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Dedicated to Professor Emil Cordoș on the occasion of his 80th anniversary

HEALTH RISK ASSESSMENT ASSOCIATED WITH NITROGEN COMPOUNDS CONTAMINATED DRINKING WATER IN MEDIAS REGION

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ABSTRACT. High concentrations of nitrogen compounds in drinking water may cause negative health effects. The aim of the present study was to assess the content of nitrogen compounds namely, nitrates, nitrites and ammonium in drinking waters from Medias region (Medias, Copsa Mica towns and Tarnava village) and to investigate the health risk associated with the consumption of drinking water contaminated with these compounds. The health risk was calculated using chronic daily intake, hazard quotient and total hazard quotient. High concentrations of nitrite, nitrate and ammonium were found, at least one of the nitrogen compounds exceeding the maximum allowable concentrations (0.5 mg/L NO_2^-, 0.5 mg/L NH_4^+, 50 mg/L NO_3^-) in about half of the analysed samples. Generally, the chronic daily intake values were lower for nitrite and ammonium than for nitrate. The hazard quotients for nitrate were higher than the critical unity value, indicating that the consumption of contaminated waters from Tarnava village and Medias town may cause potential non-carcinogenic risk. Moreover, for the same samples, the total hazard quotients were higher than the critical unity value, suggesting that potential adverse health effects may appear after the consumption of drinking water.

Keywords: *drinking water source, nitrite, nitrate, ammonium, chronic daily intake, hazard quotient, total hazard quotient*

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INTRODUCTION

Ensuring access to adequate supply of safe drinking water is a major challenge all around the world. Groundwater is an important drinking water source, thus its quality protection is mandatory.

The presence of undesirable contaminants, such as nitrate (NO_3^-), nitrite (NO_2^-) or ammonium (NH_4^+) may decrease the drinking waters quality by the unpleasant odour and taste and possible adverse health effects. The main exposure pathway to nitrogen compounds is the ingestion of water or foodstuffs that contain high levels of nitrates, nitrites and ammonium [1-5]. In the human body, NH_4^+ is oxidised to NO_3^-, while NO_3^- under the action of specific enzymes is converted into NO_2^- that further reduces into N-nitroso compounds (nitrosamides, nitrosamines), with potential carcinogenic effects. Furthermore, the gastro intestinal tract and saliva are favourable environments for the conversion of nitrogenous compounds into NO_2^- and NO_3^- [6, 7, 8]. The NO_2^- reacts with the haemoglobin which is converted into methemoglobin, which stopes carrying oxygen to all cell tissues [5, 9-10]. The most common effects that appear in case of bottled-fed infants are “blue-baby syndrome” or methemoglobinemia and developmental toxicity, which represent the main health concern regarding the NO_2^- and NH_4^+ concentrations [2, 6, 7, 11]. Moreover the high concentrations of NO_3^- in the drinking water may increase the risk for bladder cancer [12].

Although the occurrence of NO_3^-, NO_2^- and NH_4^+ is part of the nitrogen cycle, the highest concentrations are generated by the anthropogenic activities. The agriculture (livestock, use of fertilizers) and the inadequate sewage management in industrial and household activities are considered the most important diffuse or non-point sources of NO_3^-, NO_2^- and NH_4^+ contamination [1-4, 8]. The main natural source of nitrogen compounds is the anaerobic organic material decomposition [8, 9, 13]. Several studies showed that the key source of high NO_3^-, NO_2^- and NH_4^+ levels in drinking-water are the sewage effluents runoff from household and agricultural activities [2, 13-16]. In Romania, high concentrations of NO_3^- and NO_2^- in drinking waters, which exceed the corresponding maximum allowable concentrations (*MACs*) were also reported [16-19]. Studies showed possible connection between the high concentrations of nitrogen compounds and the location of the well waters close to domestic and agricultural sources [19].

To prevent these health threats, European legislation and World Health Organization guidelines set maximum allowable concentrations for the NO_2^- (0.5 mg/L), NH_4^+ (0.5 mg/L) and NO_3^- (50 mg/L) in drinking water [2, 20-22]. The health risks associated with contaminated drinking water consumption can be assessed using mathematical indices, such as chronic daily intake (*CDI*), hazard quotient (*HQ*) and total hazard quotient (*THQ*).

The aim of the current study was to assess the NO_3^-, NO_2^- and NH_4^+ levels in the drinking waters from Tarnava village, Copsa Mica and Medias towns. Furthermore, the obtained data was used to assess the health risk associated with the consumption of water contaminated with NO_3^-, NO_2^- and NH_4^+. As the reference doses were established only for nitrate and nitrite, these two parameters were used to calculate the *HQ* and the *THQ*.

RESULTS AND DISCUSSION

The results show high concentrations of NO_3^-, NO_2^- and NH_4^+ in the studied well and spring waters (figure 1).

The NO_3^- concentrations in well water samples from Tarnava village (W6, W7) and Medias town (W1, W4, W 5) exceeded almost three times the *MAC* (50 mg/L), while the NO_2^- concentrations exceeded the *MAC* (0.5 mg/L) in water samples collected from all studied localities (W1, W6-W9, S) [16-18]. The measured NO_3^- concentration in spring sample S were lower than the *MAC*, while the NO_2^- concentration exceeded four times the *MAC* and the NH_4^+ level is slightly exceeded [16-18]. Samples W7, W8 and W9 presented the highest NH_4^+ concentrations, exceeding the *MAC* [16-18].

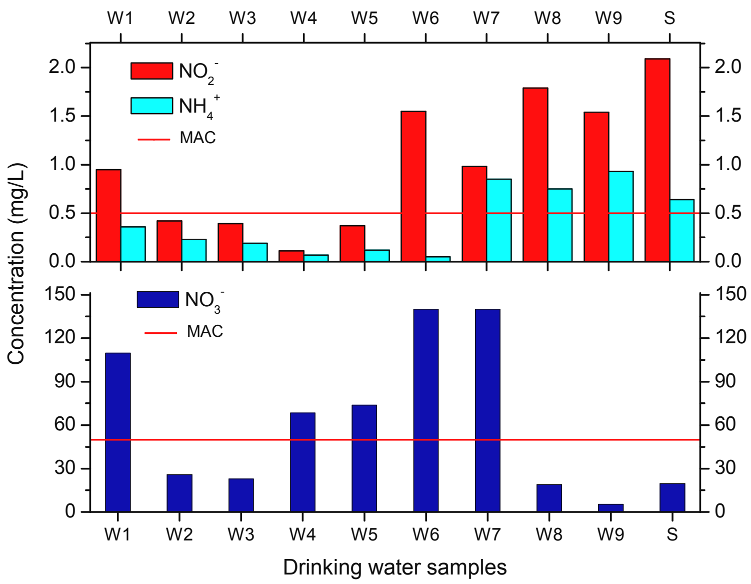

Figure 1. Concentrations of NO_2^-, $NO_3^-$and NH_4^+, in drinking waters

The *HQ* and *CDI* approaches were used to assess the non-carcinogenic risks, specifically for methemoglobinemia, associated with the ingestion of NH_4^+, NO_3^- and NO_2^- from drinking water sources. The *THQ* was used to summarize the total amount of chemicals ingested by drinking water. The *HQ* and *THQ* indices were applied only for NO_3^- and NO_2^-, since reference doses were established, by the IRIS (Integrated Risk Information System), U.S. E.P.A. (United States Environmental Protection Agency) for NO_2^- and NO_3^-, but not for NH_4^+.

Results indicate high values for the *HQ* for NO_3^-, exceeding the critical unity value in Tarnava village (W7) and Medias town (W1, W4, W5), which suggest potential non-carcinogenic effects for consumers [23, 24]. Rest of the studied well waters (W2, W3, W6, W8, W9) and spring (S) have *HQ* values below 1.00. The *HQ* results calculated for the NO_3^- concentrations range from 0.102 to 2.692 (Figure 2). Drinking water sources presented high NO_2^- levels, but low values for the *HQ*. The highest value were obtained for the spring sample (S) and the lowest value for W4 (Table 1). Possible sources that can contribute to the high concentrations NO_2^- and NO_3^- are the agricultural and the domestic activities.

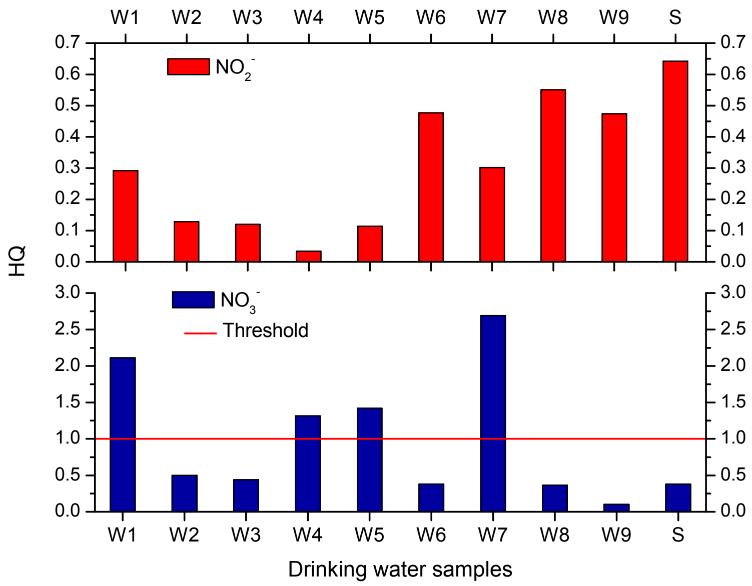

Figure 2. The hazard quotients for NO_3^- and NO_2^- in drinking waters

Table 1. The *CDI*, *HQ* and *THQ* for the drinking waters

	W1		W2		W3		W4		W5	
	CDI mg/kg/day	***HQ***	***CDI*** mg/kg/day	***HQ***	***CDI*** mg/kg/day	***HQ***	***CDI*** mg/kg/day	***HQ***	***CDI*** mg/kg/day	***HQ***
NO_2^-	0.029	0.292	0.013	0.129	0.012	0.120	0.003	0.034	0.011	0.114
NO_3^-	3.378	2.112	0.797	0.498	0.701	0.438	2.101	1.313	2.270	1.419
NH_4^+	0.011		0.007		0.006		0.002		0.004	
THQ	2.404		0.628		0.558		1.347		1.533	
	S		**W6**		**W7**		**W8**		**W9**	
	CDI mg/kg/day	***HQ***	***CDI*** mg/kg/day	***HQ***	***CDI*** mg/kg/day	***HQ***	***CDI*** mg/kg/day	***HQ***	***CDI*** mg/kg/day	***HQ***
NO_2^-	0.064	0.643	0.048	0.477	0.030	0.302	0.055	0.551	0.047	0.474
NO_3^-	0.606	0.379	4.308	2.692	4.308	2.692	0.585	0.365	0.163	0.102
NH_4^+	0.020		0.002		0.026		0.023		0.029	
THQ	1.022		3.169		2.994		0.916		0.576	

The *CDI* for NO_3^- and NO_2^- showed low values for samples from Copsa Mica and Medias towns (Figure 3) and high values for water samples collected from Tarnava village. The *CDI* ranged between 0.003 and 0.064 mg/kg/day for NO_2^- and 0.163 and 4.308 mg/kg/day for NO_3^- with a mean of 0.031 mg/kg/day and 1.922 mg/kg/day, respectively.

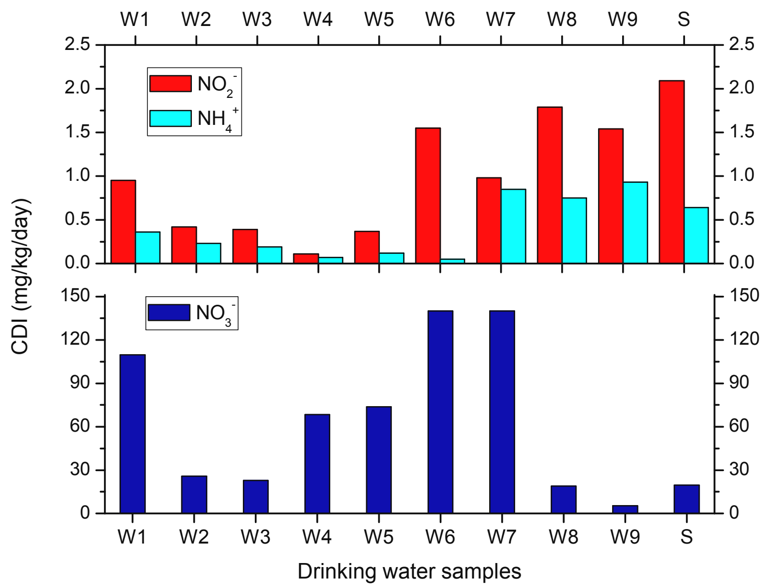

Figure 3. The chronic daily intake for NO_3^-, NO_2^- and NH_4^+ in drinking waters

The *CDI* calculated for the samples from Tarnava village (W6, W7) and Medias town (W1, W4, W5) exceeds 1.00. Obtained *CDI* values for NH_4^+ ranged from 0.002 to 0.029 mg/kg/day, with a mean of 0.013 mg/kg/day. The lowest values were obtained for W4 and W6, while the highest for W9. According to Buss et al. (2014), NH_4^+ is typically present in the wastewater discharges and landfill leachates, which could represent a possible NH_4^+ source for well waters [25]. Low *CDI* values for NO_2^- and NO_3^- (< 0.2 mg/kg/day) and *HQ* values for NO_2^- and NO_3^- (< 0.2) were found in river water samples used as drinking water sources in Poland [25]. Respective values give no cause for concern regarding the non-carcinogenic risk at NO_3^- and NO_2^- [26].

The *THQ* values were higher than 1.00 for the spring sample S and for the well waters from Tarnava village (W6, W7) and Medias (W1, W4, W5). In the case of well waters from Copsa Mica (W8, W9) and from Medias town (W2, W3) the THQ values were lower than 1.00 (Table 1).

CONCLUSIONS

The studied well water samples from Tarnava village are contaminated with NO_3^-, NO_2^- and NH_4^+. The *HQ* for NO_3^- indicated values above the critical unity value in case of one water sample, while the *HQ* for NO_2^- were below the critical unity value. Obtained *THQ* values for the two well water samples from Tarnava village were 3.169 and 2.994. Chronic daily intake of NO_2^- and NH_4^+ were below 0.100 mg/kg/day, while the CDI of NO_3^- was 4.308 mg/kg/day.

Well water and spring samples from Medias town are characterized by low NO_2^- and NH_4^+ concentrations, except one sample, which exceeds the *MAC*. Three water samples exceeded the *MAC* for NO_3^-. Three waters from Medias town showed possible non-charcinogenic risk, according to the *HQ* values, which give a cause of concern. While *HQ* calculated for NO_3^- showed values below 1.00. Results for the *THQ* ranged between 0.558 and 2.404. The obtained values for the *CDI* of NO_2^- ranged between 0.003 and 0.029 mg/kg/day, the calculated values for the *CDI* of NO_3^- ranged from 0.606 to 3.378 mg/kg/day, while the *CD*I of NH_4^+ ranged from 0.002 to 0.011 mg/kg/day.

The NO_3^- concentrations measured for well water samples collected from Copsa Mica town are lower than *MAC*. While the NO_2^- and the NH_4^+ exceeded the *MACs.* The *HQ* for NO_2^- and NO_3^- were lower as the critical unity value, indicating that the water samples present no potential non-carcinogenic risks. The *THQ* results were below 1.00, suggesting that potential adverse health effects may not appear after the consumption of waters from the studied water sources. Chronic daily intake for NO_2^- and NO_3^- were below 0.200 mg/kg/day, while for NH_4^+ below 0.100. The domestic and agricultural activities were taken into consideration as possible sources for the high nitrogen compounds concentrations. Under these circumstances it is recommended a filtration process for the drinking water before consumption and if it is possible a disinfection of the well waters, for the consumer which have no alternative drinking water sources.

EXPERIMENTAL SECTION

Study area, sampling and chemical analysis

The study region is part of Transylvania, localized in central Romania (Figure 4). This part of the country is characterized by an average annual temperature of 8.6 °C and an annual precipitation range of 700 mm [24]. Population from rural and small urban areas in the study area (Tarnava village, Copsa Mica and Medias towns) practice agricultural activities as livestock growing and crop cultivation. Private well waters and public natural springs are used as drinking water sources [17, 18].

One spring sample (S1) from Medias, two well water samples (W1, W2) from Tarnava village and two well water samples (W3, W4) from Copsa Mica were collected [17, 18]. The drinking water samples were collected during summer of 2015, one from each sampling point (Figure 4) in polyethylene bottles and kept at 4 °C in a refrigerator until the chemical analysis. Water samples were filtered using cellulose acetate membrane filters with pore-size of 0.45 μm [17, 18]. The NO_2^-, NO_3^- and NH_4^+ concentrations were measured by ion-liquid chromatography, according to ISO 10304-1:2007, using the 761 Compact IC (Methrom, Herisau, Switzerland) and the NH_4^+ as indophenol blue complex, according to SR ISO 7150-1:2001 by spectrophotometer Lambda 25, (Perkin-Elmer, Beaconsfield, UK).

The accuracy of NO_2^-, NO_3^- and NH_4^+ determinations was tested by analysing Nitrite standard solution (40 mg/L), Nitrate standard solution (15.0 mg/L), and Ammonium standard solution (1.0 mg/L) purchased from Merck. The found results were in good agreement with the certified values for all parameters. The recovery expressed as relative standard deviation degree ranged between 89 % and 100 %.

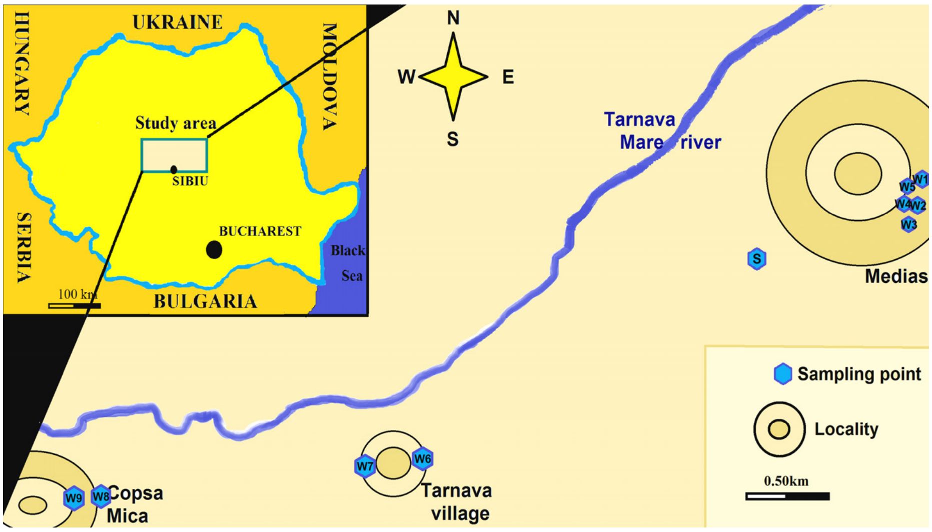

Figure 4. Study area and the location of the sampling points

Human health risk assessment

In order to estimate health risk associated with NO_2^- and NO_3^- in drinking water, the *CDI* was calculated using the following equation [27]:

$$CDI = \frac{C \times DI}{BW} \quad (1)$$

Where *C* represents the NO_3^- and NO_2^- concentrations in drinking water (mg/L), *DI* is the daily intake rate (2 l/day) and *BW* represents the body weight (72 kg) [27].

The hazard quotient (*HQ*) estimates the non-carcinogenic risk posed by NO_3^- and NO_2^- in drinking water, and was calculated using the following equation [27]:

$$HQ = \frac{CDI}{RfD} \quad (2)$$

The *RfD* represents the reference dose with values of 0.10 mg/kg/day for NO_2^- and 1.6 mg/kg/day for NO_3^-. The reference doses were set by EPA's IRIS (Integrated Risk Information System) Program [28, 29]. There are no potential non-carcinogenic risks for the exposed population in cases when the *HQ* does not exceed unity (*HQ* < 1.00) [27, 29]. In the current study the oral exposure was taken into consideration for the count of the *HQ*.

THQ represents a summation of the ingestion of NO_3^- and NO_2^- through drinking water [30].

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