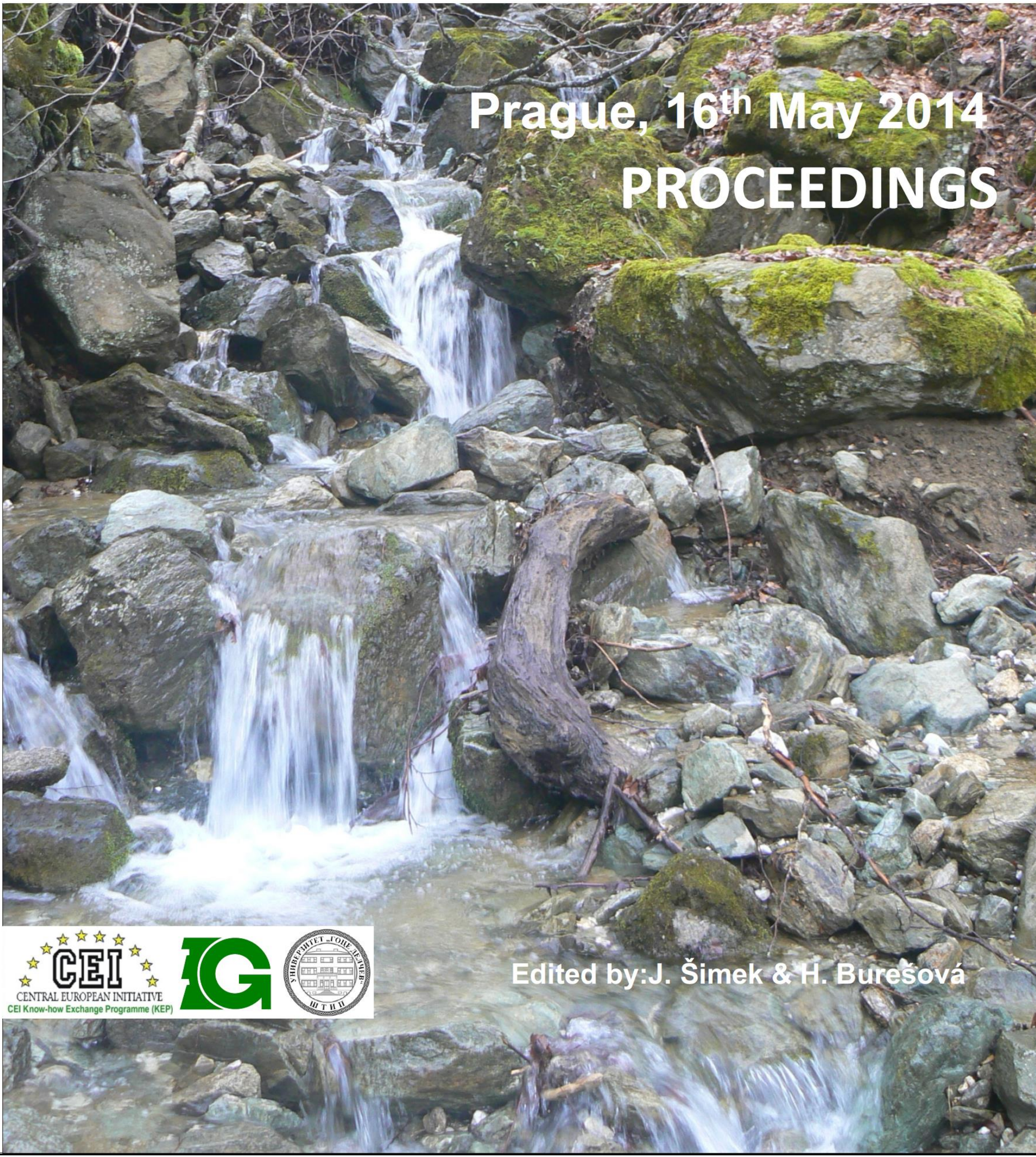
ENIGMA 2nd INTERNATIONAL WORKSHOP

GIS-GEOINDUSTRY, s.r.o., Czech Republic CEI Know-how Exchange Programme

2nd INTERNATIONAL WORKSHOP

Environmental impact assessment of the Kozuf metallogenic district in southern Macedonia in relation to groundwater resources, surface waters, soils and socio-economic consequences (ENIGMA)



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PROCEEDINGS

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ON THE PROJECT

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ENVIRONMENTAL AND HEALTH RISKS OF KOZUF METALLOGENIC DISTRICT

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Abstract: Kožuf metallogenic district is significantly affected by former exploration and exploitation which lead to increased concentrations of heavy metals in individual environmental components. These metals can enter into water environment by leaching, acid main drainage, erosion and sedimentation. Water and soil analyses of Kozuf metallogenic district performed by the team of Faculty of Natural and Technical Sciences (University "Goce Delčev"-Štip, Macedonia) and GIS-GEOINDUSTRY (Czech Republic) in 2013 detected increased concentrations of Sb, As and Tl. Health risks of these metals in drinking water as well as their legal limits are discussed.

Key words: Kožuf area, heavy metals, health risk

INTRODUCTION

Kožuf metallogenic district has been recently the subject of intense exploration and mining activities that contributed to increased concentrations of heavy metals in the surrounding environment. These metals may cause various environmental and health risks. Generally, there are several main ways how can heavy metals enter into water and influence its quality [1]:

Acid Mine Drainage

Acid Mine Drainage (AMD) is a process whereby sulphuric acid is produced when sulphides in rocks are exposed to air and water. When large quantities of rock containing sulphide minerals are excavated from an open pit or opened up in an underground mine, it reacts with water and oxygen to create sulphuric acid. The acid will leach from the rock as long as its source is exposed to air and water and until the sulphides are leached out – a process that can last hundreds, even thousands of years. Acid is carried off the mine site by rainwater or surface drainage and deposited into nearby streams, rivers, lakes and groundwater. AMD severely degrades water quality and can devastate aquatic life and make water virtually unusable.

Heavy Metal Contamination & Leaching

Heavy metal pollution is caused when such metals as arsenic, cobalt, copper, cadmium, lead, silver and zinc contained in excavated rock or exposed in an underground mine come in contact with water. Metals are leached out and carried downstream as water washes over the rock surface. Although metals can become mobile in neutral pH conditions, leaching is particularly accelerated in the low pH conditions such as are created by Acid Mine Drainage.

Erosion and Sedimentation

Mineral development disturbs soil and rock in the course of constructing and maintaining roads, open pits, and waste impoundments. In the absence of adequate prevention and control strategies, erosion of the exposed earth may carry substantial amounts of sediment into streams, rivers and lakes. Excessive sediment can clog riverbeds and smother watershed vegetation, wildlife habitat and aquatic organisms.

LOCALITY CHARACTERIZATION

The westernmost parts of the Kozuf metallogenic district reach the river Blasica (right tributary of Crna river) and the north-western side stretches in a line, from the Mrezicko village via the village Konopiste, through the course of Bosavica river to the city of Demir Kapija. Through these waterways the entire area is drained into the river Vardar. As a result of past mining activities within the area of interest there are unreclaimed dumps with anomalous concentrations of antimony, arsenic, lead, mercury and thallium at abandoned, but world-known Alshar mine, that represent a significant environmental and health hazards. Other known ore deposits/mineral occurrences are Majdan (arsenic), Dudica (copper-gold) and Arnicko (antimony). Other ore deposits are supposed to have existed here but have remained unknown due to the lack of exploration. The lack of exploration implies lack of awareness of potential risks. [2].

At the Kozuf Mt. there has been formed karstic formations and groundwater is drained through a number of karstic sources. Main karstic sources are Lukar-1, Lukar-2 and Kosmatec providing drinking water for Kavadarci and Negotino municipalities and a number of settlements. Approximate population that may be affected by negative impacts in downstream area is about 60 000 people. [2]

WATER AND SOIL ANALYSES

Water and soil analyses of Kozuf metallogenic district were performed by the team of Faculty of Natural and Technical Sciences (University "Goce Delčev"– Štip, Macedonia) and Gis-Geoindustry, s.r.o. (Czech Republic) in 2013. Previously, the major pollution in both studied areas within the Kozuf district (Alšar and Dudica) have been determined in solid samples (stream sediments, soil and mine waste) from the Alšar area. It is directly related to the former exploration and exploitation when prolonged deposition of heavy metals took place. Increased concentrations of particular metals such are Sb, Tl, As and some others at the sampling point A10 (hot water well called Toplec) can be attributed to the water with higher temperature which leaches and mobilizes former metals and transported them to the surface. In all other water samples from both areas metal concentration levels were below maximally allowed concentrations (MDK) values, in one part probably due to high water levels (ground and surface) in April 2013, resulting in dilution of the sampled media. [2]

HEALTH RISKS OF SELECTED METALS

The chemical test results indicate that the mine waste tips present in the Alshar valley are very heavily contaminated with antimony, arsenic, cadmium and thallium.

The increased arsenic, antimony and thallium concentrations could pose risk for the human environment along the River Majdanska, the river flowing through the Alshar valley, which is an upstream tributary of the River Blašnica. The Blašnica flows in a general northwards direction past Majden and then Rozden to the west, before forming a confluence with the Kozamik.

Health risks of antimony, arsenic and thallium are described in following paragraphs. In Table 1, there are showed Macedonian limits for antimony, arsenic and thallium in various classes of water. For comparison, there are mentioned Czech limits for surface water in Table 2, Czech limits for drinking water in Table 3 and EPA limits for water in Table 4.

Table 1: Macedonian limits given in the Decree on Water Classification [3]

	Limits (µg/L)		
	Class I-II	**Class III-IV**	**Class V**
Antimony (Sb)	30	50	> 50
Arsenic (As)	30	50	> 50
Thallium (Tl)		not limited	

Class I – Very clean, oligotrophic water, which is in its natural state (with eventual disinfection). It can be used for drinking and production of food products as well as for production of fish (*Salmonidae*).
Class II – Low polluted mesotrophic water, which is in its natural state and can be used for bathing, swimming, recreation and fish farming (*Cyprinidae*). With some standard treatment (coagulation, filtration, disinfection etc.) can be used for drinking and food production.
Class III – Partly eutrophic water, which is in its natural state and can be used for irrigation. After treatment it can be used in industry, but not for drinking.
Class IV – Strongly eutrophic and polluted water, which can be used in some industries only after particular treatment. So called "algae blossoming" is present. Increased decomposition of organic material may cause anaerobic conditions and death of fish. It cannot be used for recreational purposes.
Class V – Very polluted and hypertrophic water, which cannot be used in its natural state for any purpose. [4]

Table 2: Czech water quality classes and their limit values – excerpted from the ČSN 75 7221 Czech National Standard, Classification of Surface Water Quality [5]

			Limits (µg/L)		
	Class I	**Class II**	**Class III**	**Class IV**	**Class V**
Antimony (Sb)			not limited		
Arsenic (As)	< 1	< 10	< 20	< 50	≥ 50
Thallium (Tl)			not limited		

Class I – unpolluted water – surface water condition that has not been substantially affected by human activities; water quality criteria do not exceed values consistent with normal natural background in surface streams
Class II – slightly polluted – surface water condition that has been affected by human activities; however, water quality criteria attain values that enable the existence of a rich, balanced and sustainable ecosystem
Class III – polluted water – surface water condition that has been affected by human activities to such an extent that water quality criteria attain values which need not necessarily provide prerequisites for the existence of a rich, balanced and sustainable ecosystem
Class IV – heavily polluted water – surface water condition that has been affected by human activities to such an extent that water quality criteria attain values which permit the existence of an unbalanced ecosystem only
Class V – very heavily polluted water – surface water condition that has been affected by human activities to such an extent that water quality criteria attain values which permit the existence of a very unbalanced ecosystem only

Table 3: Czech limits for drinking water given in decree 252/2004 Sb. [6]

	Limits (µg/L)
Antimony (Sb)	5.0
Arsenic (As)	10
Thallium (Tl)	not limited

Table 4: EPA limits for drinking water – the maximum contaminant level (MCL) and maximum contaminant level goals (MCLG) – for selected metals.

	Limits (µg/L)	
	MCL	**MCLG**
Antimony (Sb)	6.0	6.0
Arsenic (As)	10	0
Thallium (Tl)	2.0	0.5

MCLG – Non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety.
MCL – Maximum contaminant level are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies.

Antimony

Antimony is a silvery-white metal that is found in the earth's crust. It is found in natural deposits such as ores containing other elements. Soil usually contains very low concentrations of antimony (less than 1 ppm). However, higher concentrations have been detected at hazardous waste sites and at antimony-processing sites.

Antimony ores are mined and then either changed to antimony metal or combined with oxygen to form antimony oxide. Antimony oxides (primarily antimony trioxide) are used as fire retardants for plastics, textiles, rubber, adhesives, pigments, and paper.

Antimony is also found in batteries, pigments, ceramics and glass. It is alloyed with other metals such as lead to increase its hardness and strength; its primary use is in antimonial lead, which is used in grid metal for lead acid storage batteries. Other uses of antimony alloys are for solder, sheet and pipe, bearing metals, castings, and type metal.

The major sources of antimony in drinking water are discharge from petroleum refineries; fire retardants; ceramics; electronics; and solder.

Everyone is exposed to low levels of antimony in the environment. Some people who drink water containing antimony well in excess of the maximum contaminant level (MCL) for many years could experience increases in blood cholesterol and decreases in blood sugar. Human studies are inconclusive regarding antimony exposure and cancer, while animal studies have reported lung tumors in rats exposed to antimony trioxide via inhalation. EPA has not classified antimony for carcinogenicity.

The non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). MCLG for antimony is 6 μg/L. EPA has set this level of protection based on the best available science to prevent potential health problems. EPA has also set an enforceable regulation for antimony, called a maximum contaminant level (MCL), at 6 μg /L. MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies. In this case, the MCL equals the MCLG, because analytical methods or treatment technology do not pose any limitation. [7, 8]

Arsenic

Arsenic occurs naturally in rocks and soil, water, air, and plants and animals. It can be further released into the environment through natural activities such as volcanic action, erosion of rocks and forest fires, or through human actions. Approximately 90 percent of industrial arsenic in the U.S. is currently used as a wood preservative, but arsenic is also used in paints, dyes, metals, drugs, soaps and semi-conductors. High arsenic levels can also come from certain fertilizers and animal feeding operations. Industry practices such as copper smelting, mining and coal burning also contribute to arsenic in environment.

Higher levels of arsenic tend to be found more in ground water sources than in surface water sources (i.e., lakes and rivers) of drinking water. The demand on ground water from municipal systems and private drinking water wells may cause water levels to drop and release arsenic from rock formations.

Human exposure to arsenic can cause both short and long term health effects. Long term exposure to arsenic has been linked to cancer of the bladder, lungs, skin, kidneys, nasal passages, liver and prostate. Short term exposure to high doses of arsenic can cause other adverse health effects – skin damage or problems with circulatory systems, and may have increased risk of getting cancer.

EPA has set the maximum contaminant level goals (MCLG) for thallium is 0 µg/L and enforceable regulation for thallium, called a maximum contaminant level (MCL) at 10 µg/L. [9]

Thallium

The major sources of thallium in drinking water are leaching from ore-processing sites; and discharge from electronics, glass, and drug factories.

Some people who drink water containing thallium well in excess of the maximum contaminant level (MCL) for many years could experience hair loss, changes in blood chemistry, or problems with their kidneys, intestinal and testicular tissues, or liver problems.

There is no evidence that thallium has the potential to cause cancer from lifetime exposures in drinking water.

EPA has set the maximum contaminant level goals (MCLG) for thallium is 0.5 µg/L and enforceable regulation for thallium, called a maximum contaminant level (MCL) at 2 µg/L. [10]

World Health Organization (WHO) set the upper limit of the allowed range of thallium concentrations of 1 µg/L Tl. [11]

Conclusion

With the exception of sample No. A10 analyses of water samples collected during the latest sampling campaign did not prove values over allowed limits for antimony, arsenic and thallium. Detail decription of negative influence of these paricular elements on human health, however, gives a strong incentive for regular monitoring of the quality of groundwater used for drinking purposes.

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