any disturbance to health, is the FAO / WHO established a daily amount of nitrate equivalent to 5 mg NaNO$_3$ per 1 kg of body weight (FAO / WHO, 1985).

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The minimum measured content of nitrates was in October (98.9 mg dm$^{-3}$) to a maximum of 146.3 mg dm$^{-3}$ in January and December in samples taken from spring Buganka during the year 2012. These high concentrations of nitrates, which reduce to nitrates, excluding formation of methemoglobinemia, may cause the reaction of the secondary and tertiary amines which are present in virtually everywhere (vegetables, meat, milk and cereal products, eggs, beer, wine, medicines, pesticides, etc.) the formation of nitrosamines (Muro, Stocki, Roback, 2005).

The content ranged from 69.1 mg dm$^{-3}$ in June to 95.8 mg dm$^{-3}$ in January, in the evaluated year 2013. It was found that nitrosamines are able to induce tumor formation in all organs of the body, particularly the gastrointestinal tract, urinary bladder and lymphatic system except bones. Regular intake of vitamin C can be prevented from carcinogenic nitrosamines, and on the other hand, chronically low levels of L-ascorbic acid may increase the disposition (EFSA, 2010).

We had a maximum nitrate levels - 135.8 mg dm$^{-3}$ measured in January and the minimum - 88.9 mg dm$^{-3}$ in October in the last year of assessment (2014). It can be stated that in terms of toxicological and health assessment is a specific risk group population of children in connection with such detected high levels of NO$_3^-$ in the samples.

The measured concentrations ranged from a minimum of 24.3 mg dm$^{-3}$ (April) up to the maximum established in March (44.4 mg dm$^{-3}$ NO$_3^-$) in 2014. Such concentrations are a result of increased agricultural activity or arise nitrification activity of the bacteria. Important role in fluctuations in the concentration of NO$_3^-$ have on the other hand also seasonal changes in temperature, which in practice excludes biochemical reactions in the winter.

We know from the literature (Šindelářová, 1985) that in the plants accumulate in higher concentrations when the plants cannot use nitrogen. The cause can be improper temperature, humidity and especially the light conditions. An example can be greenhouse spring vegetables, containing up to several fold higher level of nitrates as a field or garden vegetables (Valahšiková, 2005).

Nitrate in low concentrations and in non-reducing environment are not for a healthy adult harmful and therefore we can not talk about their primary toxicity.
recorded the highest average, that exceedence), the maximum deviation was recorded in January and July, and on the other hand, the minimum in April and November as documented in chart 1.

**Chart 1** Exceeding the maximum limit on the NO$_3^-$ in water from spring Buganka in 2014

![Graph showing exceeding the maximum limit on NO$_3^-$ in water from spring Buganka in 2014.](image)

Mentioned could be due mainly by the position of spring in relation to fertilization used in the surrounding garden and seductive depth of the collector source. Therefore, the use of water for human consumption from the spring Buganka in terms of the nitrate content is not recommended for drinking.

**CONCLUSION**

We were assessed the content of nitrates (NO$_3^-$) in water samples taken from groundwater resources in the administrative territory of the town Nitra and Zobor, which are still used for human consumption. We obtained from the 108 experimental results that:
The total content of nitrates which got into the ground water impact the environmental pollution, agricultural activity or arise nitrification activity of the bacteria ranged on average throughout the period in samples from Svorad's spring from 10.9 to 13.7 mg dm$^{-3}$, from the spring Šindolka from 39.1 to 39.9 mg dm$^{-3}$ and spring Buganka from 79.1 to 124.2 mg dm$^{-3}$.

Absorption of nitrate (NO$_3^-$) in the human body occurs in the upper small intestine. They are rapidly distributed in the body and then reduced to nitrite (NO$_2^-$), which are substantially toxicologically dangerous as they react with the hemoglobin and the formation occurs of nitrate alimentary methemoglobinemia. Besides formation of methemoglobinemia the reduced nitrites by reacting with secondary and tertiary amines, which are present almost everywhere (vegetables, meat, milk, cereal products, eggs, and a.) creation of risk nitrosamines.

When comparing the measurement results with current legislation in the given field and the highest limit value nitrate content in water intended for human consumption, we found that the limit was exceeded in samples taken from spring Buganka, a total of 36 times throughout the period 2012-2014. Samples of water from the spring Buganka it was on average up to 74.2 mg dm$^{-3}$ in 2012. This value was exceeded in samples of spring Buganka 29.1 mg dm$^{-3}$ in the period 2013 and by 56.3 mg dm$^{-3}$ of NO$_3^-$ in 2014.

Based on this fact in terms of establishing the overall average of the nitrate content, groundwater from a given spring Buganka that has failed in the high limit value in this parameter for drinking purposes is not recommended.

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