

# Assessment of Health Risks to Ground Water Resources for the Emergency Supply of Population in Relation to the Content of Nitrates and Nitrites

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**Abstract**—The contents of nitrates and nitrites were monitored in 15 ground water resources of a selected region earmarked for the emergency supply of population. The resources have been selected on the basis of previous assessment of natural conditions and the exploitation of territory in the infiltration area as well as the surroundings of water resources. The health risk analysis carried out in relation to nitrates and nitrites, which were found to be the most serious water contaminants, proved, that 14 resources met the health standards in relation to the assessed criterion and could be included in crisis plans. Water quality of ground resources may be assessed in the same way with regard to other contaminants.

**Keywords**—Drinking water, health risks, methemoglobinemia, nitrates, nitrites, water pollution.

## I. INTRODUCTION

**P**UBLIC authorities cannot rely that the risks arising from limited or broken supply of population with drinking water from public water supply system are low. Negative impacts may be minimized solely by becoming aware of corresponding risks and by timely preparation aimed at managing the situation. Damage caused by unsolved problems usually exceeds preventive expenses. Damage caused by unsolved problems usually exceeds preventive expenses [1]. The emergency supply of water to population may efficiently be solved by operating the alternative water resources, such as the unused structures of ground waters [2].

Water quality of assessed resource plays a significant role in the process of selecting the ground water resources for emergency supply of population during emergency and crisis situations [3].

Therefore it is necessary to pay more attention to water quality analysis of ground resource when selecting such a resource for the emergency supply of population [3]. The presence of pollutants in drinking water may cause serious health problems to its consumers [3], [4].

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## II. ANALYSIS OF CURRENT STATE

The emergency water supply of population by drinking water during emergency and crisis situations is not addressed by Community Law in the EU as a whole. The solution of this matter is the responsibility of each EU member state. The emergency water supply in the Czech Republic is provided by regional and municipal authorities through the Emergency Water Supply Service. There are several possibilities to accomplish the above mentioned task [5].

Ground water resources should also be exploited, especially vertical intake structures being built and equipped for collecting the ground waters of deeper circulation, as well as horizontal and combined intake structures [6].

The accumulation of surface waters in water reservoirs and watercourses cannot be recommended for the emergency supply due to its high level of vulnerability. Even not all hydrogeological structures are suitable, because they have different hydrogeological conditions, hydrological regimes, water quality, accessibility, and richness. Besides that they are exposed to different hazards and have resources with different levels of vulnerability [1].

According to the national Code of Law it is assumed that during emergency or crisis the source of drinking water will be capable of providing the following minimal amounts of drinking water:  $5 \text{ dm}^3 \cdot \text{person}^{-1} \cdot \text{day}^{-1}$  for the first two days;  $10\text{--}15 \text{ dm}^3 \cdot \text{person}^{-1} \cdot \text{day}^{-1}$  for other days [5]. Under the above mentioned conditions the richness of water resource  $Q (\text{dm}^3 \cdot \text{s}^{-1})$  may be calculated for the number of inhabitants  $M$  in a supplied region under the assumption there is 30 % of reserve in the interval given by relation (1) [1].

$$Q \in \left( 1,51 \times 10^{-4} \times M; 2,26 \times 10^{-4} \times M \right) \quad (1)$$

Water has to be supplied in required quality [1]. Therefore it is necessary to monitor the water quality of selected source. The assessment covers microbiological, biological, physical and chemical indicators, including organoleptic properties. If all the indicators meet hygienic standards [7] it is possible to use the assessed resource for emergency supply for unlimited period of time.

If water contains contaminants the concentrations of which exceed the values of indicators determined for drinking water even after a common water treatment, then it is recommended to apply the drinking water quality limits set for a short-term emergency supply of population [8] during the assessment of

resource exploitability. Such a resource may be exploited for one month maximum, though.

If there are more contaminants in the assessed water resource the concentrations of which are higher than the limits for drinking water [7] and at the same time they do not exceed the limit indicators for a short-term emergency supply of population [8] health risk is recommended to be assessed and the additive effects of contaminants with similar health effects considered [1].

The health risk assessment is based on the discovered concentration of contaminants, the knowledge of reference dose (RfD) for the assessed contaminants with non-carcinogenic effects, or the cancer slope factor (CSF) for the contaminants with genotoxic effects, and also the exposure equations specific for individual exposure scenarios, which stem from the US EPA prediction modules [9]. The US EPA prediction modules are also incorporated in the valid methodology of the Czech Republic [10]. If some values of exposure factors are not stated for specific exposure scenarios, they have to be determined through expert estimate [11]. It is possible to use the US EPA document for a quick orientation in the health risk assessment. The document includes health advisories for one-day and ten-day exposure of a child weighing 10kg and consuming water in the amount of  $1 \text{ dm}^3 \text{ day}^{-1}$  to approx. 210 contaminants, including inorganic anions and cations, organic substances and significant radionuclides [12].

Inorganic compounds of nitrogen belong to significant contaminants of ground water not only in the Czech Republic, but also in other countries. This contamination is caused by excessive and wrong use of synthetic fertilizers with a high content of nitrates and the leak of waste waters from cesspits and dung heaps in the resource infiltration area and its vicinity [13].

Nitrates are, after being consumed, transformed by oral bacteria to toxic nitrites and then absorbed into blood, where they inter-react with red blood pigment haemoglobin and produce methemoglobin, which is not able to transfer oxygen and cause breathing problems and often even death [14]. Mainly infants up to the age of 6 months are susceptible to methemoglobinemia, because their blood contains lower amount of enzyme called NADH-cytochrome b5 reductase, which transfers methemoglobin back to haemoglobin [15].

Nitrites further react with secondary amines from food in stomach and produce N-nitrosamines, in case of which there has been proved possible connection with cancer of pancreas, liver, kidneys, stomach, large intestine and urinary bladder. Objection defending the presence of nitrates in water is that we consume at least the same amount of nitrates in vegetables. However, such objection is unjustified, because vegetables also contain protective substances, such as vitamins C and E, derivatives of polyphenols, etc., which significantly reduce the effects of nitrates [16]. Besides that nitrates are suspected of causing a number of other illnesses [17].

The national limit concentration of nitrate anions in drinking water is  $50 \text{ mg dm}^{-3}$  [7] and is in compliance with the EU limits [18] and the WHO limits [19]. The US EPA, in its

effort to provide infants with sufficient protection in relation to the occurrence of methemoglobinemia, set the maximal limit of nitrate nitrogen to be  $10 \text{ mg dm}^{-3}$ , which is equivalent to the concentration  $44.29 \text{ mg dm}^{-3}$  of nitrate anions in drinking water [20].

As far as the concentration of nitrite anions in drinking water is concerned, the Czech Republic accepts the limit of  $0.5 \text{ mg dm}^{-3}$  [7] recommended by the EU [18]. The given limit is stricter compared both to the limit of nitrite anions set by the WHO to be  $3 \text{ mg dm}^{-3}$  [19] and to the limit  $1 \text{ mg dm}^{-3}$  of nitrite nitrogen, which is equivalent to the concentration of approx.  $3.29 \text{ mg dm}^{-3}$  of nitrite anions in drinking water as declared by the US EPA [20].

### III. APPLIED METHODS AND DEVICES

Samples of drinking water were taken in compliance with the valid standards [21].

Nitrates have been determined spectrometrically at 410 nm after adding the sodium sulfosalicylate in presence of  $\text{H}_2\text{SO}_4$  and following alkalization. Using the disodium salt of ethylenediaminetetra acetic acid prevented the hydroxides of calcium and magnesium salts from occurring in alkaline environment. The impact of nitrites was eliminated by adding the  $\text{NaN}_3$ . The limit of determinability of nitrate anions by this procedure is  $3 \text{ mg dm}^{-3}$  [22].

The concentration of nitrites was determined by molecular absorption spectrophotometry. The nitrites in the tested volume of samples inter-react in the presence of  $\text{H}_3\text{PO}_4$  and  $\text{pH} = 1.9$  with 4-aminobenzenesulfonamide and produce diazonium salt. This salt forms pink colouring with N-(1-naphthyl) ethylenediamine dihydrochloride added with 4-aminobenzenesulfonamide. Absorbance of colouring was measured at 540 nm. The level of determinability of nitrites was  $10 \mu\text{g dm}^{-3}$  [23].

The uncertainty of determining both nitrates and nitrites was about 10%.

The assessment of non-carcinogenic risks was carried out in compliance with the national legislation [10], which is based on the procedures of the US EPA [9] and adapts exposure factors to national conditions.

The hazard quotient  $HQ$  characterizes non-carcinogenic risks according to (2):

$$HQ = CDI \times RfD^{-1} \quad (2)$$

where  $CDI$  represents chronic daily intake and  $RfD$  corresponding reference dose.

When  $HQ \leq 1$  the risk is acceptable, and when  $HQ > 1$  the risk is unacceptable and the assessed resource of ground water cannot be exploited for emergency supply if water treatment does not reduce the concentration of critical pollutants.

Exposure resulting from the ingestion of drinking water is represented by chronic daily intake  $CDI$ , the value of which may be calculated according to (3).

$$CDI = c_w \times b \times IR \times EF \times ED \times BW^{-1} \times AT^{-1} \quad (3)$$

where  $c_w$  is the average weight concentration of contaminant in drinking water,  $IR$  is the daily intake rate of drinking water,  $b \in (0;1) \wedge b \in \text{Re}^+$ , where  $\text{Re}^+$  is a symbol for the set of all real numbers, specifies the contribution of particular pollution sources to the contaminant intake,  $EF$  is the exposure frequency,  $ED$  is the exposure duration,  $BW$  is the average body weight and  $AT$  is the time during which the concentration  $c_w$  of contaminant may be considered as constant.

#### IV. OUTCOMES AND DISCUSSION

There were 15 sources of ground water altogether earmarked for the needs of emergency supply of population

with drinking water in the region. Natural conditions, former exploitation of territory in the infiltration area and in the vicinity of water resource were considered during the selection. The drill holes were cleaned and water was removed by suction for 7 days prior the sampling for analysis at speed  $Q \approx 0.3 \text{ dm}^3 \text{ s}^{-1}$ .

The exposure factors for the calculation of chronic daily intake  $CDI$  from the ingestion of drinking water for the monitored age groups  $A_1 \leq 1$ ,  $A_2 \in (1; 3)$ ,  $A_3 \in (3; 6)$ ,  $A_4 \in (6; 12)$ , expressed in months, are shown in Table I together with reference doses.

TABLE I  
EXPOSITION FACTORS FOR INDIVIDUAL AGE CATEGORIES AND ORAL REFERENCE DOSES FOR NITRATE AND NITRITE

Age (month)	$IR \text{ (dm}^3 \text{ day}^{-1}\text{)}$	$BW \text{ (kg)}$	$b$	$EF \text{ (day week}^{-1}\text{)}$	$ED \text{ (week)}$	$AT \text{ (day)}$	$RfD \text{ (NO}_3^-) \text{ (mg kg}^{-1} \text{ day}^{-1}\text{)}$	$RfD \text{ (NO}_2^-) \text{ (mg kg}^{-1} \text{ day}^{-1}\text{)}$
up to 1	0.839	4.57	1.00	7	1	7		
1-3	0.896	6.10	1.00	7	1	7		
3-6	1.056	8.08	1.00	7	1	7	7.09	0.33
6-12	1.055	9.82	1.00	7	1	7		

The values of  $IR$  and  $BW$  for the assessed age groups  $A_m$ , where  $m \in \langle 1; 4 \rangle \wedge m \in \mathbb{N}$  were taken from the documents of the US EPA [24]. During an emergency or a crisis  $EF = 7$  days per week while it is assumed that the average concentration of both nitrates  $c_w \text{ (NO}_3^-)$  and nitrites  $c_w \text{ (NO}_2^-)$  in drinking water will remain constant during  $ED = 1$  week and thus  $AT = 7$  days. It has been assumed regarding constant  $b$ , that both nitrates and nitrites are adsorbed solely from drinking water, therefore  $b = 1$  for all age groups.

Oral reference dose for nitrates is according to US EPA settled as  $RfD \text{ (NO}_3^-) = 1.6 \text{ mg kg}^{-1} \text{ day}^{-1}$  nitrate nitrogen, thus it is possible to recalculate this value and  $RfD \text{ (NO}_3^-) \approx 7.09 \text{ mg kg}^{-1} \text{ day}^{-1}$  nitrate anion [25]. Reference dose for nitrites from ingestion of drinking water  $RfD \text{ (NO}_2^-) = 0.1 \text{ mg kg}^{-1} \text{ day}^{-1}$  nitrite nitrogen which after conversion corresponds with  $RfD \text{ (NO}_2^-) \approx 0.33 \text{ mg kg}^{-1} \text{ day}^{-1}$  related to nitrite anion [26].

The concentrations of nitrates and nitrites in the hydrogeological structures were monitored daily for 12 weeks. Average concentrations of nitrates  $c_w \text{ (NO}_3^-)$  and nitrites  $c_w \text{ (NO}_2^-)$  were used for calculating the  $CDI$  during the monitored period. These concentrations are shown in Table II together with the calculated values of chronic daily intakes for nitrates  $CDI \text{ (NO}_3^-)$  and nitrites  $CDI \text{ (NO}_2^-)$ , corresponding hazard quotients  $HQ \text{ (NO}_3^-)$  and  $HQ \text{ (NO}_2^-)$  and hazard indexes  $HI$ .

The values of hazard indexes  $HI$  were calculated according to (4) under the assumption, that there are neither synergic, nor antagonistic effects during the interaction of nitrates and nitrites. Equation (4) has  $n \in \mathbb{N}$  representing the number of contaminants with similar health effects, and as nitrates and nitrites are assessed  $n \in \langle 1; 2 \rangle$ .  $HQ_i$  represents hazard quotient of  $i$ -contaminant.

$$HI = \sum_{i=1}^n HQ_i \quad (4)$$

It is clear from Table II that the resources identified as HV-1 Teresov and HV-1 Lysovice are not suitable from the viewpoint of a long-term supply. The water resource HV-1 Teresov does not meet the requirements for all monitored age categories, while the water resource HV-1 Lysovice only for the category of infants at the age of 1-3 months. It can be seen in case of the second mentioned age category, that despite the fact the hazard quotients  $HQ \text{ (NO}_3^-) < 1$  and  $HQ \text{ (NO}_2^-) < 1$ , the summary effects of both contaminants in the form of hazard index  $HI$  do not slightly meet the requirements for health standards of water for a long-term supply of population. The findings correspond with national limits, as well as with the limits of the EU, the WHO, and the US EPA for drinking water.

The concentration of nitrate anions in water in the HV-1 Teresov water resource exceeds health limits almost twice, so it is not surprising that this water resource is not suitable for any of the assessed age categories. Although the water quality of the HV-1 Lysovice drill hole meets the hygienic standards for the contents of nitrates and nitrites required by the Czech Republic, the EU and the WHO, it slightly exceeds the limit of concentration of nitrate anions recommended by the US EPA. The assessment of the HV-5 Koberice water resource is interesting from the viewpoint of a long-term supply of population with drinking water. Although this resource does not meet the hygienic limits of nitrites set by national legislation, which follows the requirements of the EU, it fully meets the health limits set by the WHO and the US EPA.

TABLE II  
THE AVERAGE CONCENTRATIONS, CHRONIC DAILY INTAKES, HAZARD AND INDEX QUOTIENTS FOR NITRATE AND NITRITE

Drill hole identification	$c_w(\text{NO}_3^-)$ (mg dm <sup>-3</sup> )	$c_w(\text{NO}_2^-)$ (mg dm <sup>-3</sup> )	$A_m$ (month)	$CDI(\text{NO}_3^-)$ (mg kg <sup>-1</sup> day <sup>-1</sup> )	$CDI(\text{NO}_2^-)$ (mg kg <sup>-1</sup> day <sup>-1</sup> )	$HQ(\text{NO}_3^-)$	$HQ(\text{NO}_2^-)$	$HI$
HV-1 Detkovice	< 3	0.08	up to 1	5.51E-01	1.47E-02	7.77E-02	4.45E-02	1.22E-01
			1-3	4.41E-01	1.19E-02	6.22E-02	3.62E-02	9.84E-02
			3-6	3.92E-01	1.05E-02	5.53E-02	3.17E-02	8.70E-02
			6-12	3.22E-01	8.59E-03	4.55E-02	2.60E-02	7.15E-02
HV-1 Prusy	25.3	0.01	up to 1	4.64E+00	1.84E-03	6.55E-01	5.56E-03	6.61E-01
			1-3	3.72E+00	1.47E-03	5.24E-01	4.45E-03	5.29E-01
			3-6	3.31E+00	1.31E-03	4.66E-01	3.96E-03	4.70E-01
			6-12	2.72E+00	1.07E-03	3.83E-01	3.26E-03	3.87E-01
HV-1 Teresov	98.4	< 0.01	up to 1	1.81E+01	1.84E-03	2.55E+00	5.56E-03	2.55E+00
			1-3	1.45E+01	1.47E-03	2.04E+00	4.45E-03	2.04E+00
			3-6	1.29E+01	1.31E-03	1.81E+00	3.96E-03	1.82E+00
			6-12	1.06E+01	1.07E-03	1.49E+00	3.26E-03	1.49E+00
HV-4 Dedice	< 3	0.20	up to 1	5.51E-01	3.67E-02	7.77E-02	1.11E-01	1.89E-01
			1-3	4.41E-01	2.94E-02	6.22E-02	8.90E-02	1.51E-01
			3-6	3.92E-01	2.61E-01	5.53E-02	7.92E-02	1.35E-01
			6-12	3.22E-01	2.15E-02	4.55E-02	6.51E-02	1.11E-01
HV-5 Pustimer	< 3	0.01	up to 1	5.51E-01	1.84E-03	7.77E-02	5.56E-03	8.32E-02
			1-3	4.41E-01	1.47E-03	6.22E-02	4.45E-03	6.66E-02
			3-6	3.92E-01	1.31E-03	5.53E-02	3.96E-03	5.93E-02
			6-12	3.22E-01	1.07E-03	4.55E-02	3.26E-03	4.87E-02
well-1 Drnovice	9.00	< 0.01	up to 1	1.65E+00	1.84E-03	2.33E-01	5.56E-03	2.39E-01
			1-3	1.32E+00	1.47E-03	1.86E-01	4.45E-03	1.91E-01
			3-6	1.18E+00	1.31E-03	1.66E-01	3.96E-03	1.70E-01
			6-12	9.67E-01	1.07E-03	1.36E-01	3.26E-03	1.40E-01
M-2 Krenuvky	16.2	< 0.01	up to 1	2.97E+00	1.84E-03	4.19E-01	5.56E-03	4.25E-01
			1-3	2.38E+00	1.47E-03	3.36E-01	4.45E-03	3.40E-01
			3-6	2.12E+00	1.31E-03	2.99E-01	3.96E-03	3.03E-01
			6-12	1.74E+00	1.07E-03	2.45E-01	3.26E-03	2.49E-01
HV-1 Lysovice	46.5	0.10	up to 1	8.54E+00	1.84E-02	1.20E+00	5.56E-02	1.26E+00
			1-3	6.83E+00	1.47E-02	9.63E-01	4.45E-02	1.01E+00
			3-6	6.08E+00	1.31E-02	8.57E-01	3.96E-02	8.97E-01
			6-12	5.00E+00	1.07E-02	7.05E-01	3.26E-02	7.37E-01
HV-1 Malinky	3.5	0.01	up to 1	6.06E-01	1.84E-03	8.55E-02	5.56E-03	9.10E-02
			1-3	5.14E-01	1.47E-03	7.25E-02	4.45E-03	7.70E-02
			3-6	4.57E-01	1.31E-03	6.45E-02	3.96E-03	6.85E-02
			6-12	3.76E-01	1.07E-03	5.30E-02	3.26E-03	5.63E-02
HV-5 Koberice	< 3	1.27	up to 1	5.51E-01	2.33E-01	7.77E-02	7.07E-01	7.84E-01
			1-3	4.41E-01	1.87E-01	6.22E-02	5.65E-01	6.27E-01
			3-6	3.92E-01	1.66E-01	5.53E-02	5.03E-01	5.58E-01
			6-12	3.22E-01	1.36E-01	4.55E-02	4.13E-01	4.59E-01
HV-1 Orlovice	19.4	< 0.01	up to 1	3.56E+00	1.84E-03	5.02E-01	5.56E-03	5.08E-01
			1-3	2.85E+00	1.47E-03	4.02E-01	4.45E-03	4.06E-01
			3-6	2.54E+00	1.31E-03	3.58E-01	3.96E-03	3.62E-01
			6-12	2.08E+00	1.07E-03	2.94E-01	3.26E-03	2.97E-01

Thus it is not surprising the health risk analysis, conducted in compliance with the national methodology stemming from the methodology of the US EPA has proved that the assessed resource is suitable even for a long-term supply of population with drinking water.

By comparing the requirements set both in the Czech Republic [8] and the USA [12] for the quality of drinking water earmarked for emergency supply of infants and pregnant women it may be concluded, that only the water resource HV-1 Teresov is not suitable for the purpose of emergency

supply due to the content of inorganic nitrogenous compounds. The hygienic standards are less strict in emergency than under normal conditions. As the US EPA limit concentrations of the sums of nitrates and nitrites for 1-day and 10-day emergency supply of population are stricter than the Czech limits. The HV-1 Lysovice is slightly unsuitable when accepting the above mentioned stricter limits. On the other hand the water resource HV-1 Teresov could be used for the emergency supply of adults for up to one month in compliance with national recommendation, because

the limit up to  $130 \text{ mg dm}^{-3}$  of nitrates is accepted. The drinking water contamination limits for the emergency supply of water to infants and pregnant women set by the US EPA and the Czech Republic are similar ( $3.29 \text{ mg dm}^{-3}$  versus  $3 \text{ mg dm}^{-3}$  of nitrite anions) and therefore for a one-month emergency supply it is possible to exploit also the water resource HV-5 Koberice with the content of  $1.27 \text{ mg dm}^{-3}$  of nitrites. The above mentioned outcomes fully correspond to the outcomes of risk assessment presented in the form of  $HQ$  ( $\text{NO}_3^-$ ),  $HQ$  ( $\text{NO}_2^-$ ) and  $HI$  in Table II.

Table II does not include other assessed ground water resources HV-10001 Racice, HV-102 Drnovice, RV12 Racice and HV-7 Koberice, for which the concentrations of nitrates and nitrites were found out through chemical analysis to be below the level of determinability. The corresponding values of hazard quotients and indexes for individual age categories  $A_m$  will thus be lower than in case of HV-5 Pustimer drill hole and the resources for emergency supply will be fully exploitable.

#### V.CONCLUSION

Possible procedure of health risk assessment resulting from the contamination of ground water resources caused by nitrates and nitrites is presented in the paper. The resources have been selected for emergency supply of population and the risk assessment has been conducted for four most vulnerable age groups of infants up to the age of 1 year.

There have been 15 water resources assessed, out of which 14 meet standards concerning the national recommended limit indicators for the content of nitrates and nitrites and can be included into crisis plans. The outcomes of risk assessment mostly correspond to the recommended limits of the Czech Republic, the EU, the WHO and also the US EPA for a long-term and emergency supply of population with drinking water

The proposed procedure may be used as an example of water quality assessment of ground water resources contaminated also by other contaminants.

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