Geochemical study of arsenic mobility in secondarily influenced Kyjov brook and Ondava river (Eastern Slovakia)

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Abstract. This study describes arsenic distribution and its mobility in surface waters and stream sediments of watersheds of the Kyjov brook and partly the Ondava river, localized in Eastern Slovakia. Study area is characterized by the intensive contamination of surface waters and stream sediments with a high concentration of arsenic. It is obvious that the arsenic originates from impoundment located in the upper part of the Kyjov catchment. The impoundment operated by local chemical factory consists of waste from chemical industry and burning waste. Extreme concentrations of arsenic were found in the vicinity of impoundment: 11,39 $mg.l^{-1}$ in the sample taken from surface water in June 2000 and 3208 $mg.kg^{-1}$ in the sample collected from stream sediment in June 2005. We assume that the release of arsenic from the waste material highly depends on snow melting or higher precipitation events. Contamination of surface waters with arsenic is large-scaled and it extends more than 50 km downstream the Kyjov brook and the Ondava river. This observation suggests serious environmental load with potential negative influence on aquatic environment and human health. On the ground of these findings, a comprehensive research of different compartments of environment is highly requested.

Key words: arsenic, geochemistry, surface water, contamination, impoundment, stream sediments

1. Introduction

Arsenic is a chemical element with natural occurrence in the environment. Interest in the study of arsenic in the aquatic environment has been increased in very recent years. Arsenic belongs among the most important contaminants in the environment with the wide-range potential risk to human health. Arsenic can occur in the environment in several oxidation states (+5, +3, 0, -3), but in natural waters is mostly found in inorganic form as ox anions of trivalent arsenite [As(III)] or pentavalent arsenate [As(V)]. The most important factors controlling arsenic speciation are red ox potential (Eh) and pH. Organic As forms can be produced by biological activity, mostly in surface waters, but they may mainly occur in waters significantly impacted by industrial pollution (Smedley & Kinniburgh, 2002). The metal oxides, mainly Al, Fe and Mn oxides are the major minerals significantly binding arsenic (dissolved As forms, arsenate and arsenite; (Sullivan and Aller, 1996). Therefore Al, Fe oxides can importantly limit the mobility of arsenic in aquatic environment. It has been observed that Ca-carbonates can also affect retention of arsenates by soils and stream sediments (Hiller, 2003). Microorganisms including microscopic fungi are capable to transform inorganic arsenic forms to various inorganic and organic volatile and nonvolatile arsenic compounds (Ševc and Čerňanský, 2003).

Arsenic accumulation in the environment is due to both natural and anthropogenic sources. Increased arsenic concentration (higher than 50 $\mu g.l^{-1}$) can occur in volcanic sedimentary rocks or in geothermal areas (Rapant et al., 1996; Nimick et al., 1998). Anthropogenic sources of arsenic are mainly caused by activities such as combustion of fossil fuels, mining and smelting of ores, agricultural uses of arsenical pesticides or releasing from wastes deposed on spoil heaps and impoundments (Ďurža and Khun, 2002). By the weathering of waste material from mining activity (which contents arsenopyrite FeAsS) anomalous arsenic concentrations in natural waters can be observed, locally reaching up to thousands of μg of arsenic (e.g. Loredo et al., 2003 – range 4100–5600 $\mu g.l^{-1}$ of As).

Toxicity of arsenic and its potential risky influence on human health is one of the chief topics of many scientific works. In recent years this topic has been related to high contamination of drinking water supplies in the West Bengal (Das et al., 1996), in Bangladesh (Smith et al., 2000) and other countries (Urminská et al., 2004; Rapant and Krčmová, 2006). Long-term overexposure to As can cause skin, liver, bladder, kidney and lung cancers and many other health effects (ATSDR, 1989; Wu et al., 1989; Jain and Ali, 2000).

Arsenic distribution and its mobility in surface waters and stream sediments of watersheds of the Kyjov brook and partly the Ondava river is presented in this paper. Pollution of aquatic environment by arsenic in the study region (Eastern Slovakia) was observed in the late 1990s for the first time (Kordík and Slaninka, 2001). Arsenic comes from impoundment located in the upper part of the Kyjov catchment near the Poša village (Fig. 1). The impoundment operated by local chemical factory consists of waste from chemical industry and

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burning waste. During the first research, extremely high concentrations of arsenic were found in the surface water in the vicinity of impoundment with maximum value of 11.39 $mg.l^{-1}$ in the sample from June 2000 (Kordík and Slaninka, 2001). In 2005, a comprehensive research was started in the contaminated area to obtain more information on arsenic distribution in various compartments of the environment and to define the actual extent of arsenic contamination.

The main objectives of this paper are following:

- identification of spatial pattern of arsenic contamination in surface waters and description of its trends,
- comparison of arsenic contents in surface waters with water quality guidelines,
- synthesis and interpretation of new information and allocation of potential risk and impact of contamination to natural equilibrium in the aquatic environment.

The research results will create the information base for representatives of decision makers (Ministries) as well as local authorities. The knowledge obtained during the scientific activities should lead to the final implementation of a strategy focused on reduction of the negative impact of contamination in the area. Information will support the water management system by many important issues such as identification of contamination "hot spots" etc. that requires relevant scientific data and information.

2. Methods

2.1 Sampling, laboratory techniques and data sources

Geochemical research for presented part of study includes sampling and subsequent analysis of surface water. Regarding water-sample collection, the used data are based on a criterion of ecological objective, e.g. sampling sites are situated in the areas with expected natural background concentrations of analysed parameters as well as in the contaminated part of the study area.

Water samples were received from the following data sources:

- Geochemical atlas of Slovakia – part Groundwater for description and calculation of referenced condition (Rapant et al., 1996),
- National monitoring program of surface water quality realized by SHMI (SHMI Annual report on surface water quality),
- Research related to study of geological factors of environment – TIBREG region (Kordík and Slaninka, 2001),
- Research realized in 2005.

Water samples were collected into the PVC bottles and stabilized by 5 ml of concentrated HNO_3. The water samples were analysed in a hydrochemical laboratory of INGEO Inc. Žilina and ŠGÚDŠ Bratislava. A review of analytical technique and detection limits applied to arsenic (also for stream sediments) is given in Tab. 1. The accuracy of analytical data was continuously assured by the system of analytical quality assurance (AQA) corresponding to the European standards. The polysulphone vacuum filtration instrument NALGENE (USA) and nitrocellulose membrane filters SYNPOR with 0.45 μm pores were used in membrane filtration (samples collected in 2005 and samples used from Geochemical atlas).

All data are stored in the database programme MS Access and used in GIS.

Tab. 1. Laboratory parameters for determination of arsenic in water and stream sediment.

Element	Detection limit		Method
	INGEO Žilina	ŠGÚDŠ Bratislava	INGEO Žilina, ŠGÚDŠ Bratislava
As	0.001 $mg.l^{-1}$	0.0001 $mg.l^{-1}$	AAS-HG – Atomic Absorption Spectrometry - Hydrid Genering

2.2 Data processing

The distribution of arsenic, determination of environmentally significant concentrations as well as the background and critical values are discussed in the paper. Several approaches to process the data gained from the research are used:

- application of statistical analysis,
- comparison of the results with a baseline or background distribution given in Rapant et al. (1996) and Kordík and Slaninka (2001),
- comparison of the results with legislative standards (legislative approach).

Basic statistics is a standard method used for assessment of analytical results. Arithmetic mean, median, standard deviation, minimum and maximum values of analysed components are the parameters applied to describe the central tendency and variability of element distribution in waters (Tab. 4). Moreover the individual contents of arsenic are presented as well (Tab. 2).

The legislative approach is based on comparison of observed concentrations with the limit values that are given as a standard and defined for particular components of the geologic environment. To evaluate the content of contaminants in waters, Decree of Slovak Health Ministry No. 151/2004 on drinking water demands and drinking water quality control and Slovak Technical Standard (STN 75 7221) were used for the of comparison. This legislation strictly limits arsenic contents in waters (Tab. 2).

Interpretation of the results is supported by graphical visualization providing comprehensive information about arsenic distribution in the study region.

3. Results

Based on the results from regional research of environmental geological factors (Kordík & Slaninka, 2001) and the results of long-time monitoring of surface waters performed by the Slovak Hydrometeorological Institute (SHMI), a large-scale contamination of the Kyjov catchment by highly toxic element – arsenic was observed. Furthermore, the high values of total dissolved solids (TDS), ammonium ions, sulphates and nitrates in surface water were determined in studied area. High arsenic concentrations (much higher than a background value) were observed also in the Ondava river into which the Kyjov

Tab. 2. Concentrations of arsenic in the Kyjov brook and the Ondava River and important values of arsenic content in waters (all values in $\mu g.l^{-1}$).

Sample No.	Sampling date							
	05/1999	*07/1999*	*06/2000*	*07/2002*	*01/2003*	*07/2003*	*01/2004*	*08/2004*
109 (Ondava)	12.59	10.00	5.4	11	113	17	-	3.1
112 (Ondava)	-	0.26	-	-	-		-	-
113 (Ondava)	-	77.60	-	-	-		-	-
122 (Kyjov)	**10667**	**-**	**11385**	**2870**	**7000**	**3460**	**1932**	**2208**
129 (Kyjov)	-	**6700**	-	-	-		-	-
131 (Kyjov)	-	**7150**	-	-	-		-	-
Regional background mean value for surface water	According to data given in Kordík & Slaninka, 2001 2.6							
Geochemical atlas – groundwater (Rapant et al., 1996)	Arithmetic mean 1.9				Median 0.5			
Drinking water standard	According to decree of Slovak Health Ministry No. 151/2004 10							
Surface water standards (STN 75 7221)	I. class 10	II. class 20	III. class 50	IV. class 100	V. class > 100			

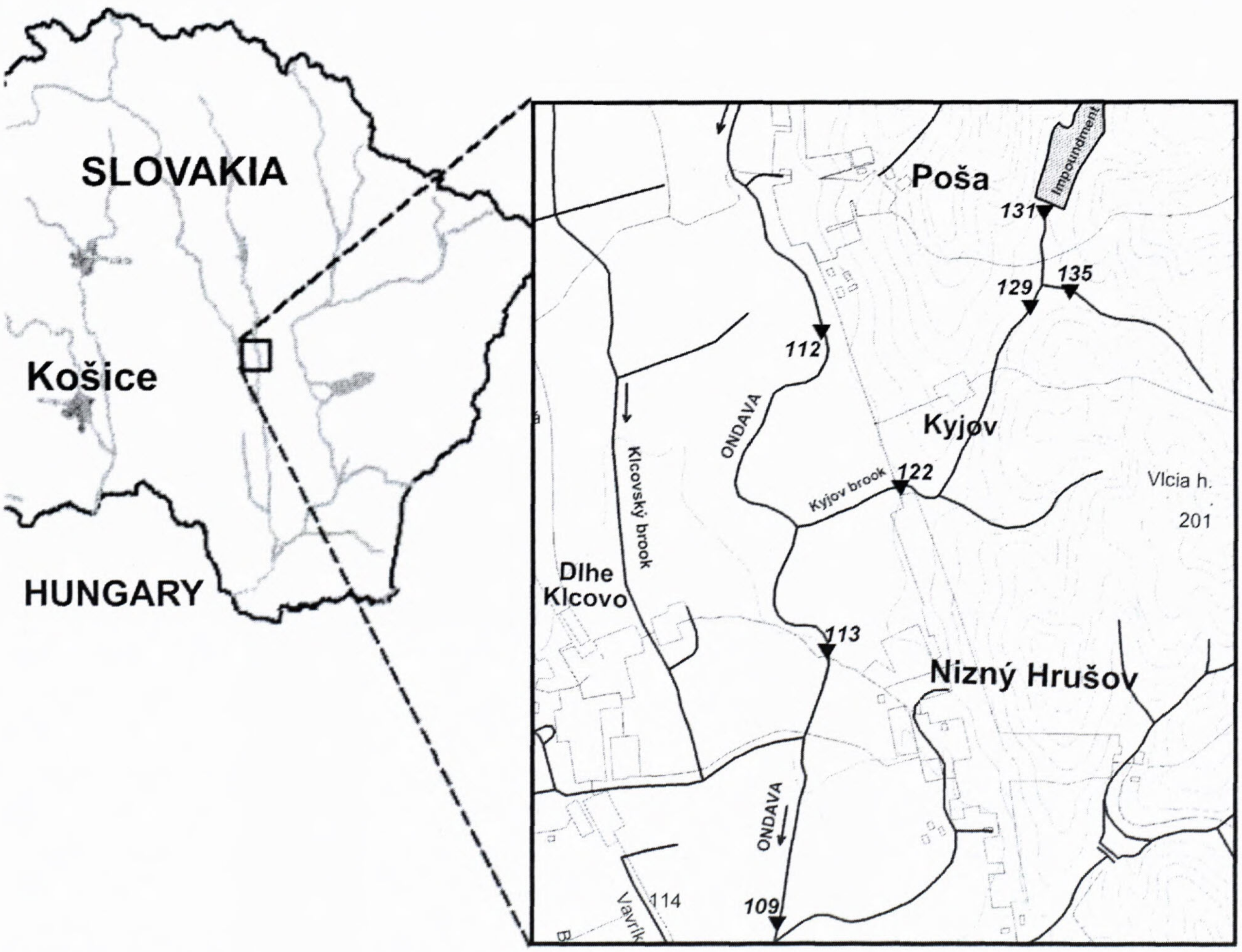

Fig. 1. Schematic map of the study area and sampling sites of the surface water during the period 1995 – 2004.

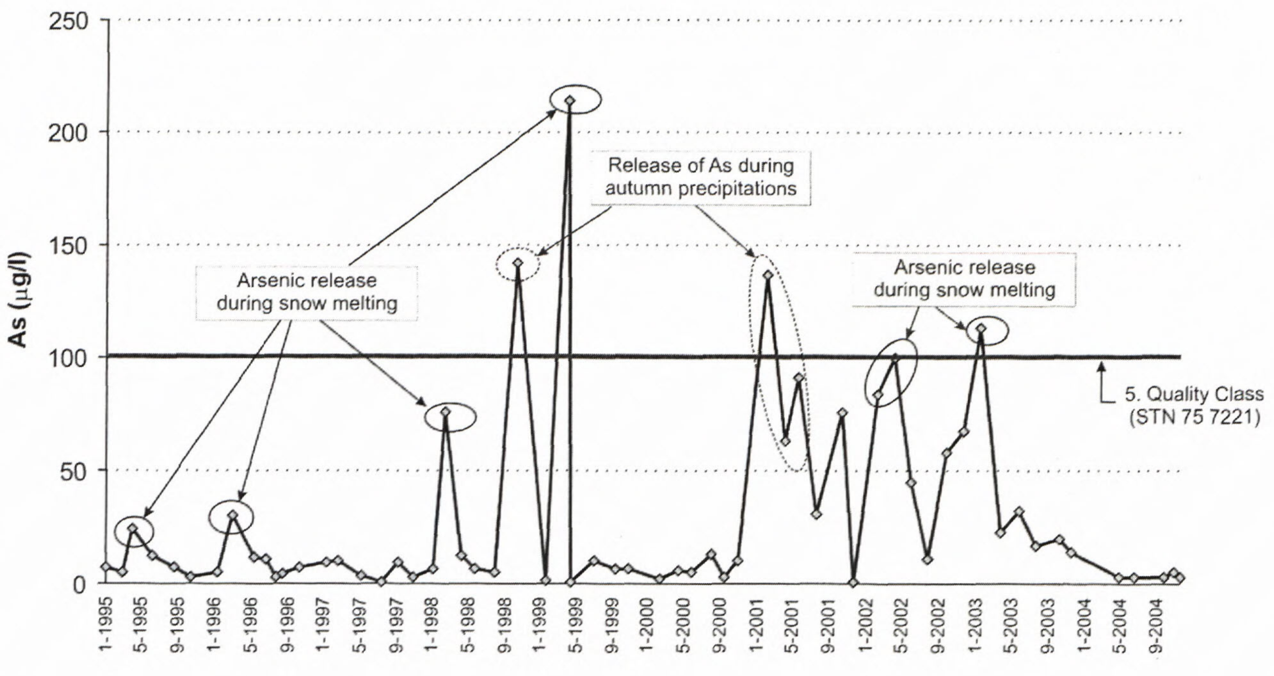

Fig. 2. Seasonal variation of As concentration in the Ondava river during 1995 – 2004 (SHMI sampling site No. 109 near the Nižný Hrušov village – SHMI, 1995-2004).

brook inflows nearby the village of Nižný Hrušov. The investigated area and the sampling points of the surface waters are presented in Fig. 1.

The source of As contamination in the study region is put down to an impoundment located in the upper part of the Kyjov catchment. Impoundment was built in 1977 and was designed for depositing the burning waste and waste from burning coal (Pivovarčiova et al., 1989). The founder and owner of the impoundment is chemical concern. with production targetted at basic products of organic and inorganic chemistry – benzene chemistry, productions of cyclohexane, cyclohexanol, manufacture of industrial fertilizers, products based on ammonia, manufacture of concentrated nitric acid for nitration purposes and other (Annual Report, 2004)

Selected analytical results of arsenic contents of the sampled Kyjov brook and the Ondava river are presented in Tab. 2 (period 1999 – 2004). The quality of surface water in the Ondava river (sampling site Nižný Hrušov – No. 109) is permanently monitored by the Slovak Hydrometeorological Institute. Geological Survey of Slovak Republic regularly monitors sampling site No. 122 (located at the border of Nižný Hrušov village). Other sampling sites represent one-shot measures taken during the study of geological factors of the environment in the "TIBREG" region in 1999 (Kordík and Slaninka, 2001). Moreover, a background mean value of arsenic and limit concentrations valid for drinking waters and surface water quality are given in Tab. 2 in order to compare significant values of arsenic with the measured arsenic contents in the area.

Sampling point No. 112 (Ondava river – located upstream to the confluence with the Kyjov brook) shows very low As concentration (0.26 $\mu g.l^{-1}$), typical for background natural conditions in the area. Much higher arsenic contents have been observed in the contaminated part of the Ondava river located downstream to the confluence with the Kyjov brook (up to 113 $\mu g.l^{-1}$). Extreme values of arsenic are characteristic for the whole Kyjov catchment (reach the values in thousands $\mu g.l^{-1}$).

Concentrations of arsenic in groundwaters of Slovakia range from 0.5 $\mu g.l^{-1}$ to 887.5 $\mu g.l^{-1}$, with the mean As concentration only 1,9 $\mu g.l^{-1}$ and median 0,5 $\mu g.l^{-1}$ (Rapant et al., 1996). Arsenic distribution pattern in surface waters of Slovakia is very similar to the groundwaters. Arithmetic mean of As concentration for surface waters of Eastern Slovakia is 2.6 $\mu g.l^{-1}$ with minimum values under the detection limit (0.5 $\mu g.l^{-1}$) and the highest concentration 118 $\mu g.l^{-1}$ (extreme arsenic concentrations from the Kyjov brook were excluded from the calculation of statistical parameters). Decree of the Slovak Health Ministry No. 151/2004 on drinking water demands and drinking water quality control and Slovak Technical Standard (STN 75 7221) strictly limit the arsenic contents in waters (values are given in Tab. 2). Based on the above mentioned arsenic concentrations and legislative standards it is obvious, that the measured concentrations of As especially in the contaminated Kyjov catchment show very high values. In other words, the arsenic concentrations in the Kyjov brook are app. 20 to 100 times higher in comparison to the arsenic limit value for V. quality class of surface water (100 $\mu g.l^{-1}$) and app. 2000 to 10000 times higher than the upper permissible value of arsenic for drinking water. In addition, arsenic contents in the contaminated part of the Ondava river (downstream to the confluence with the Kyjov brook) frequently reach values exceeding drinking water standard.

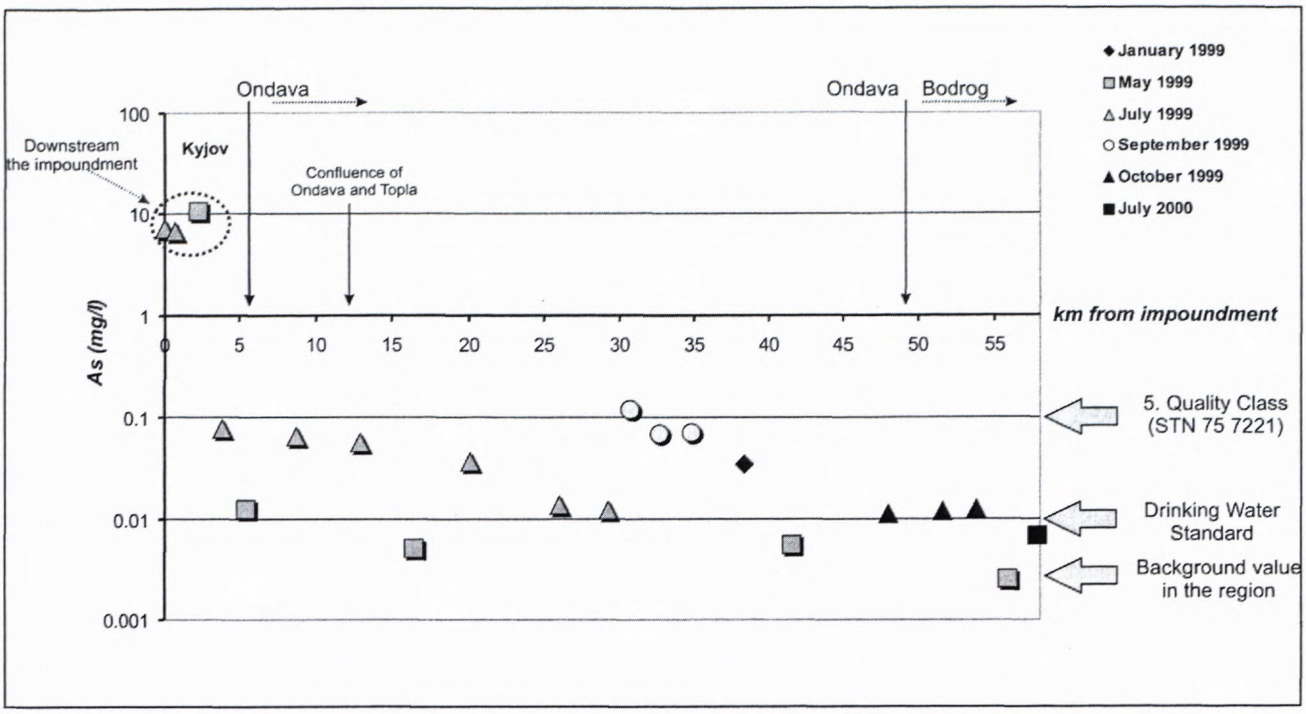

Fig. 3. Profile of arsenic distribution in the Kyjov brook, the Ondava and the Bodrog Rivers.

According to the results, the research of surface waters quality during the period 1995 – 2004 clearly shows very high level of arsenic contamination of the whole Kyjov catchment and partly the the Ondava river. These observations suppose an environmental load with potential influence on human health. For instance, epidemiological studies in areas with As concentration ranging from 350 to 1140 $\mu g.l^{-1}$ in drinking waters reported increased cancer risk (EHIS, 2000). We assume that the large amount of the As from the waste material. Mainly entered technological waters and rainfall in surroundings of impoundment affect the release of As and induce contamination of surface waters and stream sediments in the Kyjov brook and the Ondava river.

Data from the national monitoring programme performed by SHMI display concentration variability of arsenic in surface waters (Fig. 2). Variability of As concentration is obviously influenced also by seasonal conditions. It was found out that snow melting or higher precipitation events have also eminent influence on arsenic contents in surface water. Moreover, seasonal climatic changes could have a serious impact on variability of dissolved As forms as well. Gault et al. (2003) showed a seasonal difference in the dissolved arsenic concentration and its speciations by changing of As(V)/ΣAs ratio in surface water.

It was found out in the course of the research that contamination of aquatic environment by arsenic is really vast; it reaches up to more than 50 km downstream the Kyjov brook and the Ondava river. Increased arsenic concentration (above background mean value) has been detected also after the Ondava River joins the Latorica river as well as nearby the Slovak-Hungarian border (the Bodrog river). Profile of arsenic distribution in the Kyjov catchment, the Ondava and the Bodrog rivers is given in Fig. 3. Outstanding concentrations of arsenic are typical of the Kyjov catchment. Although the concentration rate of As is gradually decreasing downstream the Ondava and the Bodrog rivers, at the end of the rivers profile reach still high values.

The territory of Ondava watershed is a very important water supply area consisting of the fluvial sediments of the Ondava river (Hydrogeological region QN-106). This area belongs to large water resources available in Eastern Slovakia with possible total withdrawal 91 $l.s^{-1}$ (Jetel, 2001). Although no strong contamination of this water-bearing aquifer has been observed yet, the problem with arsenic contamination in the Kyjov catchment could pose serious danger to the groundwater quality of potential water supply (groundwater quality can become worse as a result of other potential sources of contamination such as high population density, industry etc.). In the assumption that mean flow rate of the Kyjov brook is 10 $l.s^{-1}$ (no real data at disposal) and mean As content is 1 $mg.l^{-1}$ downwards the impoundment, it is expected that 315 kg of As is released to the aquatic environment of the Ondava river annually (in several $mg.l^{-1}$).

Significant contamination was observed also in stream sediments (research under the study). For example, concentration of As in sample No. 122 (Kyjov) reached a value of 284 $mg.kg^{-1}$ (August 2004) and concentration of As close to the impoundment was extremely high reaching 3208 $mg.kg^{-1}$. The stream sediment in the Ondava river monitoring site (Tab. 3) is also significantly contaminated but showing strong variation of arsenic values. All obtained analytical results of arsenic in stream sediments of the study area significantly exceed natural background level of arsenic (average concentration is 8 $mg.kg^{-1}$) calculated according the data given in (Kordík and Slaninka, 2001) and represent high environmental risk to the environment.

Tab. 3. Concentrations of arsenic in stream sediments from the Ondava River (in $mg.kg^{-1}$).

Sample No.113	Sampling date							
	06/1996	06/1998	05/1999	06/2000	08/2001	07/2002	07/2003	08/2004
	38.9	16.7	17.4	105.4	101.5	42.3	60.3	11.9

Tab. 4. Statistical parameters of analytical results in surface waters (all data in $mg.l^{-1}$).

	TDS	*Na*	*K*	*NH_4*	*Cl*	*SO_4*	*NO_3*	*PO_4*	*As*	*TOC*
Kyjov brook (n = 6)										
Mean	1353.18	199.20	37.57	26.15	131.71	307.66	28.97	1.937	1.7781	30.68
Median	1049.33	103.90	35.87	26.14	125.72	250.65	29.07	2.013	0.4587	29.95
St. Dev.	561.23	215.50	5.02	10.55	16.86	127.30	11.77	0.586	2.5129	2.14
Min.	965.46	99.40	33.80	11.11	120.49	231.45	12.40	1.015	0.3935	29.00
Max.	2340.00	584.65	45.90	39.00	161.01	532.50	40.31	2.50	6.70	33.80
Ondava river (n = 10)										
Mean	399.44	19.83	4.18	0.21	20.90	53.42	5.60	0.198	0.0266	5.33
Median	412.85	19.14	3.84	0.24	21.39	51.25	5.58	0.111	0.0088	5.45
St. Dev.	35.44	7.21	0.78	0.16	6.31	7.11	2.51	0.144	0.0297	0.43
Min.	310.00	10.61	3.18	0.00	9.98	45.25	3.01	0.080	0.0022	4.70
Max.	428.00	34.04	5.90	0.44	26.94	69.15	10.32	0.418	0.0776	5.70
Referenced brooks (n = 17)										
Mean	528.29	25.73	4.63	0.73	29.02	47.45	12.93	0.174	0.00097	
Median	535.00	23.69	4.10	0.20	25.33	45.70	8.95	0.107	0.00075	
St. Dev.	108.62	10.99	3.13	2.06	12.37	18.63	11.92	0.156	0.00053	
Min.	297.00	12.27	1.42	0.01	10.62	14.00	0.79	0.061	0.00050	
Max.	747.00	47.74	13.12	8.65	51.16	90.55	37.79	0.666	0.00232	

For the sake of more detailed geochemical study, additional samples of surface waters were collected in June 2005. Situation map of the sampling sites is presented in Fig. 4. Analytical results showed totally different character of chemical distribution between catchment of the Kyjov brook, the Ondava river and the referenced brooks in the region (Tab. 4). Except for arsenic, statistical parameters of the main ions, TDS and TOC are given in Tab. 4.

Significantly higher values of TDS, ammonium ions, sulphates, nitrates, chlorides and arsenic are typical for the secondarily influenced Kyjov brook. It is very interesting that higher values of total organic carbon (TOC) were obtained in surface waters downwards the impoundment. This might point to organic contamination of the Kyjov brook from impoundment material. Comparison of analytical results from filtered and non-filtered water samples is also considered rather important for assessment of arsenic contamination. In 2005, both the filtered and non-filtered water samples were analysed. The results of this comparison showed that majority of arsenic in the study area is presented in soluble forms.

Relation between arsenic concentration and TDS for the different surface waters (Kyjov catchment, the Ondava river, impoundment and referenced brooks) is presented in Fig. 5. The figure shows a different level of the surface water contamination in the study region. In the referenced brooks low As concentrations up to 2.32 $\mu g.l^{-1}$ and TDS contents ranging app. from 300 to 700 $mg.l^{-1}$ has been observed. In the Ondava river higher As concentrations are typical and depend on the position to the

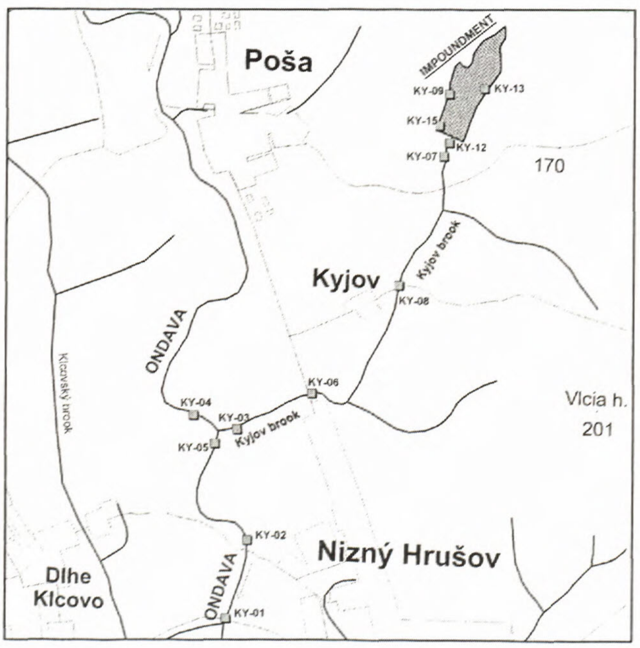

Fig. 4. Schematic map of samples localization during June, 2005.

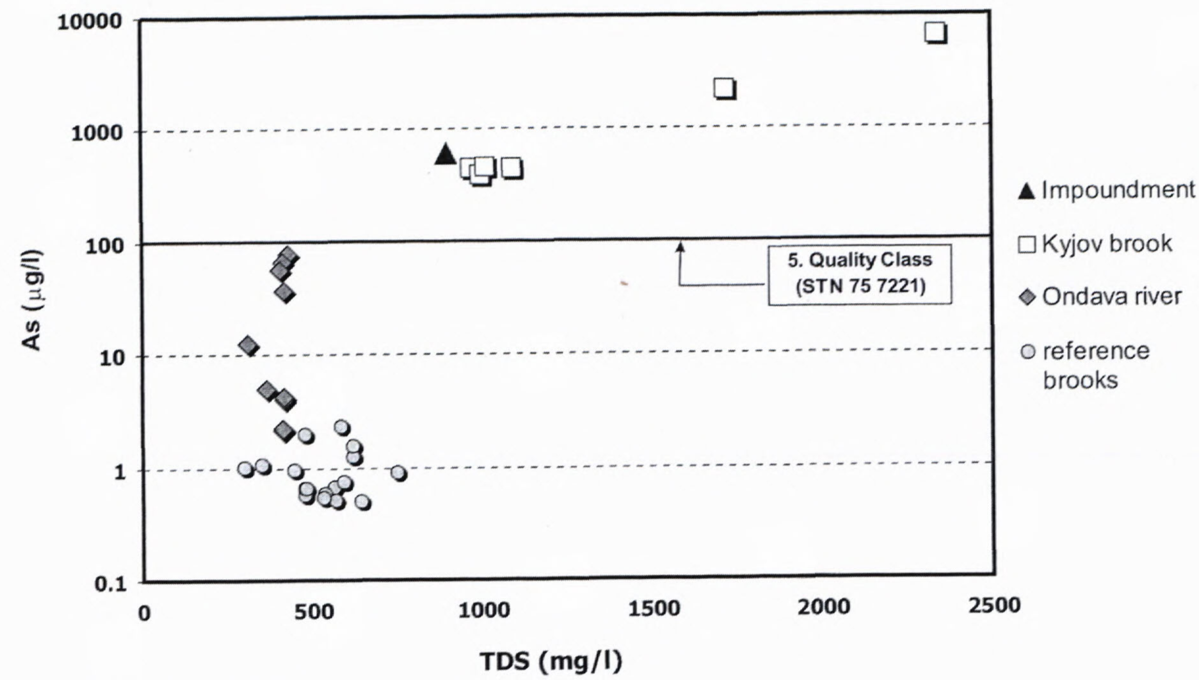

Fig. 5. Distribution and relation of As and TDS in surface waters.

Kyjov brook. The As contents upstream the confluence with the Kyjov brook reach values of about 3-7 μg.l^{-1} and downstream the confluence of about 10-100 μg.l^{-1}. Contents of TDS are slightly lower than in the referenced brooks (around 400 mg.l^{-1}). Outstanding values of both arsenic and TDS are typical of the Kyjov catchment and impoundment ranging from about 400 to 6700 μg.l^{-1} for arsenic and from about 1000 to 2300 mg.l^{-1}.

4. Conclusions

Basic information about arsenic contamination of aquatic environment in the Kyjov and Ondava catchments (Eastern Slovakia) are presented in the paper. The detailed field research focused on waste material from impoundment, stream sediments and surface waters results in a wide-range arsenic contamination of aquatic environment in the study region.

Significantly higher values of TDS, ammonium ions, sulphates, nitrates, chlorides and especially arsenic are typical of the secondarily influenced Kyjov brook. Increased values of total organic carbon showed organic contamination of the Kyjov brook from impoundment material. Moreover we assume, that large release of As from the waste material is partially influenced also by seasonal conditions (depending on snow melting or higher precipitation events). For risk assessment of As mobility it is important that major amount of arsenic in the locality is present in soluble form.

Significant arsenic contamination is detected also in stream sediments of the Kyjov brook and particularly in the Ondava river (extreme As values downwards the impoundment). This observation supposes serious environmental load with potential negative influence on aquatic environment and human health. In addition, a potential entry of arsenic into the food chain can pose a serious health risk as well. Increased arsenic values were measured also in biological material from the impoundment, e.g. Ceratophyllum demersum 254 mg.kg^{-1} of total As (under the current study). In order to sort out this problem, thorough description and justification of the mobile As-forms, its bioavailability and experimental estimation of sorption and desorption behaviour of As in aquatic environment will be necessary. All obtained field and analytical data should predict the potential risk of arsenic contamination to the water environment.

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