

Assessment of Risk of Ground Water Resources for the Emergency Supply in Relation to Their Contamination by Metals

Frantisek Bozek, Alexandr Bozek, Alena Bumbova, Jiri Dvorak, and Lenka Jesonkova

Abstract—The contamination of 15 ground water resources of a selected region earmarked for the emergency supply of population has been monitored. The resources have been selected on the basis of previous assessment of natural conditions and the exploitation of territory in their surroundings and infiltration area. Two resources out of 15 have been excluded from further exploitation, because they have not met some of the 72 assessed hygienic indicators of extended analysis. The remaining 13 resources have been the subject of health risk analysis in relation to the contamination by arsenic, lead, cadmium, mercury, nickel and manganese. The risk analysis proved that all 13 resources meet health standards with regard to the above mentioned purposefully selected elements and may thus be included into crisis plans. Water quality of ground resources may be assessed in the same way with regard to other contaminants.

Keywords—Contamination, drinking water, emergency supply, health risk, hygienic limits, metals, risk assessment.

I. INTRODUCTION

It is necessary to analyze water quality when selecting the ground water resources for emergency supply of population during emergency and crisis situations. Water quality of ground water resource is one of the crucial criteria for the classification of these resources on the basis of risk analysis [1].

There are many pollutants the presence of which in drinking water may cause serious health problems to consumers [2], [3]. A significant group of pollutants include cations and metal compounds. The paper is focused on the assessment of health risks and quality of ground water resources potentially earmarked for emergency supply with regard to their contamination by selected metals.

II. ANALYSIS OF CURRENT STATE

The emergency water supply of population by drinking water is not addressed by Community Law in the EU. The solution of this matter is the responsibility of individual

EU member states, which often transfer responsibility to their citizens [4]. The emergency water supply in the Czech Republic is provided by regional and municipal authorities through the Emergency Water Supply Service [5]. There are several possibilities to accomplish the above mentioned task. As far as the efficiency of water supply is concerned water supply system should be employed as a matter of priority and despite lower water quality. Moreover, the ground water resources are less vulnerable than surface water resources [4].

The process of efficient supply of population with drinking water in case public water supply system is out of operation requires crisis plans to have ground water resources earmarked and, ideally, classified on the basis of risk analysis. Significant factors for such a classification include mainly the assessment of natural and anthropogenic risks, water quality, availability, accessibility and richness of water resource [1].

According to the national legislation it is necessary to have water resource capable of providing the following minimal amounts of drinking water: $5\text{dm}^3 \text{ person}^{-1} \text{ day}^{-1}$ for the first two days; $10\text{--}15\text{dm}^3 \text{ person}^{-1} \text{ day}^{-1}$ for other days of emergency or a crisis [5].

Water quality is one of the crucial criteria of classification of ground water resources on the basis of risk analysis. Therefore it is necessary to monitor water quality permanently not only in the process of selecting the ground water resource, but also when such a resource is included into a crisis plan. The assessment covers physical, chemical, biological and microbiological indicators, including organoleptic properties. If all the indicators meet hygienic standards [6] 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 limit concentrations even after a common water treatment through sedimentation, filtration, coagulation, flocculation and disinfection [6] then it is recommended to apply the drinking water quality limits set for a month [7], a day, or a 10-days emergency supply at maximum [8].

If there are more contaminants in the assessed water resource the concentrations of which are higher than the limits for drinking water [6] and at the same time they do not exceed the limit indicators for a short-term emergency supply of population [7], [8], health risk is recommended to be assessed and the additive effects of contaminants with similar health effects considered in case antagonistic, or synergic effects of mix of contaminants are not known [1].

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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 U.S. EPA prediction modules [9]. The U.S. EPA prediction modules are also incorporated in the 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].

Inorganic cations and anions belong to significant contaminants of ground water not only in the Czech Republic, but also in other countries. The contamination is caused mainly by extensive industrial, agricultural, mining and transport activities in the vicinity of the source or its infiltration area [2], [12], [13].

The concentration of the following metals and ions have been monitored in the water of ground resources in compliance with national legislation [6]: Na, K, Li, NH_4^+ , Ca, Mg, As, Cd, Pb, Hg, B, Al, Cu, Mn, Fe, Be, Cr, Ni, Se, Ag, Sb, SO_4^{2-} , NO_3^- , NO_2^- , Cl^- , F^- , PO_4^{3-} , HCO_3^- , BrO_3^- and ClO_2^- , including the sum of cations and anions.

The paper is focused on the health risk assessment in relation to the detected content of As, Cd, Pb, Hg, Ni and Mn. Toxicity of As, Pb, Cd, Hg, Ni and Mn is described by the US EPA [14] and by the WHO, as well. [15]. As far as the carcinogenicity is concerned the compounds of arsenic are classified by the US EPA into the group A [14]

and by the IARC into the group 1 [16] as proven human carcinogens. According to the US EPA classification the Pb belongs to the B2 group with sufficient evidence of carcinogenicity for animals and insufficient or no evidence of carcinogenicity for humans, while Cd and Hg are not included as human carcinogens and belong to the group D [14]. The IARC classifies Cd into the group 2A as probable human carcinogens and Pb and Hg into the group 2B as possible human carcinogens [16]. The carcinogenic effects of Mn and Ni have not been proved [14], [16].

The toxicity of As is described in detail by Ratnaike [17]. The summary of toxic effects of Pb is presented by Papanikolaou [18] and Cd by Flick [19], who demonstrates that Cd does not have genotoxic effects if taken orally or through dermal contact. The effects of Hg are described by Wiship [20] and acute and chronic effects of Ni are analyzed by Bencko [21]. Xenophon presents an adverse effect of Mn on human health [22] although Mn intake from drinking water is normally substantially lower than from the food. In addition, the concentrations of Mn higher than 0.1 mg dm^{-3} may negatively affect the sensorial properties of drinking water [8], [15], [23].

Table I presents the Czech limit concentrations for the analyzed metal elements in drinking water [6] together with the limits defined by the EU [24], the WHO [15] and the US EPA [8]. It can be seen that the national limits strictly follow the EU limits. At the same time Table I shows the hygienic limits for a short-term emergency supply of population by drinking water valid in the Czech Republic [7] and determined by the US EPA [8].

TABLE I
LIMIT CONCENTRATIONS OF MONITORED ELEMENTS IN DRINKING WATER AND IN WATER FOR A SHORT-TERM EMERGENCY SUPPLY

Element	Drinking water				Emergency supply		
	Limit concentrations [mg dm^{-3}]				Limit concentrations [mg dm^{-3}]		
	CR	EU	WHO	US EPA	CR One-month	US EPA One-day	US EPA Ten-days
As	0.010	0.010	0.010	0.010	0.030	-	-
Pb	0.010	0.010	0.010	0.015	0.010	-	-
Cd	0.005	0.005	0.003	0.005	0.030	0.040	0.040
Hg	0.001	0.001	0.006	0.002	0.002	0.002	0.002
Ni	0.020	0.020	0.070	0.100	0.250	1.000	1.000
Mn	0.050	0.050	-	0.050	1.000	1.000	1.000
Mn ^a	0.200	-	0.400	0.300	-	-	-

^a Possible limit concentration, if the concentration of element in water is affected by a bedrock

III. APPLIED METHODS AND DEVICES

Samples of drinking water have been taken in compliance with the valid standards [25]. Standard operational procedures have been followed when determining the concentrations of monitored metal elements in the ground water resources. The concentration of metal elements in drinking water has been determined by inductively coupled plasma atomic emission spectroscopy in compliance with national standard [26], stemming from the EU standards. The limits

of determinability for individual elements with uncertainty $\pm 10\%$ are presented in Table II.

Non-carcinogenic risk is characterized by hazard quotient HQ in compliance with (1):

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

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

When $HQ \leq 1$, the risk may be considered as acceptable, when $HQ \in (1; 4)$ the risk is tolerable, especially during emergency supply. Under normal conditions the risk should be reduced by implementing suitable countermeasures within

set time limits. When $HQ > 4$ the risk is unacceptable and the assessed resource of ground water should not be exploited even for emergency supply, unless the concentration of critical contaminants is reduced by water treatment.

TABLE II
THE LIMITS OF DETERMINABILITY OF THE MONITORED ELEMENTS

Element	As	Pb	Cd	Hg	Ni	Mn
Limit of determinability [mg dm ⁻³]	0.005	0.003	0.0005	0.00025	0.001	0.050

Exposure resulting from the ingestion of drinking water is represented by chronic daily intake CDI , the value of which may be calculated according to (2):

$$CDI = c_w \times b \times IR \times EF \times ED \times BW^{-1} \times AT^{-1} \quad (2)$$

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 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.

The acceptability of genotoxic risk is given by excess lifetime cancer risk $ELCR$ value, which can be calculated from the chronic daily intake CDI and the known cancer slope factor CSF for individual exposure pathways according to the relation (3):

$$ELCR = 1 - e^{-(CSF \times CDI)} \quad (3)$$

when $ELCR \leq 10^{-4}$, the risk may be considered as socially acceptable, especially in emergency or crisis situation. According to the US EPA requirements the tendency under normal conditions of supplying the population with drinking water should lead to the value of $ELCR \leq 10^{-6}$. However, it is difficult to reach the above mentioned requirement in practice, especially in relation to the occurrence of many monitored metal elements in natural geological bedrock of resource. The US EPA tolerates the genotoxic risk during emergency supply corresponding to the value of $ELCR \leq 10^{-3}$.

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 vicinity of water resource and its infiltration area were considered during the selection. The drill holes were cleaned and water was removed by suction for seven days prior the sampling for analysis at speed $Q \approx 0.3 \text{ dm}^3 \text{ s}^{-1}$.

Out of the whole range of analyzed metals, their cations and the monitored concentrations of anions within the extended

water analysis [6] the attention is paid to the health risk assessment in relation to the content of As, Pb, Cd, Hg, Ni and Mn. Arsenic has been selected, because it is an element with proved human carcinogenicity and Pb has been selected, because it belongs to the group of metals, which probably have carcinogenic effects. The metals with non-carcinogenic effects included in the health risk assessment are Cd, which is carcinogenic only when inhaled, and also Hg, Ni and Mn. Mn has been selected, because it represents the elements with adverse cosmetic effects resulting in the colouring of teeth and skin and also aesthetic effects resulting in bad taste, smell and colour of drinking water.

The risk has been calculated for one of the most vulnerable age group of infants up to the age of one year. The exposure factors for the calculation of chronic daily intakes CDI from the ingestion of drinking water have been found out in the following way. The value of water intake rate $IR = 0.295 \text{ dm}^3 \text{ day}^{-1}$ has been determined as the median of the mean intake water rate for the age categories $A_1 \leq 1$, $A_2 \in (1; 3)$, $A_3 \in (3; 6)$, $A_4 \in (6; 12)$ months [27]. Body weight $BW = 6.60 \text{ kg}$ has been calculated as the median of the 50 % smoothed percentile of the male and female body weights for the age categories birth, $A_1 \leq 1$, $A_2 \in (1; 3)$, $A_3 \in (3; 6)$, $A_4 \in (6; 9)$, $A_5 \in (9; 12)$ months [28]. It is assumed in the paper that the maximum time of emergency supply is one month, i.e. $EF = 30 \text{ days month}^{-1}$, which is in compliance with national methodology. At the same time it is assumed that the average concentration of individual elements c_w in drinking water will remain constant during the exposure duration $ED = 1$ month and thus $AT = 30$ days. It has been assumed regarding constant b , that metal elements are adsorbed solely from drinking water, therefore $b = 1$ for all monitored metals.

Table III shows the values of reference doses and oral cancer slope factors for the monitored metals [8], [14], necessary for the calculation of non-carcinogenic and genotoxic risks. It also shows the tolerable daily intakes TDI defined by the US EPA [28], the WHO [15] and the National Institute of Public Health of the Czech Republic [7].

The concentrations of metal elements in the assessed 15 hydrogeological structures were monitored 5 days a week for 12 weeks. Average concentrations c_w have been used for calculating the CDI during the monitored period and are shown in Table IV for the assessed elements.

The concentrations of As, Pb, Cd, Hg and Ni have not been monitored in the drill holes HV-5 Koberice and HV-1 Teresov, because they have been excluded from the list of potential resources suitable for emergency supply.

The reason was that water from the HV-5 Koberice drill hole contained over-limit concentrations of SO_4^{2-} , NO_2^- and the sum of minerals and thus did not meet even the limits of conductivity. Moreover, water did not meet

the microbiological requirements due to the occurrence of coliform bacteria, which indicate sewage contamination and the KTJ 100cm^3 of which significantly exceeded even an incident limit. The HV-1 Teresov drill hole have been excluded from further assessment due to almost double excess of limit concentrations of NO_3^- and the microbiological image showing the presence of live organisms.

TABLE III
VALUES OF THE ORAL REFERENCE DOSES, CANCER SLOPE FACTORS AND TOLERABLE DAILY INTAKES

Element	RfD [$\text{mg kg}^{-1} \text{ day}^{-1}$]	CSF [$\text{mg}^{-1} \text{ kg day}$]	TDI [$\text{mg kg}^{-1} \text{ day}^{-1}$]		
			US EPA	WHO	CR
As	0.0003	1.5000	0.0003	-	-
Pb	-	-	0.0005	0.0036	0.0035
Cd	0.0005	-	-	0.0010	0.0070
Hg	0.0003	-	-	0.0020	0.0005
Ni	0.0200	-	0.0200	0.0120	0.0050
Mn	0.1400	-	0.0200	0.0600	0.0600

TABLE IV
THE AVERAGE CONCENTRATIONS OF MONITORED ELEMENTS IN THE SELECTED DRILL HOLES

Drill hole identification	Concentration of element [mg dm^{-3}]					
	As	Pb	Cd	Hg	Ni	Mn
HV-1 Dedkovice	< 0.005	< 0.003	< 0.0005	< 0.00025	0.00321	0.0900
HV-1 Prusy	< 0.005	< 0.003	< 0.0005	< 0.00025	0.00634	0.0800
HV-10001 Racice	< 0.005	< 0.003	< 0.0005	< 0.00025	0.00379	0.1500
HV-102 Drnovice	< 0.005	< 0.003	< 0.0005	< 0.00025	< 0.001	0.0900
HV-4 Dedice	< 0.005	0.00762	< 0.0005	< 0.00025	0.02270	0.4200
HV-5 Pustimer	< 0.005	< 0.003	< 0.0005	< 0.00025	0.00744	0.1200
Vrtl Drnovice	< 0.005	< 0.003	< 0.0005	< 0.00025	0.00495	< 0.050
M-2 Krenuvky	< 0.005	< 0.003	< 0.0005	< 0.00025	< 0.001	< 0.050
RV12 Racice	< 0.005	< 0.003	< 0.0005	< 0.00025	< 0.001	< 0.050
HV7 Koberice	< 0.005	< 0.003	< 0.0005	< 0.00025	0.00256	< 0.050
HV1 Lysovice	< 0.005	< 0.003	< 0.0005	< 0.00025	0.0285	< 0.050
HV1 Malinky	< 0.005	< 0.003	< 0.0005	< 0.00025	0.00102	0.0700
HV1 Orlovice	< 0.005	< 0.003	< 0.0005	< 0.00025	< 0.001	< 0.050
HV-5 Koberice	-	-	-	-	-	0.0850
HV-1 Teresov	-	-	-	-	-	< 0.050

The concentration of As, Cd and Hg in water of all 13 monitored drill was below the level of determinability and met even the strictest limit set for drinking water. The analogous outcomes have been acquired for the concentration of Pb, which exceeded the level of determinability only in the HV-4 Dedice drill hole, but has still been below the lowest limit for drinking water. The limit value of determinability of Ni has been exceeded in 9 monitored drill holes, out of which in 7 cases the strictest national and European standard for drinking water has been met. The limit has been slightly exceeded in the water of 2 drill holes. However, it has met the hygienic limits of WHO and EPA for drinking water. The concentration of Mn has been measured in all 15 resources of ground water. The concentration higher than the limit for drinking water has been detected in 8 cases and only in the HV-4 Dedice drill hole it has been higher than the national limit for ground waters due to bedrock. The concentration has still not exceeded the limits for emergency supply.

The critical concentration of metals c_{na} in ground water resource corresponding to still acceptable non-carcinogenic risk has been calculated under the assumption that $HQ = 1$, with the use of (1), (2) and the known RfD for ingestion. Similar procedure has been applied when calculating the critical concentration c_{ga} in relation to genotoxic risk, which may be considered to be still socially acceptable, when $ELCR = 10^{-4}$. Relation (3) has been applied together with the substitution of CDI from (2) while knowing the CSF for oral exposure in the above mentioned procedure. The critical concentrations c_{nt} for still tolerable non-carcinogenic risk has been acquired in the same way, when $HQ = 4$ and c_{gt} is still tolerable genotoxic risk under the assumption that $ELCR = 10^{-3}$.

The situation has been slightly different for inorganic Pb. Neither CSF nor RfD of oral exposure have been assigned to this contaminant, because its content in blood is decisive for its toxic effects. Some health effects connected

with the presence of Pb in blood occur already in extremely low concentrations, so the compounds of inorganic Pb are effective as substances with non-threshold effect. The critical concentration of Pb in blood is considered to be the value of $100\mu\text{g dm}^{-3}$ [29]. The content of Pb in blood, which is the basis for risk assessment, is assessed according to the specific models in relation to the intake of water and food. The models have not been available, though. Therefore the value of TDI for oral exposure, recommended by national legislation [7] has been used for calculating the critical concentration of Pb in water. The value of critical concentrations c_{nt} and c_{gt} of inorganic Pb for still tolerable risk

could be thus calculated according to (4) in which the other symbols have the same meanings as in (2):

$$c_{nt} = c_{gt} = TDI \times BW \times IR^{-1} \quad (4)$$

The critical concentrations calculated for the monitored elements in the ground water resources in relation to non-carcinogenic and genotoxic risks for the age group of children up to the age of one year are clear from Table V.

It is clear from the comparison of the critical concentrations of the assessed elements from Table V and the limit concentrations for drinking water from Table I that all limits for drinking water result in acceptable risk. The exceptions are arsenic and lead.

TABLE V
CRITICAL CONCENTRATIONS OF THE MONITORED METAL ELEMENTS IN WATER OF HYDROGEOLOGICAL STRUCTURES

Type of risk	Acceptable risk						Tolerable risk					
	Critical concentration c_{na} for non-carcinogenic risk and c_{gc} for genotoxic risk [mg dm^{-3}]						Critical concentration c_{nt} for non-carcinogenic risk and c_{gt} for genotoxic risk [mg dm^{-3}]					
	As	Pb	Cd	Hg	Ni	Mn	As	Pb	Cd	Hg	Ni	Mn
noncarcinogenic	0.0067	-	0.0112	0.0067	0.4475	3.1322	0.0268	0.0783	0.0447	0.0268	1.7898	12.529
genotoxic	0.0015	-	-	-	-	-	0.0149	0.0783	-	-	-	-

For As the critical concentration c_{nc} corresponding to acceptable non-carcinogenic risk is approximately 1.5 times lower than the hygienic limit for drinking water and the critical concentration c_{gc} characterizing the genotoxic risk is even 7 times lower. The WHO states that the concentration of As in natural waters is in the interval $[As] \in (0.001; 12) \text{ mg dm}^{-3}$. It is technically quite difficult to reduce the concentration of arsenic below $5\mu\text{g dm}^{-3}$ through conventional methods, e.g. coagulation, even when the water treatment processes are thoroughly optimized. Besides that there are significant uncertainties in the risk determination and therefore the limit $10 \mu\text{g dm}^{-3}$ for as is set as temporary [15].

As far as lead is concerned the critical concentration for still tolerable risk could not be calculated with regard to the fact that neither RfD nor CSF is defined for oral exposure to this metal. The TDI value has been used for determining the tolerable contamination of water by Pb.

It is clear from Table V that the critical concentration of Mn significantly exceeds the limit set for drinking water earmarked also for emergency supply. This fact may be explained by omitting the requirements for the quality of drinking water from cosmetic and aesthetic viewpoints when determining the critical concentrations of Mn. Moreover, it is known that higher concentrations of Mn negatively influence organoleptic properties of water, such as taste, smell and colour.

It results from the values of critical concentrations that the hygienic limits for all the monitored elements are below the limit of tolerable risk, which is required for emergency supply. Out of 15 selected ground water resources there are 13 which may be included into the category of resources exploitable for the emergency supply of population with drinking water. The above mentioned

statement results from the comparison of concentrations of metal elements in water of these resources with the critical concentrations corresponding with tolerable risk.

V. CONCLUSION

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

There have been 15 water resources assessed, out of which 13 meet standards concerning the recommended 72 limit indicators and can be included into crisis plans. The outcomes of risk assessment of these 13 resources in relation to the contamination by As, Pb, Cd, Hg, Ni and Mn mostly correspond to the recommended limits of the Czech Republic, the EU, the WHO and also the U.S. EPA for emergency and even long-term 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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