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CONTAMINATION OF INDIVIDUAL SOURCES OF DRINKING WATER LOCATED IN ENVIRONMENTALLY POLLUTED CENTRAL SPIŠ REGION (SLOVAKIA)

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ABSTRACT

The aim of the present paper was to evaluate individual sources of drinking water in a village located in environmentally polluted Central Spiš region (Slovakia) which has been affected negatively by mining activities and subsequent processing of complex Fe and Cu ores. Altogether 20 wells were examined chemically (pH, NH_3, NO_2, NO_3, Cl^-, Cl_2, COD_{Mn} and 71 elements including heavy metals) and microbiologically focusing on selected indicators of contamination (KM_{22}, KM_{36}, KB and *E. coli*). The results obtained were evaluated on the basis of a Statutory order of SR 354/2006 of the Civil Code (of May 10, 2006) on requirements on water intended for human consumption. Limits for heavy metals were exceeded in 3 wells (Ni, Sb and Sb and As). The acceptable concentration of NH_3 was exceeded in one well, of NO_2 in 3, NO_3 in 3 and Cl^- in 10 wells. Higher concentrations of Cl_2 were determined in 1 well and of COD in 5 wells. In the majority of cases only 1 or 2 parameters were exceeded with the exception of 3 wells (3 parameters in two and 5 in one well). Some of the wells could present risk from the chemical point of view. None of the wells could be considered completely safe from the bacteriological point of view.

Keywords: Drinking water, chemical, microbiological determination, heavy metals

INTRODUCTION

Decrease in water quality on our Earth is a consequence of anthropogenic pressure on the environment and because of that it poses an international problem. People realise that the maximum pollution threshold cannot be exceeded without disturbing the global-ecological balance with all related catastrophic consequences (**Demeterová, 2002**).
The pollution of water belongs to global problems. The biggest danger is industry (crude oil and its products, heavy metals: lead, mercury, arsenic), agriculture (artificial and nature fertilisers, pesticides, waste water), public aglomerations (production of solid waste) and transportation (emissions).
Water is essential to most bodily functions. Importance of good quality of drinking water is stressed by the fact that the recommended daily fluid intake by adults is 2.25 litres per day. Xenobiotics that penetrate into organisms from the external environment can affect significantly many body functions, react in the internal environment, change their toxicity and accumulate in some organs or be eliminated from the bodies. Because of their chemical resistance and spreading under various natural conditions they can occur in all components of the environment including water
Quality of water is defined as a set of representative data characterising its physical, chemical and biological properties related to its potential use for various purposes. Since 2006 the **Slovak Republic Government Order No. 354/2006 Coll.** (**2006**) has been in force defining requirements for water intended for human consumption and quality control of water intended for human consumption. Water complying with this regulation will not cause health problems even after long-term consumption. The number of pollutants that may penetrate into ground water and thus also into human food chain increases. Because of increasing demands on drinking water supplies and present deficiency of sources in some locations it is inevitable to increase protection of existing ground and surface sources of drinking water (**Podhrázská and Toman, 2000**) and improve monitoring of their quality.
Systematic monitoring of quality of ground water in SR as a part of national monitoring programme has been initiated in 1982. Currently monitoring takes place in 26 areas important from the point of view of water management. This monitoring showed that ground water is most polluted in the western (2) and eastern (25) regions of Slovakia (**Report of MŽP SR and SAŽP, 2011; Jankulár *et al.*, 2009**). The regions endangered by former anthropogenic activities include central Spiš region. Quality of surface and ground water in this region is affected by long-term mining and mineral processing activities (Želba Rudňany, Kovohuty and SEZ Krompachy and activities in the area around Prakovce, Slovinky and Gelnica) (**Hrušková, 2011**).
The importance of quality of surface water and its protection against pollution increases in the Slovak Republic because its use as a source of drinking water after appropriate treatment increases so does its use in agriculture. Moreover, with regard to the interaction of surface and ground water, surface water determines quality of ground water and the importance of ground water constantly increases in relation to increased demands on drinking water supply.
The aim of our study was to examine water from individual sources in an endangered central Spiš region in relation to potential sources of their pollution.

MATERIAL AND METHODS

In the period from October 2010 to December 2011, water samples from 20 wells of various depth (4–14 m) from a village in central Spiš region not connected to public water supply were collected and examined chemically and bacteriologically (Figure 1).

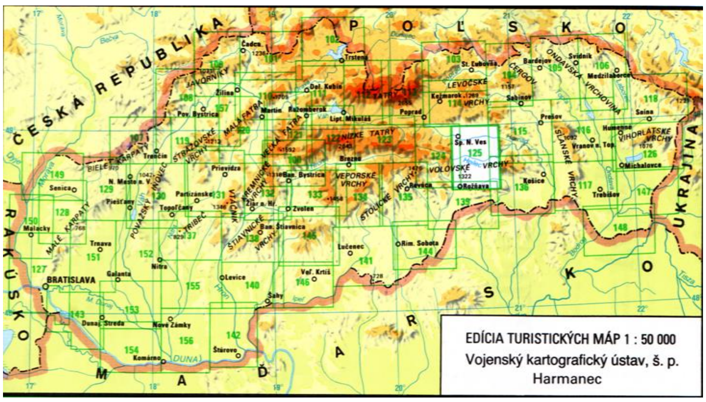

Figure 1 Sampling places in central Spiš region (Slovakia)

The main sources of pollution in the area were industrial locations Rudňany, Krompachy and Spišská Nová Ves with mining activities and processing of complex iron and copper ores. Although air pollution decreased in the area in the recent period. contamination of soil with metals, particularly with Hg, Cu, Pb, Cd and Zn, may still affect the quality of surface and ground water.

Chemical examination included determination of pH, NH_3, NO_2, NO_3, PO_4, COD, Cl^-, Cl_2 and COD_{Mn} (Order No. 354/2006) and 71 chemical elements including heavy metals (AAS method).

Quantitative determination of ammonium ions, nitrites, phosphates and free chlorine was determined only in samples that showed positivity at qualitative examination. Although the Government Order No. 496/2010 Coll. does not require determination of phosphates for evaluation of quality of drinking water, this parameter serves as an indicator of pollution of water sources with human and animal excreements or sewage.

The level of pH and was determined potentiometrically, nitrates were determined by ion exchange electrode inoLab pH/ION 735 (WTW) and chlorides by argentometric titration (**STN ISO 9297**). The level of COD_{Mn} was determined by **STN EN ISO 8467**. Determination of ammonia, nitrites and phosphates was carried out spectrophotometrically according to HACH methods using HACH LANGE DR 2800 spectrophotometer. Free chlorine was determined by titration with sodium thiosulphate (**STN EN ISO 7393-3**).

Bacteriological examination focused on determination of plate counts of bacteria cultivated at 22 and 37 °C (BC_{22}, BC_{36}), total coliforms (TC) and *E. coli* according to respective STN ISO and STN EN ISO.

Colony forming units (CFU) of BC_{22}, BC_{37} were determined by STN EN ISO 6222 using a pour-plate method and counting colonies after cultivation on meat-peptone agar at 20°C for 72 h and 37 °C for 48 h, respectively

Total coliforms and *E. coli* were determined according to STN EN ISO 9308-1 by membrane filtration using 10 ml volume of examined water Fermentation test was used to confirm the presence of coliform bacteria.

RESULTS AND DISCUSSION

Chemical determinations and heavy metals

Results of chemical examination of parameters indicating potential pollution of water compared with limit values stipulated by Slovak Republic Government Order No. 496/2010 of the Code are presented in Tab 1.

Table 1 Levels of chemical indicators of water pollution range and mean of 3 determinations; *mg/L

Limits	pH 6.5-8.5	NH_4^+ 0.5 *	NO_2^- 0.01*	NO_3^- 50*	Cl^- 100*	PO_4 1.0*	COD_{Mn} 3.0*	Cl_2 0.3
1	**5.8-6.2**	-	0.005	4.6-5.4	18-**245**	+	1.5-2.0	-
m	**6.03**			5.0	98.1		1.8	
2	**6.2-6.4**	0.1	-	3.2-8.7	5.3-10.6	+	0.7-1.0	-
	6.30			6.0	8.0		0.8	
3	**6.3**-7.5	-	0.004	17-40	170-**399**	0.1-0.95	**3.1-4.6**	0.1 - 0.3
	6.9	0.3	**0.12**	25.5	**271**	0.44	**4.5**	
4	**6.2**-6.7	-	-	3.5-13	14.2-19.5	+	**3.1-4.2**	-
	6.5			7.0	16.8		**4.1**	
5	6.6-7.2	0.1	0.05	5.5-14.0	**133-367**	0.025	**3.2-3.9**	0 – 0.2
	6.9			9.0	**250**		**3.7**	
6	**6.1**-7.2	0.26-**1.44**	0.04-**0.17**	37-**89**	**108-112**	0.01-0.26	**8.0-8.5**	0 – 0.2
	6.7	**0.85**	0.1	**57.3**	**110**	0.02	**8.3**	
7	6.8-7.6	0.28	0.07-**0.68**	8.4-31	5-58.5	+	1.8-2.25	0.2 – **0.8**
	7.2		**0.38**	18.1	44.2	0.11	2.1	
8	6.9-8.2	-	0.02	26-**64**	37-**113.4**	0.075	2.0-2.3	0.1 - 0.2
	7.5	-	0.08	39.5	75.0		2.2	
9	6.8-7.3	-	0.02	18-**100**	39-**239**	0.025	1.5-2.7	-
	7.1			**58.5**	**124**	0.08	2.3	
10	6.7-7.8	-	-	24-30	33.7-39.4	-	2.6-2.8	0 – 0.1
	7.2	+	+	26	36.6	0.15	2.7	
11	6.8-7. 9	-	-	7.3-18	17.0-51.4	-	2.2-2.4	-
	7.5			12.1	34.2		2.3	
12	6.5-7.6	-	+	7.8-31	26.5-**233**	0.05	1.5-1.7	-
	7.3			17.0	106.6		1.6	
13	**6.2**-7.6	-	-	4.1-14	34-**223**	0.56-0.89	0.3-0.5	-
	6.92			12	**157.3**	0.72	0.4	
14	6.9-7.7	0-0.1	-	8.5-29	13.5-**117**	+	1.8-1.8	-
	7.3			18.5	67.1		1.8	
15	6.5-7.0	-	+	2.1-2.5	1.8-49.6	0.05	0.6-0.8	-
	6.8			2.3	25.7		0.7	
16	**6.4**-7.6	-	-	0.63-4.1	6.4-30.1	0.16	2.6-2.9	0 – 0.1
	7.0			1.9	16.2	0.5	2.7	
17	6.9-8.5	+	0.08	7.1-16	30-**170.2**	**1.43**	**3.3-4.0**	0 – 0.1
	7.7	-	0.01	11.7	84.4	**1.18**	**3.7**	
18	6.8-7.5	+	+	7.3-17	9.2-23	+	**4.2-5.7**	-
	7.3			10.7	16.1		**5.2**	
19	**6.2**-7.3	-	-	14-29	30.5-72.7	+	2.5-2.7	-
	6.8			21.5	51.6		2.6	
20	6.9-7.5	-	-	3.4-4.6	31.2-95.7	+	2.5-2.9	-
	7.4			4.0	63.5		2.7	

Legend: m – mean, + – traces, bold – parameters exceeding the acceptable limits

Our examination showed that only in 4 of 20 examined wells none of the chemical parameters was exceeded at any sampling. The limit value for ammonium ions (0.5 mg/L) was exceeded in one well (1.44 mg/L), for nitrites (0.1 mg/L) in 3 wells (W3 – 0.12, W6 – 0.168 and W7 – 0.68 mg/L), for nitrates (50 mg/L) in 3 wells (W6, W8 and W9, 55–100 mg/L) and chlorides (100 mg/L) in 10 wells (W1, 3, 5, 6, 8, 9, 12, 13, 14, 17, levels ranged from 108 to 399 mg/L). In W7 we detected increased level of active chlorine (0.8 mg/L vs. max 3 mg/L). Increased level of COD_{Mn} (max. 3 mg/L) was detected in 5 wells (W3, 4, 6, 17, 18, range 3.7–8.25 mg/L).

The effects of high level of chemical pollutants in the body will not occur immediately, but in the long term can contribute to most serious health problems.

Chemical composition of ground water depends on composition of soil layers through which it passes. A range of groundwater pollution problems can be associated with mining activities.

One of the most sensitive parameters of equilibrium state in natural water is pH. According to Government Order No. 354/2006 Coll. pH of drinking water should range from 6.5 to 9.5. Shift to the alkaline zone is caused by intensive photosynthetic assimilation. Acidity in water is not in itself harmful to health. However, low pH (wells No. 1, 2, 3, 4, 6, 13, 16, 19) can allow toxic elements and compounds to become mobile and "available" for uptake by aquatic plants and animals. Even mildly acidic water can dissolve lead or copper that may be present in plumbing pipes and fixtures.

Presence of ammonium ions in water is an indicator of ongoing decomposition processes and thus of potential pollution of water with N-substances present in faeces. This is related to health risk associated particularly with microbiological content of faecal material. Ammonium ions exceeding the limit were found in well No. 6.

Nitrates are a transient stage of decomposition (biochemical oxidation of ammonia) of organic N-substances. They are very unstable in water and thus their presence in ground and surface water indicates fresh organic pollution. Nitrates in drinking water are particularly dangerous to babies as they cause methamoglobinemia or "blue babies" syndrome. They pose some risk also to adults as in the gastrointestinal tract they may react with secondary amines and be converted to carcinogenic nitrosamines (**Directive 91/676/EC, 1991**). Our study showed their higher levels in three wells and particularly high one in well No. 7. in drinking water present some risk to humans in levels exceeding the acceptable limit (**Tôlgyessy 1989**). In the gastrointestinal tract they can be reduced to nitrites that may cause methaemoglobinemia in babies or become precursors of nitrosoamines. In our study the levels of nitrates acceptable for adults were exceeded in three wells.

Phosphates occur in water in dissolved and undissolved forms. If they are of organic origin they serve as indicators of faecal pollution. The limit was exceeded only in one well. Anthropogenic sources of inorganic phosphorus include artificial fertilizers and detergents. Phosphorus of organic origin is found in animal and human wastes. Man eliminates about 1.5 g P which finds its way into sewage.

Chlorides are a permanent component of ground water. They are not harmful in higher concentrations but affect taste of drinking water. Presence of chlorides of animal origin indicates faecal pollution. Increased level of chlorides is one of the signs of insufficient protection of water sources (**Pisaříková 1996**). Its level was exceeded in 10 examined wells.

Free chlorine is a chemical most frequently used for disinfection of water. Residual chlorine (from 0.05 up to 0.3 mg/L) is found in water sources that were disinfected for the purpose of elimination of potential microbiological contamination of water. Free chlorine is very active and may react with present organic substances and form various chlorderivatives including trihalomethanes, the substances identified as carcinogens and mutagens Total content of organic substances in water is evaluated by means of COD. Increased COD poses a risk to human health if the water is disinfected with chlorine. We detected residual chlorine in 8 examined wells, in one of them exceeded considerably the limit value. Evidently, some people tried to disinfect their wells. The water in 4 of 8 wells containing residual chlorine showed increased level of COD_{Mn} (indicator of total oxidisable organic substances). The risk of development of cancer is particularly high after long-term consumption of such water. The highest level of COD_{Mn} (8.25 mg/L) was determined in W6.

Results of AAS examination (71 elements) showed that only 3 elements, for which the Regulation No. 354/2006 gives the maximum allowed level (MAL), were exceeded, namely nickel in W6 reached 0.027 mg/L (MAL = 0.02 mg/L), antimony in W16 was detected at the level of 0.012 mg/L, (MAL = 0.005 mg/L) and water in W18 exceeded the levels for both antimony (0.0086 mg/L vs. 0.005 mg/L) and arsenic (0.019 mg/L vs. MAL = 0.01 mg/L). The maximum allowable levels of Cr and Cd were not exceeded.

In humans, nickel influences iron absorption and metabolism, and may be an essential component of the haemopoietic process. Only in high doses in water nickel becomes toxic and carcinogenic. Allergic contact dermatitis is another prevalent effect of nickel in the general population.

The acceptable level of arsenic was exceeded only in one well. Chronic toxicity of arsenic is manifested by changes in skin and mucosa, neurologic and haematological changes and mutagenic and carcinogenic effects. Carcinogenic effects appear after long-term consumption of water contaminated arsenic.

Increased level of antimony and arsenic in water can also be linked to geological background of the respective territory, e.g. in case of water reservoir Bukovec (**Holéczyová *et al.*, 2003**).

Antimony in water is monitored on the basis of WHO recommendations due to its carcinogenic effects. The toxicity of antimony is a function of the water solubility and the oxidation state of the antimony species under consideration. In general, antimony (III) is more toxic than antimony (V), and the inorganic compounds are more toxic than the organic compounds (**WHO/SDE/WSH/03.04/74 Antimony in Drinking-water).**

Microbiological determinations

Very serious were the results of bacteriological examination (Figures 3 and 4).

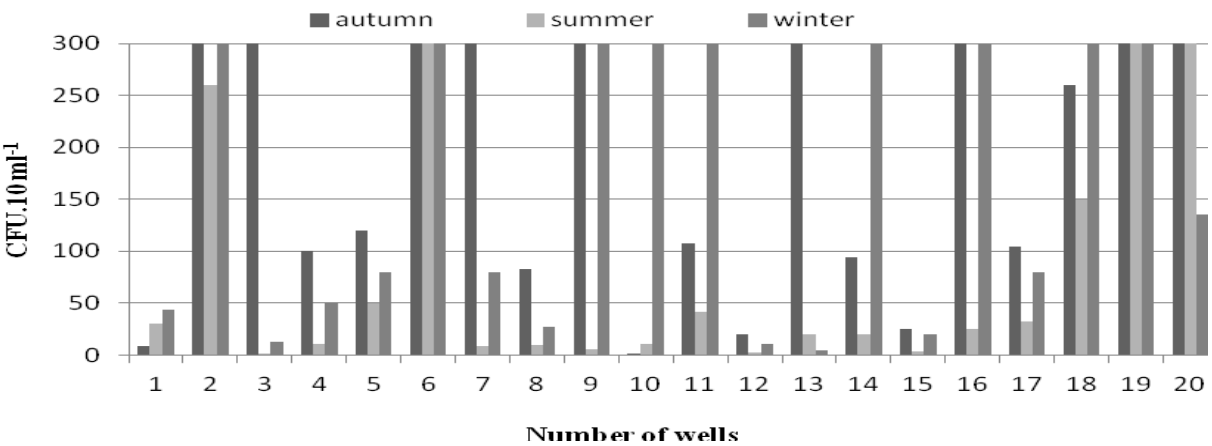

Figure 3 Coliform bacteria – KTJ.10 ml/L
Legend: > 300 = uncountable

Microbiological contamination of water results in immediate disease outbreaks that can affect many people and can have lifelong consequences. The level of bacterial contamination differed according to seasons and indicated some influence of manipulation with excrements in autumn. Total coliform (TC) bacteria that serve as an indicator of potential faecal contamination were recovered from 10 ml of water from all wells over the examination period, occasionally in very high numbers (>300 CFU). Moreover *E.coli*, considering a proof of faecal contamination, were also detected in all wells at least at one sampling. This was particularly serious finding because it is related to considerable risk of spreading of diseases through animal or human faeces.

BC_{22} in 1 ml water reached >300 CFU in 4 wells at one or more samplings and most likely exceeded the limit value (500 CFU) for this parameter and counts of BC_{37} were exceeded in 3 wells, 2 of them showing also high level of BC_{22}.From the bacteriological point of view the worst was well W6 (Figure 3) in which we detected also increased levels of 5 chemical indicators of contamination and increased content of Ni. There was a septic tank located not far from this well.

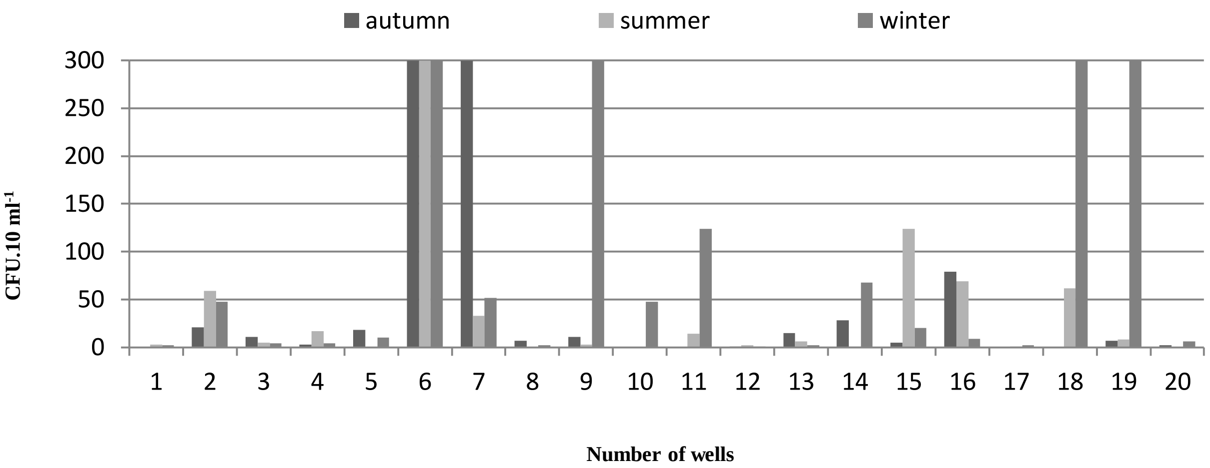

Figure 4 *Eschericia coli* – KTJ.10 ml/L
Legend: > 300 = uncountable

Bacteriological finding provides picture of the immediate quality of water. It serves as the most sensitive indicator of faecal pollution. **Macler and Merkle (2000)** implied that all persons who drink water from ground sources which were not subjected to hygiene control or were not subsequently disinfected run the risk of infection with pathogenic micro-organisms. Wells that serve as sources of drinking water for individual supply and mass supply should comply with the hygiene principles and regulations. In order to protect water in wells from bacteriological, chemical and hydrological point of view it is necessary to inspect the immediate surroundings of the wells for potential sources of pollution, such as septic tanks, sewage pipelines, storage of liquid fuels, animal houses and dung heaps, before starting to draw water from such wells.

Figure 3 Well No. 6

CONCLUSION

Our results indicated potential pollution of the entire examined area even to a depth of 12 meters. The levels of chemical indicators of pollution that can affect the health of people after long term consumption were exceeded in a number of examined wells and were associated with serious bacteriological contamination. Examination of water from well No. 6 (approx. 11 m deep), which was the most contaminated one, showed that in this water 6 of 8 examined chemical parameters were exceeded, the level of Ni was increased, and counts of all examined bacterial groups were highly exceeded in all seasons. Particularly serious were the high counts of *E. coli* which are considered the proof of faecal contamination and serious risk of spreading of diseases.

According to our results none of the wells could be evaluated as safe from the bacteriological point of view and some could affect the health of people, particularly babies, also from the chemical point of view. Although we obtained good results for some wells at one sampling, at other samplings they contained coliform bacteria in 10 ml volumes (none may be present according to Regulation No. 354/2006). This may be related to the fact that some families in the village keep farm animals and apply their excrements to soil, although the number of animals has been decreasing. Another reason of poor quality of water in investigated wells may be the location of wells and absence of the required adjustment and protection of their immediate surroundings.

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REFERENCES

DEMETEROVÁ, B. 2002. Management of Water Sources (In Slovak). Košice, SHMÚ.
DIRECTIVE 91/676/EC on the protection of waters against pollution caused by nitrates from agricultural sources.
HOLÉCZYOVÁ, G., HUDÁK, A., RIMÁROVÁ, K. 2003. Occurrence of heavy metals in drinking water in Košice and the Košice area (In Slovak). *Military Health Letters*, 4, 183-185.
HRUŠKOVÁ, T. 2011. The impact of environmental contamination in natural waters of Slovakia – Review (In Slovak). *Ecology and veterinary Medicine VIII.* (Proceeding of International Scientific Conference) Košice: 159 – 161.
JANKULÁR, M., HILLER, E., JURKOVIČ, Ľ., VESELSKÁ, V., MAJZLAN, J. 2009. Arsenic and zinc in impoundment materials and related stream sediments from a poluted area in Eastern Slovakia: distribution, mobility, and water quality. *J. Hydrol. Hydromech.* , 57(3), 200-211.
LANGER, P., KOCAN, A., TAJTÁKOVÁ, M., RÁDIKOVÁ, Z., PETRÍK, J., KOSKA, J. 2007. Fish from industrially polluted freshwater as the main source of organochlorinated pollutants and increased frequency of thyroid disorders and dysglycemia. *Chemosphere*, 67, 379-385.
MACKLER, B.A, MERKLE, J.C. 2000. *Hydrogeol. J.*, 8, 1, 29-40.
PÍSAŘIKOVÁ, B., HERZIG, I., ŘÍHA, J. 1996. Inorganic anions with stumigenous potential impact in drinking water. *Vet. Med.-Czech*, 41, 33-39.
PODHRÁZSKÁ, J., TOMAN, F. 2000. Importance of differentiated protection of catchment area of water reservoirs in landscape planning (In Slovak). *Proceedings Bioclimatology and the Environment* Košice.
REPORT of MŽP SR and SAŽP. 2011. (In Slovak).
SKALICKÁ M., NAĎ, P., DEMETEROVÁ M., KORÉNEKOVÁ, B. 2007. Influence of Cr and Cd on quality of Japanese quails eggs. *Risk Factors in Food Chain* (Proceedings 7*th* International Scientific Conference) Nitra, 197–199.
SLOVAK REPUBLIC GOVERNMENT ORDER NO. 354/2006 Coll. defining requirements for water intended for human consumption and quality control of water intended for human consumption.
SLOVAK REPUBLIC GOVERNMENT ORDER NO. 496/2010 Coll. defining requirements for water intended for human consumption and quality control of water intended for human consumption.
STN 75 5115. 1993. Water management. Wells for individual water supply (In Slovak).
STN ISO 9297. 2000. Water quality. Determination of chlorides by argentometric titration (In Slovak).
STN EN ISO 8467. 2000. Water quality. Determiínation of COD_{Mn} (In Slovak).
STN EN ISO 7393-3. 2000. Water quality. Determination of free chlorine with sodium thiosulphate (In Slovak).
STN EN ISO 6222. 2000. Water quality. Determination of bacteria cultivated. (In Slovak).
STN EN ISO 9308-1. 2000. Determination of total coliforms and *E.coli.* (In Slovak).
TÓLGYESSY, J.1989. Chemistry, biology and toxicology of water and air. Bratislava: Science, 531p. ISBN 80 22 400 343.
WHO/SDE/WSH/03.04/74 Antimony in Drinking-water. Background document for development of WHO *Guidelines for Drinking-water Quality).*
ŽÁČEK, E. 1994. Organic substances in drinking water. *Aquaculture*, 5/6, 39.