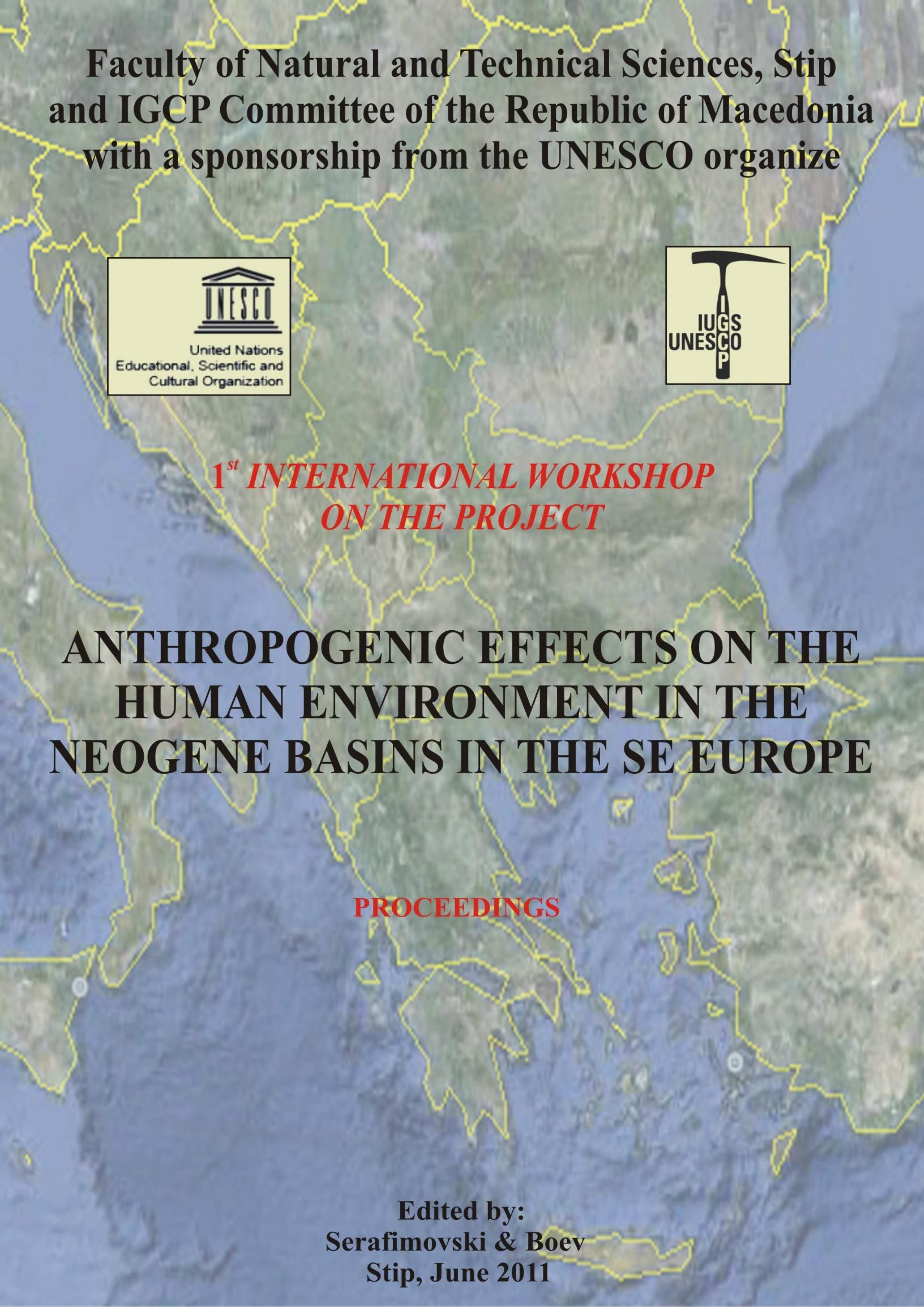

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1st *INTERNATIONAL WORKSHOP ON THE PROJECT*

ANTHROPOGENIC EFFECTS ON THE HUMAN ENVIRONMENT IN THE NEOGENE BASINS IN THE SE EUROPE

PROCEEDINGS

Edited by:
Serafimovski & Boev
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National UNESCO-IGCP Committee in the Republic of Macedonia has long tradition and active work in area of correlation in geology. More than five decades this Committee brings together scientific researchers in the area of geology within the Republic of Macedonia and creates basis for animation of geological problems in the country and abroad. Numerous active memebers of the Macedonian IGCP-Committee took participation in numerous scientific projects that were financially supported by UNESCO, but there are few teams in the Republic of Macedonia that have managed to be leaders of important projects in the area of geology and human environment, also.

During the last decade the Macedonian Nationa UNESCO-IGCP Committee successfully was involved in studies of anthropogenic effects on the human environment in a wider region that occupies area of former Yugoslavia, Mediterranean and presently Southeastern Europe. As main partners of the Macedonian UNESCO-IGCP Committee in these important activities participate national UNESCO-IGCP Committees of the Republic of Slovenia and Republic of Croatia, regularly supported by National UNESCO-IGCP Committees, groups and individual researchers from the UK, France, Switzerland, Bulgaria, Russia, Greece, Romania, Slovakia, Czech Republic, Germany etc.

The ongoing UNESCO-IGCP Project "Anthropogenic effects on the human environment in the Neogene basins in the SE Europe", which financially have been supported by the Participation Programme 2010-2011, represents just confirmation of the continuity of scientific activities of the National UNESCO-IGCP Committee and opens an opportunity for new studies and enclosure of more younger scientific workers in the country and from abroad. In that context speaks already organized 1st International Workshop on this project at 3-4 June 2011 in Stip, Republic of Macedonia where active participation took more than 40 participants from few European countries. These project activities have resulted with preparation of a Proceeding Book containing 14 selected scientific papers, which have been presented at the aforementioned Workshop.

Aknowledgement:

This Workshop was organized with a financial support from the UNESCO-IGCP Participation Programme 2010-2011through the National Commission for UNESCO in Skopje, Republic of Macedonia

CONTENTS

INSTEAD OF PREFACE

GENERAL FEATURES RELATED TO HUMAN ENVIRONMENT CHANGES

Anthropogenic effects as an integral part of so called anthrosphere may be defined as *that part of the environment made or modified by humans and used for their activities.* Of course, there are some ambiguities associated with that definition. Clearly, a factory building used for manufacture is part of the anthrosphere as is an ocean-going ship used to ship goods made in the factory. The ocean on which the ship moves belongs to the hydrosphere, but it is clearly used and affected by humans. A pier constructed on the ocean shore and used to load the ship is part of the anthrosphere, but it is closely associated with the hydrosphere. During most of its time on Earth, humankind made little impact on the planet, and its small, widely scattered anthropogenic artifacts—simple huts or tents for dwellings, narrow trails worn across the land for movement, clearings in forests to grow some food—rested lightly on the land with virtually no impact. However, with increasing effect as the industrial revolution developed, and especially during the last century, humans have built structures and modified the other environmental spheres, especially the geosphere, such that it is necessary to consider the anthrosphere as a separate area with pronounced, sometimes overwhelming influence on the environment as a whole.

Components of the Anthrosphere

As the various spheres of the environment are each divided into several subcategories. (ex.: the hydrosphere consists of oceans, streams, groundwater, ice in polar icecaps, and other components), the anthrosphere, too, consists of a number of different parts. These may be categorized by considering where humans live; how they move; how they make or provide the things or services they need or want; how they produce food, fiber, and wood; how they obtain, distribute, and use energy; how they communicate; how they extract and process nonrenewable minerals; and how they collect, treat, and dispose of wastes. With these factors in mind, it is possible to divide the anthrosphere into the following categories:

- Structures used for dwellings
- Structures used for manufacturing, commerce, education, and other activities
- Utilities, including water, fuel, and electricity distribution systems, and waste distribution systems, such as sewers
- Structures used for transportation, including roads, railroads, airports, and waterways constructed or modified for water transport
- Structures and other parts of the environment modified for food production, such as fields used for growing crops and water systems used to irrigate the fields
- Machines of various kinds, including automobiles, farm machinery, and airplanes
- Structures and devices used for communications, such as telephone lines or radio transmitter towers
- Structures, such as mines or oil wells, associated with extractive industries

From the list given above it is obvious that the anthrosphere is very complex with an enormous potential to affect the environment.

Anthropogene effects on the Earth

Anthropogenic effects on Earth have been many and profound. Persistent and potentially harmful products of human activities have been widely dispersed and concentrated in specific locations in the anthrosphere as well as other spheres of the environment as the result of human activities. Among the most troublesome of these are toxic heavy metals and organochlorine compounds. Such materials have accumulated in painted and coated surfaces, such as organotincontaining paints used to prevent biofouling on boats; under and adjacent to airport runways; under and along highway paving; buried in old factory sites; in landfills; and in materials dredged from waterways and harbors that are sometimes used as landfill on which buildings, airport runways and other structures have been placed. In many cases productive topsoil used to grow food has been contaminated with discarded industrial wastes, phosphate fertilizers, and dried sewage sludge. In some cases the contamination has been so pervasive and persistent that the effects will remain for centuries. Some of the most vexsome environmental and waste problems are due to contamination of various parts of the anthrosphere by persistent and toxic waste materials. Potentially harmful wastes and pollutants of anthropogene origin have found their way into water, air, soil, and living organisms. For example, chlorofluorocarbons (Freons) have been released to the atmosphere in such quantities and are so stable that they are now constituents of "normal" atmospheric air and pose a threat to the protective ozone layer in the stratosphere. Lake sediments, stream beds, and deltas deposited by flowing rivers are contaminated with heavy metals and refractory organic compounds of anthrospheric origin. The most troubling repository of wastes in the hydrosphere is groundwater. Some organisms have accumulated high enough levels of persistent organic compounds or heavy metals to do harm to themselves or to humans that use them as a food source.

Integration of the anthropogenicaly induced effects into the total environment

Over the eons of Earth's existence, natural processes free from sudden, catastrophic disturbances (such as those that have occurred from massive asteroid impacts, for example) have resulted in a finely tuned balance among the systems composing Earth's natural environment. Fortuitously, these conditions-adequate water, moderate temperatures, an atmosphere that serves as a shield against damaging solar radiation have resulted in conditions amenable to various life forms. Indeed, these life forms have had a strong impact in changing their own environments. According to the well known *Gaia hypothesis* (advanced by the British chemist James Lovelock), organisms on Earth have modified Earth's climate and other environmental conditions, such as by regulating the CO_2/O_2 balance in the atmosphere, in a manner conducive to the existence and reproduction of the organisms. To a degree, the early anthropogene impact created by pre-industrial humans integrated well with the environment and caused minimal environmental degradation. That this was so resulted less from any noble instincts of humankind toward nature than it did from the lack of power to alter the environment. In those cases where humans had the capability of modifying or damaging their surroundings, such as by burning forests to provide cropland, the effects on the natural environment could be profound and very damaging. In general, though, preindustrial humans integrated their influence, such as it was, with the natural environment as a whole.

The relatively harmonious relationship between the anthropogene activities and the rest of the environment began to change markedly with the introduction of machines, particularly power sources, beginning with the steam engine, that greatly multiplied the capabilities of humans to alter their surroundings. As humans developed their use of machines and other attributes of industrialized civilization, they did so with little consideration of the environment and in a way that was out of synchronization with the other environmental spheres. A massive environmental imbalance has resulted, the magnitude of which has been realized only in recent decades. The most commonly cited manifestation of this imbalance has been pollution of air or water. Because of the detrimental effects of human activities undertaken without due consideration of environmental consequences, significant efforts have been made to reduce the environmental impacts of these activities. The first approach to dealing with the pollutants and wastes produced by industrial activities-particulate matter from power plant stacks, sulfur dioxide from copper smelters, and mercury contaminated wastes from chlor-alkali manufacture-was to ignore them. However, as smoke from uncontrolled factory furnaces, raw sewage, and other by-products of human activities became more troublesome, "end-of-pipe" measures were adopted to prevent the release of pollutants after they were generated. Such measures have included electrostatic precipitators and flue gas desulfurization to remove particulate matter and sulfur dioxide from flue gas; physical processes used in primary sewage treatment; microbial processes used for secondary sewage treatment; and physical, chemical, and biological processes for advanced (tertiary) sewage treatment. Such treatment measures are often very sophisticated and effective. Another kind of endof-pipe treatment is the disposal of wastes in a supposedly safe place. In some cases, such as municipal solid wastes, radioactive materials, hazardous chemicals, power plant ash, and contaminated soil, disposal of sequestered wastes in a secure location is practiced as a direct treatment process. In other cases, including flue-gas desulfurization sludge, sewage sludge, and sludge from chemical treatment of industrial wastewater, disposal is practiced as an adjunct to other end-of-pipe measures. Waste disposal practices later found to be inadequate have spawned an entirely separate end-of-pipe treatment called **remediation** in which discarded wastes are dug up, sometimes subjected to additional treatment, and then placed in a more secure disposal site. Although sometimes unavoidable, the production of pollutants followed by measures taken to control or remediate them to reduce the quantities and potential harmfulness of wastes are not very desirable. Such measures do not usually eliminate wastes and may, in fact, transfer a waste problem from one part of the environment to another. An example of this is the removal of air pollutants from stack gas and their disposal on land, where they have the potential to cause groundwater pollution. Clearly, it is now unacceptable to ignore pollution and to dump wastes, and the control of pollutants and wastes after they are produced is not a good permanent solution to waste problems. Therefore, it has become accepted practice to "close the loop" on industrial processes, recycling materials as much as possible and allowing only benign waste products to be released to the environment.

Warfare activities within the region and in a such manner introduced contaminations

During the nineties of the last century and beginning of this one the Balkan experienced intensive warfare activities and associated consequences. Just to mention some war clashes in the region: Croatia, Bosnia, Kosovo and Macedonia. Those war clashes have caused considerable environmental damage to the broader Balkan region. War clashes in Macedonia, which happened during the 2001 have increased treat of the warfare introduced pollution within the country. Realization of the proposed project and its results would help the social, political and economical development of that part of the country.

A large number of industrial facilities were reportedly attacked and destroyed during those various war clashes in aforementioned countries. As a consequence of this, significant amounts of hazardous chemicals have been released into surface waters, ground waters, air and soil, affecting the wider Balkans region. However, these transboundary pollution events have caused less public concern than subsequent admittance that the alliance had used depleted uranium (DU) ammunition both in Kosovo and during the earlier military operations in Bosnia and Herzegovina.

Increased public concern regarding the dumping of unspent ordnance and the use of depleted uranium (DU) ammunition during military operations, has resulted in several field preliminary investigations, which have shown that some components of DU ordnance contain trace amounts of transuranics and fission products indicating the use of reprocessed uranium in the manufacture of these components. A simple calculation yields the result that at least 10 tons of DU have been deployed. Some of this ammunition still litters various parts of the area, causing concerns about environmental contamination and human health risks in the basin. UNEP's Depleted Uranium Assessment Group, during its field assessment mission in November 2000, visited 11 of the 112 sites that were identified as being targeted by DU ordnance. Altogether, 340 samples were collected for analysis in 5 european laboratories. The samples include 247 soil samples, 30 vegetation samples, 10 smear tests, 8 parts of munition parts (sabots and penetrators). The final report was published in March 2001-UNEP report, confirming preliminary reports which stated that in addition to the "expected" uranium isotopes, parts of DU ordnance contained U-236 (0.0028 % of the total uranium content) and traces of other fission products, implying that these components were made from reprocessed uranium. Following this disclosure, a report by the Department of the Army of the United States of America, dated January 2000, was made public. The report states that DU components used by the US armed forces may contain trace amounts of transuranics (TRU) and Tc-99 (Kniewald and Bermanec, 2005). The TRU may contain Am-241, Np-237, Pu-238, Pu-239 and Pu-240. However, the TRU contamination of DU components contributed an additional 0.8 % to the radiation dose from the DU itself, considering this a very low radiological hazard associated with the primary DU material. Subsequently, international agency missions also assessed the situation both in Serbia-Montenegro-UNEP report, and Bosnia and Herzegovina-UNEP report and found that DU ammunition has also been used against targets in these countries.

Mining activities and anthropogenic effects to the human envrionments

All three principal activities of the mining industry-mining, mineral processing, and metallurgical extraction-produce wastes, such as solid mining, processing and metallurgical wastes and mine waters:

Mining wastes either do not contain ore minerals, industrial minerals, metals, coal or mineral fuels, or the concentration of the minerals, metals, coal or mineral fuels is subeconomic. *Mining wastes* include *overburden* and *waste rocks* excavated and mined from surface and underground operations. *Waste rock* is essentially wall rock material removed to access and mine ore. The physical and chemical characteristics of mining wastes vary according to their mineralogy and geochemistry, type of mining equipment, particle size of the mined material, and moisture content. The primary sources for these materials are rock, soil, and sediment from surface mining operations, especially open pits, and to a lesser degree rock removed from shafts, haulageways, and underground workings. Usually mining wastes are placed in large heaps on the mining lease, often generating very large amounts.

Processing wastes. Ore is usually treated in a physical process called beneficiation or mineral processing prior to any metallurgical extraction (simple washing of the ore; gravity, magnetic, electrical or optical sorting; and the addition of process chemicals to crushed and sized ore in order to aid the separation of the sought after minerals from gangue during flotation). These treatment methods result in the production of "*processing wastes*". Processing wastes are defined herein as the portions of the crushed, milled, ground, washed or treated resource deemed too poor to be treated further. The definition thereby includes tailings, sludges and waste water from mineral processing, coal washing, and mineral fuel processing. "*Tailings*" are defined as the processing waste from a mill, washery or concentrator that removed the economic metals, minerals, mineral fuels or coal from the mined resource. Processing wastes can be used for backfilling mine workings or for reclamation and rehabilitation of mined areas, but an alternative method of disposal must be found for most of them. Usually, this disposal simply involves dumping the wastes at the surface next to the mine workings. Most processing wastes accumulate in solution or as a sediment slurry. These tailings are generally deposited in a tailings dam or pond which has been constructed using mining or processing wastes.

Metallurgical wastes. Processing of metal and industrial ores produces an intermediate product, a mineral concentrate, which is the input to extractive metallurgy. Extractive metallurgy is largely based on hydrometallurgy (e.g. Au, U, Al, Cu, Zn, Ni, P) and pyrometallurgy (e.g. Cu, Zn, Ni, Pb, Sn, Fe), and to a lesser degree on electrometallurgy (e.g. Al, Zn). These metallurgical processes destroy the chemical combination of elements and result in the production of various waste products including atmospheric emissions, flue dust, slag, roasting products, waste water, and leached ore. "*Metallurgical wastes*" are defined as the residues of the leached or smelted resource deemed too poor to be treated further. At many historical metal mines, ore or ore mineral concentrate was smelted or roasted in order to remove sulfur and to produce a purer marketable product. Consequently, roasted ore, slag, ash, and flue dust are frequently found at historical metal mine sites.

Mine waters. Mining, mineral processing and metallurgical extraction not only involve the removal and processing of rock and the production and disposal of solid wastes, but also the production, use and disposal of mine water. "*Mine water*" originates as ground or meteoric water which undergoes compositional modifications due to mineral-water reactions at mine sites. The term "mine water" is collective and includes any water at a mine site including surface water and subsurface ground water. The term "*mining water*" is used here in a general sense to refer to waters which run off or flow through a portion of a mine site and had contact with any of the mine workings. "*Mill water*" is water that is used to crush and size the ore. "*Process water*" is water that is used to process the ore using hydrometallurgical extraction techniques. The water commonly contains process chemicals. At some stage of the mining operation, water is unwanted and has no value to the operation, so it is disposed of at various stages during mining, mineral processing or metallurgical extraction. Water of poor quality requires remediation as its uncontrolled discharge, flow, drainage or seepage from the mine site may be associated with the release of heat, suspended solids, bases, acids, and dissolved solids including process chemicals, metals, metalloids, radioactive substances or salts. "*Acid mine drainage*" (AMD) refers to a particular process whereby low pH mine water is formed from the oxidation of sulfide minerals. A number of other terms are also used to describe this process such as "*acid drainage*" or "*acid rock drainage*" (ARD). These latter two terms highlight the fact that there are naturally outcropping sulfide orebodies and sulfidic rocks, which actively weather, oxidize, and cause acidic springs and streams. In fact, the acid streams draining such ores and rocks can contain high levels of metals and metalloids that exceed water quality standards and result in toxic effects to aquatic life.

CHALCOPHILE ELEMENTS IN KALIMANCI LAKE SURFACE SEDIMENTS (REPUBLIC OF MACEDONIA)-PRELIMINARY STUDY

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Abstract

In this preliminary study we examine the chalcophile element contents in Klaimanci Lake surface sediments (eastern Macedonia). The mineral composition of Sasa Mine tailings material is dominated by quartz, pyrite, galena, sphalerite, magnetite and others. Geochemical investigation revealed very high concentrations of chalcophile elements in lake sediments – with average values [ppm]: Co 19.89, Ga 21.13, Mo 2.69, Cu 415.12, Pb 6059.00, Zn 8420.32, Ni 44.99, As 67.69, Cd 56.58, Sb 1.77, Bi 10.08, Ag 5.58 and Au 25.23 ppb. Because of such high concentrations of chalcophile elements we have also calculate enrichment factor with average values: Co 2.01, Ga 1.26, Mo 1.84, Cu 17.02, Pb 312.86, Zn 121.08, Ni 2.28, As 46.92, Cd 0.59, Sb 9.27, Bi 0.08, Ag 0.12 and Au 13.96.

Key words: Chalcophile elements, enrichment factor, lake sediments, Kalimanci Lake.

Introduction

Among all innumerable contaminants is pollution by heavy metals global problem because of its toxicity, persistence of several decades in the aquatic environment and consecutiveness the bioaccumulation in food chain (Gochfeld, 2003; Valls & Lorenzo, 2002). Toxic heavy metals are usually present in low concentrations in aquatic environment, and it mainly originate from anthropogenic activities what usually cause increase of the concentrations of toxic elements in lakes, rivers etc. Within the polluting elements are the highly toxic chalcophile elements, which are extremely hazardous to the environment and also human health (Dauvalter et al, 2009).

The purpose of these research was to detect and define geochemical patterns of distribution of the chalcophile elements Ga, Cu, Pb, Zn, As, Cd, Ag, Au and Se in surficial sediments in Kalimanci Lake, which is influenced by emissions and waste waters from the mining activities in nearby Sasa Mine.

Kalimanci Lake is located to the East of the Republic of Macedonia (Figure 1). The Kalimanci Lake is artificial lake, its longest length is 14 km and greatest width is 0.3 km, lake reaches a maximum depth of 80 meters (Figure 2). The surface area of the lake is 4.23 km^2 and accumulates approximately 127 million m^3 of water. The basic purpose of Kalimanci water-storage is to irrigate about 30,000 hectares, mainly rice fields in Kočani valley and Ovce Pole. The lake has two channels, the left is 36 km long and it irrigate Kočani field and the right is 98 km long and carries water to Ovce Pole.

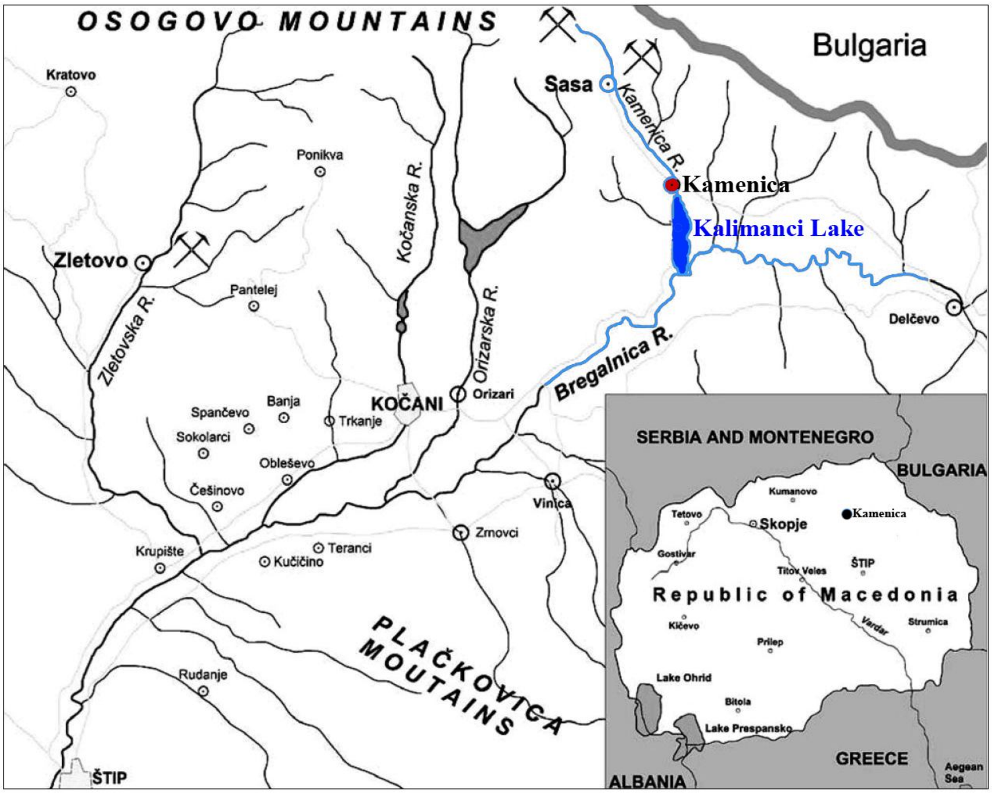

Fig. 1. Map of the study area.

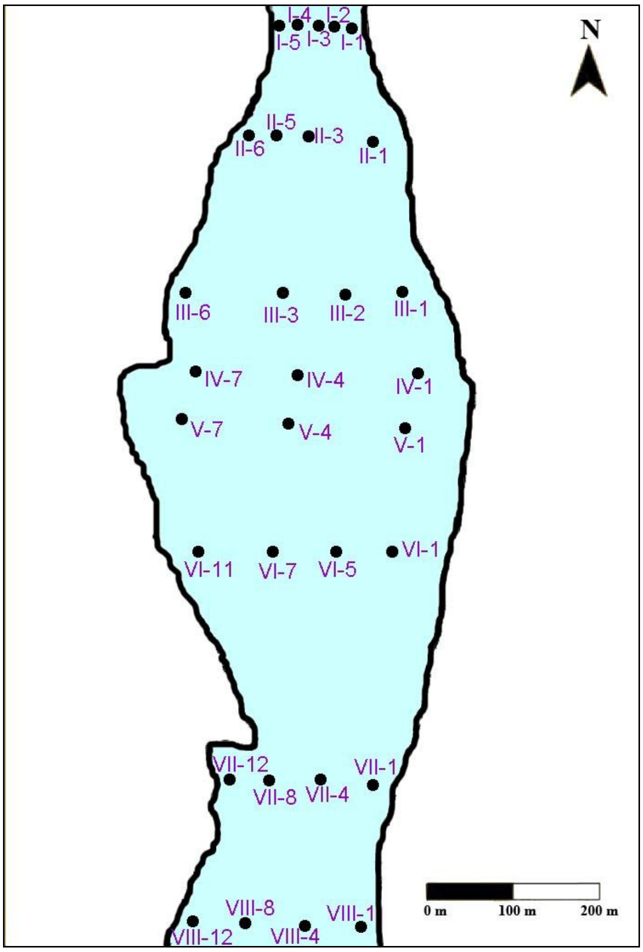

Fig. 2. Sampling locations on the Kalimanci Lake.

Exploitation of the Sasa Mine Pb-Zn deposit since 1954 has caused the surrounding area including Lake Kalimanci to become polluted with suspended substances (Vrhovnik et al., unpublished). The Sasa Mine is located in 2000 m high Osgovo Mountains, near the small town of Makedonska Kamenica north of the Kalimanci Lake in eastern Macedonia (Figure 1). This area is part of the Serbo-Macedonian Massif. It comprises highly metamorphic rocks containing gneiss, micas, amphibolites and schist. Typical mineral assemblage around the Sasa Mine area is represented by ore minerals: pyrite, galena, sphlareite, sometimes chalcopyrite and traces of ceruzite, anglesite and malachite (Tasev et al, 2005).The tailings material from Sasa Mine is located between the mine and Kalimanci Lake. Tailings material is deposited near the Kamenica River and therefore poses severe threats of trace metal pollution in the surrounding area and further downstream towards both the river and the lake. In year 2003 a major environmental disaster happened in the eastern Republic of Macedonia, when a part of the Sasa Mine tailings dam collapsed and caused an intensive flow of tailings material through the Kamenica River valley. Between 70 000 an 100 000 m^3 of tailings material was discharged into the Kalimanci Lake.

Materials and Methods

Sampling and analysis

Thirty one sediment samples from Lake Kalimanci were taken in September 2007. Sampling locations were arranged through the Kalimanci Lake (Figure 2). The samples were collected with the 10 cm long with 10 cm internal diameter plastic corers, and after that packed into plastic bags and stored in the laboratory at 4^oC. The collected lake sediment samples were dried at 50^oC for 48 hours and than sieved through a 0.315 mm polyethylene sieve to remove plant debris and homogenised by mechanical agate grinder to a fine powder for subsequent analysis.

The geochemical analysis of chalcophile elements, Ga, Cu, Pb, Zn, As, Cd, Ag, Au and Se was obtained in a certified Canadian laboratory (Acme Analytical Laboratories, Ltd.). 0.5 g of samples were leached in hot (95^oC) Aqua Regia and analysed by ICP Mass Spectrometry. The analytical precision and accuracy were better than ±5 % for the analysed elements.

Basic statistical analyses were performed by the original statistical software program Statistica 8. Pearson multiple correlation analysis was also applied.

Environmental factor

Potential contamination with heavy metals in the environment can be assessed by means of enrichment factors (EFs). It is a good tool to differentiate the metal source between anthropogenic and naturally occurring. The concept of enrichment factor was developed in the 1970s to evaluate the anthropogenic contribution and is expressed with:

$$EF= (M/Al)_{sample}/(M/Al)_{crust}$$

The numerator stands for the ratio of the concentration of the examined element to the reference element in a sample. The denominator represents the ratio of concentration of the examined element to the reference element in a reference material (Abubakr, 2008). The reference element in our study was aluminum, because ratios between metal and aluminum are widely adopted, supposedly because the concentration of Al in weathering products and their parent materials are generally comparable (Rogan Šmuc, 2009). And Al is also the normalizing element assumed not to be enriched owning to local contamination. Baseline values for M_{crust} reference material were adopted from Taylor and McLennan (1985).

The enrichment factor values are interpreted as the levels of heavy metal pollution that were suggested by Birth (2003) and the assessment criteria are generally based on the EF values.

Table 1. Assessment criteria suggested by Birth (2003).

EF<1	indicated no enrichment
1<EF<3	minor enrichment
3<EF<5	moderate enrichment
5<EF<10	moderately severe enrichment
10<EF<25	severe enrichment
25<EF<50	very severe enrichment
EF>50	extremely severe enrichment

Results and Discussion

Table 2. Concentrations of chalcophile elements.

	Co	Ga	Mo	Cu	Pb	Zn	Ni	As	Cd	Sb	Bi	Ag	Au
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb
I-1	11,7	18,8	1,9	195,4	2272	2944	24,1	54,2	16,5	1,1	4,4	1,8	9,1
I-2	19,9	19,5	2,2	238	2720,5	5913	37,3	54,8	48,1	1,4	4,5	2	9,5
I-3	12,3	16,8	1,7	168,5	1931,1	2949	21,7	62	21	1,1	3	1,5	11,9
I-4	18,8	20,9	2,9	672,3	9200	10700	47,4	68,8	74	2,4	12,2	10,3	24,2
I-5	14	16,5	2,9	540,3	7979,8	8627	35,4	45,5	61,1	2,4	11	8,9	13,2
II-1	24	22,1	3,1	415	4460,5	9596	52,4	86,7	77,2	2,2	8,3	3,6	18,9
II-3	24,3	22	4,6	1161,9	16300	20900	79,3	77,2	136	3,6	22,9	17,3	25,6
II-5	20,4	21,2	4,2	928,7	13800	17600	63,6	70,1	111,6	3,2	24,3	15,2	17,9
II-6	16,7	20,3	2,6	344,9	5065,5	6335	34	53,3	41,9	1,6	9,7	4,5	15,2
III-1	22,8	23	3,1	477,6	6600	10800	50,8	62,7	79,9	1,7	11,7	6,9	34,5
III-2	19,1	22,5	4,1	514,1	9500	11900	46,1	61,6	71,2	2,1	14,2	7,2	18,8
III-3	19,7	22,6	3,7	723	10900	14000	50,7	73,2	89,6	2,7	15,8	11,1	31,6
III-6	23,2	20,6	3,3	692,5	9600	14000	53,6	57,6	86,8	2,1	15,3	10,4	41,3
IV-1	17,7	21,6	3	413,1	6695,1	8105	41,6	66,1	59	1,7	9,4	5,1	18,9
IV-4	16	20,7	2,3	341,4	5343,4	6734	32,6	61,6	47,6	1,6	7,8	4,2	21,7
IV-7	19,4	23,1	3	343,2	4754,6	6641	40,8	68,5	43,1	1,3	8,3	3,9	15,6
V-1	18,4	23	2,4	303,2	4446,8	5677	37,1	61,6	40	1,3	7,5	3,6	23,5
V-4	14,4	16,5	1,8	144,4	2564,1	3052	26,3	77,8	23	1,6	5,7	2	9,3
V-7	20,5	21,2	3,7	595,7	8600	12600	53,7	66	81,1	2	12,9	8,1	39,8
VI-1	20,7	20,3	1	161,8	1873,7	4587	38,6	67,9	27,9	0,7	3,2	1,4	30,4
VI-5	17,8	21,9	2,6	287,8	4776,2	5188	35,4	70,1	39	1,7	8,2	3,8	15,9
VI-7	20,3	21,1	3,6	315,4	7885,1	7181	46	128,2	54,2	3,3	18,1	5,6	15,9
VI-11	24,3	21,9	2,5	545,7	6700	11600	53,2	58,6	77,6	1,6	11,1	7,1	54,7
VII-1	27,7	21,3	1,9	372,5	4200	10400	63,6	77,8	61,3	1,1	8,1	3,6	56,3
VII-4	22	24,9	2,6	292,5	4510,2	5965	47,3	71,2	41,4	1,4	8,4	3,5	16
VII-8	13,5	15	1,8	147,1	2598,2	3376	26,3	74,4	24,6	1,5	5,2	1,9	9,1
VII-12	25,3	21,4	2,7	398,1	5144	9326	56,1	66,4	53,5	1,2	9	4,5	39,6
VIII-1	23	24	2,2	311,9	5091,5	7224	54,2	69,8	47,9	1,4	10,3	3,8	35,9
VIII-4	20	20,7	2,4	269,7	4990,6	5553	48,9	95,2	40,3	1,9	9,3	3,9	23,1
VIII-8	23,5	23,3	2,3	327,6	4863,2	7056	48,5	61,5	46,8	1,4	8,8	4,1	38,7
VIII-12	25,1	26,3	1,2	225,4	2462,9	4501	48,3	27,9	30,8	0,6	3,8	2,3	46,1
*****	/	/	10	60	85	200	50	20	1	/	/	/	/

*permissible levels of heavy metal content – Ur.list RS 68/96

The average concentrations of examinated elements were [ppm]: Co 19.89, Ga 21.13, Mo 2.69, Cu 415.12, Pb 6059.00, Zn 8420.32, Ni 44.99, As 67.69, Cd 56.58, Sb 1.77, Bi 10.08, Ag 5.58 and Au 25.23 ppb. The tailings dam accident in 2003 mostly affected the northern part of the Kalimanci Lake, therefore in this part (second profile II) were measured the maximum concentrations of most chalcophile elements. With the expectance of Mo most of the chalcophile elements exceed the permissible levels of metal contents.

Table 3 Descriptive basic statistics of the chalcophile elements in the surficial sediments of the Lake Kalimanci.

Variable	**Mean**	**Min**	**Max**	**Variance**	**Std.Dev.**
Co	19,887	11,700	27,70	16	4,043
Ga	21,129	15,000	26,30	6	2,459
Mo	2,687	1,000	4,60	1	0,850
Cu	415,119	144,400	1161,90	54498	233,447
Pb	6059,000	1873,700	16300,00	11814567	3437,233
Zn	8420,323	2944,000	20900,00	18567615	4309,016
Ni	44,997	21,700	79,30	160	12,643
As	67,687	27,900	128,20	274	16,542
Cd	56,581	16,500	136,00	741	27,228
Sb	1,771	0,600	3,60	1	0,713
Bi	10,077	3,000	24,30	27	5,166
Ag	5,584	1,400	17,30	15	3,929
Au	25,232	9,100	56,30	180	13,401

Table 4 Pearson correlation matrix showing inter-elemental relationship (n=13).

Vari.	**Co**	**Ga**	**Mo**	**Cu**	**Pb**	**Zn**	**Ni**	**As**	**Cd**	**Sb**	**Bi**	**Ag**	**Au**
Co	1,00000												
Ga	0,70179	1,00000											
Mo	0,18678	0,20560	1,00000										
Cu	0,33435	0,20078	0,82591	1,00000									
Pb	0,24988	0,18864	0,89922	0,96128	1,00000								
Zn	0,48765	0,26735	0,82424	0,96740	0,92753	1,00000							
Ni	0,84054	0,55817	0,57554	0,73998	0,68673	0,82997	1,00000						
As	0,09056	-0,08135	0,29791	0,02741	0,17099	0,08483	0,19473	1,00000					
Cd	0,47605	0,26644	0,83946	0,95944	0,92001	0,98474	0,81332	0,12690	1,00000				
Sb	0,04359	-0,04780	0,85538	0,77308	0,86811	0,72116	0,47588	0,49098	0,76624	1,00000			
Bi	0,29427	0,20883	0,89660	0,88095	0,95582	0,87578	0,69675	0,34093	0,87145	0,89523	1,00000		
Ag	0,24062	0,13408	0,82827	0,98222	0,97902	0,92990	0,67413	0,06694	0,92198	0,82650	0,91658	1,00000	
Au	0,78032	0,49846	-0,0483	0,23590	0,12937	0,36662	0,60974	-0,1748	0,31040	-0,1801	0,11549	0,16276	1,00000

A Pearson correlation matrix was used to assess element associations and their origins (Table 4). The correlation matrix presents a significantly positive correlation between Mo, Cu, Pb, Zn, Ni, Cd, Sb, Bi and Ag from what can conclude that all those contaminants were from similar sources; in this case this would be Sasa tailing dam material as also it is to be expected as it reflects the mineral composition of the samples. Conversely no correlations were noted between As and other chalcophile elements, what indicate that As may be from different source.

Table 5 Enrichment factor of chalcophile elements

EF	Max	Min	Average
Co	2,694565	1,214081	2,012717
Ga	1,564766	1,087888	1,260178
Mo	3,400548	0,636297	1,841026
Cu	51,53605	6,242534	17,01829
Pb	903,7327	90,36338	312,8653
Zn	326,4152	43,02703	121,0833
Ni	4,396687	1,19441	2,284512
As	107,7489	14,79389	46,92402
Cd	1,538846	0,174711	0,59033
Sb	20,80175	2,386112	9,268509
Bi	0,209419	0,023798	0,082186
Ag	0,383671	0,027007	0,115588
Au	30,79755	5,196227	13,96337

The value of enrichment factor across all samples ranged from 0.59 to 312.86. According to assessment criteria suggested by Birth (2003) can we slightly conclude that the Kalimanci Lake sediments are much polluted with most of chalcophile elements. The lake sediments have extremely severe enrichment with Pb and Zn and very severe enrichment with As. Quoted elements Cu, Au and Ni, Co, Mo, Ga have also increased concentrations in the investigated lake sediments.

Conclusions

In the present preliminary study we examined the geochemical characteristics of the surficial Kalimanci Lake sediments. Analysed concentrations of the most chalcophile elements are much higher than permissible levels. According to the Enrichment factor, the surficial lake sediments contain extremely high levels Pb and Zn; and are also polluted with As, Cu, Au, Ni, Co, Mo and Ga. However, after this preliminary study many questions remain unanswered, therefore further investigations are required.

References

Dauvalter, V.A., Kashulin N.A., Lehto J. & Jernström, J. (2009): Chalcophile elements Hg, Cd, Pb, As in Lake Umbozero, Murmansk Region, Russia. *International Jurnal Environmental Research.* 3 (3): 411-428.

Tasev, G., Serafimovski, T., Lazarov, P.: New K-Ar, ^{87}Sr/^{86}Sr, and XRF data for Tertiary volcanic rocks in the Sasa-Toranica ore district, Macedonia. (2005).

Vrhovnik P., Rogan Šmuc N., Dolenec T., Serafimovski T., Tasev G. & Dolenec M. (2010) Determination of heavy metals in surficial lake sediments (Kalimanci Lake, Republic of Macedonia) – unpublished.

Gochfeld, M., 2003. Cases of mercury exposure, bioavailability, and adsorption. Ecotoxicol. Environ. Safety 56, 174–179.

Valls, M., Lorenzo, V.D., 2002. Exploiting the genetic and biochemical capacities of bacteria for the remediation of heavy metal pollution. FEMS Microbiol. Rev. 26, 327–338.

A REVIEW OF THE ANTHROPOGENIC EFFECTS ON THE HUMAN ENVIRONMENT IN THE REGIONS OF THE PERNIK, BOBOV DOL AND MARITZA EAST COAL BASINS, BULGARIA

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Introduction

Coals are organo-mineral sedimentary rock (Yurovskii, 1968). They have been used worldwide as a fuel for centuries and around 1800 they became the main energy source for the Industrial Revolution. People used coals to: (1) manufacture goods; (2) power steamships; (3) railroad engines; and (4) to make iron and steal. By the end of the 1800s, people began using coals to make electricity.

At present, the major producers of coals are: Chine (2 782.0 million tones), USA (1 061.8 million tones), India (515.8 million tones), Australia (397.6 million tones), Russian Federation (326.5 million tones), South Africa (251.0 million tones), Indonesia (229.0 million tones), Germany (194.4 million tones), Poland (144.0 million tones), Kazakhstan (104.9 million tones) (Catelin, M., 2010). The producing of coal in some countries from SE Europe is the following: Turky -78.8 million tones, Greece – 65.7 million tones, Serbia – 37.4 million tones, Romania – 35.2 million tones, Bulgaria – 28.8 million tones, Macedonia – 7.3 million tones, and Slovenia – 4.5 million tones (Catelin, M., 2010).

The use of coals is expected to rise by over 60% by 2030, with developing countries responsible for around 97% of this increase (Catelin, M., 2010).

On the other hand, the mining, preparation and burning of coals influence upon the environment and human health, because these technological processes originate different waste products: (1) host rocks from the mining of coal; (2) host rocks, slime, and waste waters from the preparation of coal; and (3) gas emissions, fly-ash (FA), lagooned-ash (LA), bottom-ash (BA), and waste waters from the burning of coals.

The goal of this paper is to present a review about the environment in the regions of Pernik, Bobov Dol and Maritza East coal basins, Bulgaria (Fig. 1).

Fig. 1. Location of the Pernik, Bobov Dol and Maritsa-East coal basins.

Environmental geochemistry

The Pernik, Bobov Dol and Maritza East coal basins are the biggest units among the exploited Bulgarian coal deposits.

Pernik coal basin

Geological setting and general information

The Pernik coal basin is located in southwestern Bulgaria, 30 km from Sofia (Fig. 1). This basin belongs to the Sofia Srednogorie area (Bonchev, 1962) and it is part of the Pernik coal province (Minchev, 1961). The basin was formed in one small graben structure confined within the Pernik deep-seated fault in the south and Liulin fault zone in the north (Bonchev, at al., 1960). The Pernik coal-bearing sediments are represented by coarse-clastic, clay-sandy and clay-marly rocks divided to five formations: Basal, Bituminous, Mudrock, Coal-bearing and Marl Formations. The thickness of the individual formations varies significantly as the total thickness varies from 1000 to 2000 m. The coal-bearing formation includes five coal seams, but only three of them are economically significant (Kamenov, 1964). The age of coal-bearing sediments was not completely specified, but Late Oligocene-miocene age was accepted (Šiškov et al., 1986). The Pernik coals are brown to black in colour, semi-bright, and banded. They consist of clarain, vitrain, and fusain. The Pernik coals were selected as a standard for subbituminous coal types in Bulgaria (Šiškov et al., 1982). This text is a part of a publication by Yossifova (2007).

Except the mines "Teva", "Republika" and |Beli breg", a plant preparation, a thermo-electric power station (TEPS) and some depots/ponds for host rocks, slime and ashes are included in the area of Pernik coal basin. The Central Preparation Plant (CPP) "Pernik" was closed in 2005-2006 and today the mined Pernik coals are putted to sieving only. Previously the TEPS "Republika" burned mostly Pernik coals, but at present it uses a blend of coals (Pernik coal, Maritza East coal, Chukurovo coal, etc.). CPP and TEPS are located in Pernik town.

Previous ecological investigations

Volatilization. - Except the gases of S, C and N, it was established that the next elements show susceptibility to release into the atmosphere as a result of the combusting of Pernik coal: Br, Na, Ce, Cr, Hf, Mo, Sc, La, Zn, Co, Eu, Al, As, Ba, Be, Cs, Cu, Ge, Pb, V, and Y (Vassilev et al., 2001).

Characterization of the waste waters from CPP "Pernik". - The factors that influence on the solid waste coal products (host rocks, slime, ashes) are the waters (technological, rainwater), atmospheric air and the change in the atmospheric temperature. The combination of these physical-chemical factors leads to weathering of the waste products connected with oxidation, hydration, dehydration dissolution, and hydrolysis. During preparation the coal, slime and host rock reside in water medium where dissolution and extraction of the most mobile components take place. During transport and later during preservation of the waste products (especially slime and lagooned ash) there takes place an additional extraction of components, when even the phases more resistant to weathering can be altered (as quartz, plagioclase, clay minerals, etc.).

The content of 25 components in the waste water studied samples are compared to their respective admissible values (AV) according to Regulation N 7/1986. The values of these components, which exceed several times the normative for the separate categories of surface flowing waters are: NH_4, PO_4, NO_2, NO_3, SO_4, F, As, Pb, Mn, B, V, Cu, etc. In this case of interest are the components of higher concentrations, which fall in categories II and III (as NO_2, NO_3, SO_4, Mn, F, and As) because according to these norms these waters are determined as unsuitable for irrigation, fish-breeding, watering, aquatic sports (II category) and even for industrial needs (III category).

The radiological studies for U, Ra^{226} and total β-radioactivity in the waste waters, running out from the slime-storage are within the norms for admissible values.

The concentration of 32 elements in the waste waters tested are compared to their Clarke values for surface waters according to Dobrovolskii, 1983 (in Kist, 1987) for Li, Al, Si, P, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Ge, As, Sr, Mo, Ag, Cd, Sb, Ba, La, Hg, Pb, Th, and U and for B, C, N, F, Na, Mg, S, Cl, K, Ca, and Br according to Bowen, 1966 (in Kist, 1987). Their enrichment/depletion factor (EDF) is given in Table 1. (Yossifova, 2003; Yossifova, 2005a)

Table 1. Over-Clarke concentrations of elements in the waste water from CPP “Pernik”

Sample	EDF of elements
Waters from Strouma river (taken from CPP)	$P_{26}>N_{22.4}>Pb_{13.1}>Li_{12}>F_{11}>S_{8.1}>Sr_{8.0}>Na_{6.0}>Mg_{4.5}>Ca_{3.8}>C_{3.5}>(V=Mn)_{3.0}>Zn_{2.7}>Cl_{2.1}>$
Waters from the slime-pound	$Mo_{90}>V_{60}>Li_{44}>N_{31.3}>F_{30}>S_{21.9}>Sr_{14.8}>Ba_{11.7}>Na_{10.0}>P_{9.5}>Ca_{6.0}>Cu_{5.7}>Mg_{5.5}>K_{3.4}>Cl_{3.3}>Ni_{3.2}>C_{2.5}$
Waters transporting slime (taken from CPP)	$(La=Mo)_{90}>N_{31.4}>Li_{28.2}>Ti_{24.1}>F_{22.5}>Sr_{22.0}>S_{20.6}>Ba_{15.1}>V_{14.0}>Mg_{12.2}>P_{7.5}>Ca_{5.1}>K_{3.5}>Cl_{3.3}>C_{2.7}$
Waters transporting slime and fly-ashes (taken from the pipes of the slime-pound)	$Mo_{90}>V_{85.3}>As_{75}>F_{44.4}>Li_{41.0}>N_{31.4}>Ga_{28.5}>Pb_{21.1}>S_{19.5}>Sr_{18.5}>Ba_{18.4}>Ti_{17.7}>Na_{10.0}>P_{9.0}>(Ca=Ni)_{5.8}>Mg_{5.2}>K_{3.9}>Cr_{3.1}>C_{2.9}>Cl_{2.6}$
Waters entering in Strouma river (taken from the collector)	$Ti_{343.3}>Mo_{82.0}>V_{80.0}>F_{35.8}>Li_{32.0}>S_{26.8}>N_{25.2}>Sr_{20.0}>Ba_{15.9}>Na_{11.1}>P_{10.0}>Ca_{8.0}>Mg_{6.6}>Ni_{5.7}>K_{4.5}>Cl_{3.8}>C_{3.3}>Zn_{2.0}$
Draining waters (taken from the region of slime-pound	$Mn_{42.2}>S_{40.6}>Sr_{24.7}>N_{21.8}>F_{21.1}>Li_{17.3}>Ba_{15.3}>B_{14.4}>Mo_{13.9}>Ca_{12.4}>Na_{10.5}>Mg_{7.7}>(K=Cl)_{4.9}>C_{4.0}>(P=V)_{3.0}>Zn_{2.0}$

Notes: The table includes this elements with EDF>2

Characteristics of the soils and plants in the region of CPP “Pernik” and TEPS Republika. **-** It is difficult to reproduce exactly the influence of the waste waters upon the soil due to the following reasons: (1) primary contents of some elements in the soils; (2) the availability of dust from the CPP and the depots as well as from the smoke emissions from TEPS; (3) other secondary contaminants-road transport impact, public activities; (4) migration of the elements; (5) influence of the atmospheric precipitation and the drinking waters in case of their utilization for irrigation.

The data from the chemical analyses of the soils were compared to the Clarke values by Vinogradov, 1957 (Kist, 1987) and by Bowen, 1966 (in Kist, 1987). In Table 2 are shown the elements with two times over-Clark values or their EDF.

Table 2. Concentration of elements in the soil with EDF>2

Sample	K>2
Soil from the greenhouse of the CPP (autumn)	$Pb_{4.5}>Cu_{4.1}>Zn_{3.9}>(V=Cr)_2$
Soil from the greenhouse of the CPP (winter)	$(Zn=Pb)_6>Co_{3.8}>(Cu=Ag)_3>V_2$
Soil from the greenhouse of the CPP (summer)	$Cu_{4.8}>Mn_{4.1}>Pb_{3.1}>Co_{2.6}>V_2$
Soil from the shore of the slime-depot (autumn; at 2-3 m distance)	$Zn_4>(Cu=Pb)_3>S_{1.6}$
Soil from the shore of the slime-depot (winter; at 2-3 m distance)	$(Zn=Pb)_6>Cu_3>Cr_2$
Soil from the shore of the slime-depot (autumn; at 5-15 m distance)	$Pb_{6.7}>Cu_4>Zn_{3.3}>Mn_{1.9}$

Comparing the data for Pb, Cu and Zn in the soil samples to the maximum admissible concentrations (MAC) (Regulation N 3), it proved that the soils are within the admissible norms. For other elements there is no data in MAC.

The data from the chemical analyses of 27 plant ashes were compared to the Clarke values by Tkalich, 1969 (in Kist, 1987). Some of the elements show over-Clarke values (Table 3).

These results confirm the previous research with coal wastes and waste waters for migration of the elements as well as their increased concentration in the soils within the region of Pernik CPP. The results also show that the above mentioned elements are available in such forms of presence, allowing them to be easily absorbed by the plants.

In some of the plant species it is observed affinity to some of the elements as well as that the concentrations of the elements is higher at the high-stemmed plants and in the samples from the autumn and winter. Some samples from the slime-depot are characterized by the greatest collection of elements and comparatively high concentrations. It is logical, considering that in these projects exist permanent humid environment and feeding is being performed by elements migrating from the water. As a result of the investigations held, it has been established that the soil samples are characterized by the availability of one and the same elements (Pb, Cu, Zn, V, Mn), their concentrations being close and don't exceeding more than 6 times the Clarke.

Contrary to these samples however, the presence of Pb, Sr, Li, Ba is dominant in the plant ones with contents being tens and hundreds times above the Clarke values. So, the components in the waste waters of Pernik CPP are found in easily movable forms and are not concentrated in substantial degree in the soils. That is why, they can provoke significant pollution of the surface and ground waters, as well as of the plant cover.

This on its turn, impacts directly or indirectly the health of the people from the region (Yossifova, 2000a; Yossifova, 2005a).

Table 3. Concentration of elements in the plant ashes with EDF>2

Sample	EDF>2
Slime-depot	
Blossom and stalks of *Rumex elegnos* (autumn)	$Pb_{11.6}>Sr_{10}>Ba_6>Li_{3.5}>Ag_{2.4}$
Leaves and stalks of *Salix elegnos* (autumn)	$Sr_{33.3}>Co_{6.7}>(Ba=Pb)_3$
Buds and stalks of *Salix elegnos* (winter)	$Sr_{66.7}>Zn_{15.2}>Pb_{7.7}>Ba_6>Rb_4>Mn_{2.3}$
Leaves and stalks of *Salix elegnos* (spring)	$Li_9>Sr_{6.7}>Ba_6$
Leaves and stalks of *Salix elegnos* (summer)	$Pb_{20}>Sr_{10}>V_{3.3}>(Ba=Ti=Cu)_3>Li_{2.7}>(Co=Sn)_2$
Leaves, blossom, stalks of *Tagetis patula* (autumn)	$V_{3.3}>Pb_3>Ni_2$
Leaves, blossom of *Xanthium italicum* (autumn)	$Sr_{33.3}>(Pb=Ag)_2$
Mix of blossoms of *Pharagmites australis* and *Tipha latifolia* (winter)	$Pb_{27}>Sr_{10}>Ba_6>Rb_{2.6}>Co_2$
Leaves, blossom, stalks of *Verbascum eriophorum* (spring)	$Pb_{30}>Sr_{10}>Ba_3$
Leaves, stalks of *Salix purpurea* (spring)	$Sr_{10}>(Ba=Pb)_6>Ag_2$
Leaves, blossom, stalks of *Prassicaea Lepidium Ruderale* (spring)	$Sr_{6.7}>Li_{2.7}$
Leaves, blossom, stalks of *Cardus nutans*	$Li_{27.3}>Sr_{10}>Cu_3$
Greenhouse near to CPP	
Leaves and stalks of tomato and pepper (autumn)	Sr_{10}
Leaves of *Spinacia oleracea* (winter)	$Sr_{10}>Ba_3$
Leaves of *Lycopersicon esulentum* (tomato) (winter)	$Sr_{20}>Ba_3$
Leaves of *Lycopersicon esulentum* (summer)	$Pb_{60}>Sr_{33}>Ba_6>Cu_3>Ag_2$
Leaves, stalks of *Capsicum annuum* (pepper) (sum.)	$Sr_{100}>Ba_6>Pb_3$
Leaves of *Lactuca sativa* (winter)	$Sr_{33.3}>Ba_6$
Host rock- storage	
Leaves, blossom of *Xanthium italicum* (autumn)	$Sr_{33.3}>Ba_3>Pb_2$
Leaves, stalks of *Lepidium campestre* (spring)	$Sr_{20}>Ba_3$
Leaves, blossom of *Xanthium italicum* (summer)	$Sr_{33.3}>Zn_{3.3}>Pb_3$
Leaves, blossom, stalks of *Chenopodium botrags* (summer)	$Pb_{100}>Sr_{33.3}>Ba_6>Zn_{5.6}>Cu_5>Ti_3$

Characteristics of the sickness rate in Pernik region.- According to published data (Ketris, 1987; Kalojanova, 1991) some of the above tested components influence the health of the people. For example: NO_2, Pb, Br, Mn – diseases of the respiratory system and the lungs NO_2, V, Co, Pb, Cd, Br, Cu, Mn – diseases of the nervous system; Zn, La, Pb, Pb, B, Mn – diseases related to the blood circulation, mutation action; Zn- heart diseases; Pb, Cu, V, Mn, As, Cd, Hg – diseases of the kidneys and the liver; Ba, Br, Cu – diseases of the skin and the mucous membrane of the eyes.

Having in mind this data as well as the data from the investigations held, it should be expected increased degree of sickness related to the above mentioned diseases among the population in the regions with developed coal industry.

Confirmation about thus is the statistical data from the years 1996 and 1997, received from the National Centre for Health Information (Table 4). They show that these indices namely characterize the higher degree of sickness among the population in Pernik Municipality compared to the average one about the country.

The proximity of "Republika" TEPS is of great significance, that impacts dominantly and permanently the environment by its smoke emissions and its waste products.

Fly-ash are also characteristic by water soluble phases. A proof in this respect are the present investigations (the contents of the water, transporting coal slime and fly-ashes) as well as the investigations, held by other authors (Vassilev et al., 2001). The following factors could be emphasized about the sickness among the population: the coal mining and coal preparatory activities in the region almost a century long; the free outflow of the waste waters and their impact upon surface and ground waters; the usage of these waters for irrigation, fish-farming and cattle water-feeding; the pasture of the cattle (Yossifova, 2000b; Yossifova, 2005a).

Table 4. Data about the sickness rate in Pernik District
(considered for1000 persons from the population)

Types of diseases	1996						1997					
	Pernik District			Mean for Bulgaria			Pernik District			Mean for Bulgaria		
	Total;	0-17;	18^+	Total;	0-17;	18^+	Total;	0-17;	18^+	Total;	0-17;	18^+
Disease of the endocrine glands, nutrition diseases, metabolism and immune system distortion	29	23	31	21	6	25	27	7	31	22	8	26
Diseases of the nervous system and the sense organs	187	180	189	167	132	177	191	208	188	158	150	161
Diseases of the blood circulation organs	140	11	172	107	8	135	146	10	177	111	13	137
Diseases of the respiratory system	675	1917	373	563	1458	314	702	2166	360	564	1622	280
Diseases of the urino-genital system	89	44	100	78	26	93	101	50	112	81	44	91

The data is statistical and is calculated on the grounds of the method of the averagely assessed value. It is impossible to be submitted more updated data due to the health reform, held in the country. Data about traumas, silicose and gas intoxications, typical for the regions of mining industry is not requested.

Bobov Dol coal basin

Geological setting and general information

The Bobov Dol coal deposit, which is located in southwestern Bulgaria (Fig. 1), is part of the Pernik coal province (Minchev, 1961). This Paleogene deposit was formed in one of the small post-orogenic graben basins in the Kraishtide region (Kamenov et al., 1978). The most important structures of the Bobov Dol deposit are two synclines associated with normal-slip faults and flexures (Valčeva,1990). The basement rocks of the basin consist of Paleozoic to Upper Cretaceous schists, gneisses, amphibolites, diorites, sandstones, limestones, marls, conglomerates and shales (Kamenov, 1958). Lithostratigraphically (Fig. 1 b,c), the Paleogene is divided into several formations: (1) basal mudrock and flysch; (2) bituminous (kerogen) rock; (3) variegated mudrock; (4) coal-beating; and (5) fine-bedded shale, slightly bituminous (kerogen) rock (Kamenov et al., 1978).

The coal-bearing formation is of late Oligocene age (Šiškov et al., 1988). It includes 14 coal seams, but only 6 are economically significant. The coal is clark brown to black in colour, bright, banded and consists of clarain and vitrain, with rare semifusain and fusain (Valceva, 1990). Some of the characteristics of these subbituminous coals are: moisture = 6-12%; VM^{daf} = 43-51%; A = 15-65%; C^{daf} = 7 l - 75%; H^{daf} = 5.3-5.8%; S^{daf} = l.8-3.7%; Q^{daf} = 31.38 MJ kg^{-1}, and R_o = 0.42-0.43% (Kamenov, 1958; Valčeva, 1990). This text is a part of a publication by Vassilev et al. (1994).

Except the mines, a plant preparation, a thermo-electric power station (TEPS) and some depots/ponds for host rocks, slime and ashes are included in the area of Bobov Dol coal basin. Previously the TEPS "bobov Dol" burned mostly Pernik coals, but at present it uses a blend of coals (Pernik coal, Oranovo coal, Katrishte coal, Stanyantzi coal, etc.). CPP and TEPS are located in the area of Bobov Dol town.

Previous ecological investigations

Volatilization. - Some trace elements show susceptibility to scattering in the atmosphere by stack emissions in solid, liquid and gas states. Thus, for example, from TEPS into atmosphere there could be emitted: Sn, Be, Y, Ga, Zr, Mo, As, Sb, Cu, Zn, and U (Vassilev, 1994).

Characterization of the waste waters from CPP "Bobov Dol". - Mixture water from "Dyakovo" dam and water sent back by the slime-storage is being used for dressing in 'Bobov Dol' CPP.

High migrating abilities display a number of elements, irrespectively thet they essentially belong to group of different geochemical characteristic. For example, the distinctive migration display Li, Mo, Sr, Ba, and Na from the group of the lithophilic metals (the classification by Solodov et al., 1987 is used); P, F, S, N from the group of non-metals; V, Ti, and Mn from the group of siderophilic metals; As, Cd, and Cu from the chalcophilic metals. Their concentrations exceeds the Clarke values of the order of several dozens to several hundreds times. High concentration in some individual samples show Ag, Zn, Ga, Ge, Pb, Hg, La, Mg, B, C, Cl, Zr, K, Al, Si, Ca, Ni, P, F, N, and Cr.

According to the degree of pollution, the technological and waste waters from Bobov Dol CPP could be classified in the following order: mixed water for dressing < waters flowing into the slime-pound ≤ waters running out the slime-pound < draining waters (Yossifova, 2000b).

As a result of the studies held, it was established that the soils samples are characterized by a number of elements – Pb, Cu, Zn, Cr, La, Co, V, Li, S, Mg, Br, and Co which concentrations are close and exceed no more than thirteen times the Clarke values. In comparison with the soils, the prevailing availability of Sr and Ba in the plant samples were found to exceed hundred times the Clarke values.

Characteristics of the soils and plants in the region of CPP "Bobov Dol". - The samples studied are given in Table 5.

Table 5. Concentration of elements in the soils and plants (ash basis) with EDF>2

Place of sampling	Sample	EDF
Soils		
Shore of the lake with draining water	Soil (summer)	$Pb_4>(Cu, Li)_{3.7}> Cr_3>Zn_{2.8}>V_2$
Private garden, irrigated with waste waters	Soil (autumn)	$Zn_6>Pb_3>La_{2.7}>S_{2.4}$
	Soil (spring)	$(Cr, Zn, Pb)_6>Co_{2.5}>Mg_{2.4}>V_2$
	Soil (summer)	$Br_{13.4}>Pb_{4.3}>(Cr, Cu)_3> Zn_{2.4}>Co_2$
Plants		
Private garden, irrigated with waste waters	Leaves of *Lycopersicon esulentum* (tomato) and *Capsicum annum* (peppers) (autumn)	$Li_{7.9}>Pb_{4.0}>Sr_{3.3}>Ni_2$
	Leaves and stalk of *Lycopersicon esulentum* (tomato) (spring)	$Sr_{10}>(Ba, Pb)_6>Li_{2.7}$
	Leaves of Zea mays (cabbage) (autumn)	$Sr_{3.3}$
	Leaves of Brassica oleracea (corn) (autumn)	$Sr_{33.3}>Ba_3$
Closed slime-pound	Blend of blossoms of wild growing plants (*Pharagmites australis* and *Tipha latifolia*) (autumn)	Sr_{10}
Slime-pound	Blend of leaves and stalks of *Tipha latifolia* (summer)	$(Sr, Ba)_{100}$
	Blend of blossoms and leaves of *Xantium italicum* (summer)	$Sr_{333.3}>Pb_6>Ba_3>Sn_2$
Host rock-storage	Blend of blossoms, leaves and stalks of *Thlaspiarvence* (spring)	$Sr_{10}>Li_9$
	Blend of leaves and stalk of *Tipha latifolia* (summer)	$Sr_{100}>Ba_3$

That shows that the components are in easy-movable water soluble forms and may provoke substantial pollution of the surface and ground waters as well as of the vegetation, thus affecting directly and indirectly upon the health condition of the population in the region examined (Yossifova, 2000a).

Maritza East coal basin

Geological setting and general information

The mining and power producing enterprise “Maritza East” (Fig. 1) is the biggest unit for lignite mining and thermo-electric power generation in Bulgaria. It includes three large open-pit mines, three thermo-electric power stations (TEPSs), and a briquette plant. The total area of the coal and power-producing enterprise includes more than 200 km^2.

The Maritza East lignite basin is a part of the Zagore depression of the Upper Thracian tectonic trough and has a complex geological structure (Valčeva et al., 2000). Three formations have been divided, namely: basement, coal-bearing and superstructure (Nedyialkov, 1979, 1985; Šiškov et al., 1986). The basement consists of granites, metamorphic and sedimentary rocks of different age (from Late Cambrian to Late Cretaceous), and degree of alterations. The Miocene coal-bearing formation is well developed with a sandy-clayey suite at bottom (Nedyialkov, 1985) and Troynovo coal level (Panov, 1982) being, respectively, the correlative of Marishka Formation (Kamenov and Panov, 1976). The coal-bearing level consists of three lignite seams interbedded by grayish-black thinly layered clays. The second seam with maximum thickness of 24 m bears the main coal reserves. The ash yields of lignites commonly determine their selective utilization as briquettes or fuel for TEPSs (Valčeva et al., 2000). The superstructure – Gledachevska Formation (Nedyialkov and Kojumdgieva, 1983) covers the Maritza coal-bearing sediments. It lies in conformity with Marishka Formation and is covered, on its turn, by Quaternary sediments. The lithology of Gledachevska Formation consists of clays, sands, and limestones. The clays are the dominant rocks in the sedimentary sequence. They are grey to bluish-green or light green, and rust-yellowish in colour, layered, dense with variable quantity of sand. The sands and sandstones form lenses or pinching out intercalations between the clayey layers, mostly in the upper-most parts of the sediments covering the coal complex (Valćeva et al., 2000). This text is a part of a publication by Yossifova et al. (2007).

Previous ecological investigations

Volatilization. - Some trace elements show susceptibility to scattering in the atmosphere by stack emissions in solid, liquid and gas states. Thus, for example, from TEPS into atmosphere there could be emitted: Nb, Co, Cu, Zr, Ce, Eu, V, Cr, As, Sc, Hf, Zr and U (Vassilev, 1995) as well as and Hg (Yossifova, 2009).

Trace elements in soils.- The soils used for restoring LA disposals were taken from the Maritza East area. Their phase composition includes mainly quartz, plagioclase, mica, amphibole, kaolinite, chlorite (Valćeva et al., 2000), and some organic matter (4.4-11.8%). The mean concentrations of Be > Sn > Ag > Ga > Ti > Ba > Rb = Co > Mo = Ni = Cu in these soils have over Clarke concentrations. The EDF is normally low and only Be, Sn, and Ag reveal significant enrichment (EDF ≥ 2.0). It should be emphasized that elements such as Be, Cr, Cu, Li, Ni, and Sn show significant variations in their concentrations for the individual soil samples. However, some correlation trends between the elemental contents and sampling places were not detected for these restored LA disposal sites. As pointed above, some elements (Rb, Be, Ti, Pb, Ba, Sn, V, Ga) are even more enriched in soils than LAs. Hence, the abundance of elements such as Ag, Ba, Be, Co, Cu, Ga, Mo, Mn, Ni, Pb, Rb, Sn, Ti, V, and Zn (in particular Ag, Ba, Be, Cu, Pb, Rb, Sn, Ti, Zn) in soils is probably related to some occurrence of discrete minerals and phases containing these elements. Such phases could be formed by infiltration of rainfall water trough the soils and covered LA. However, such discrete phases could be also a result of particulate materials deposited from the stack emissions of Maritza East 1 TEPS. For example, it was found that elemental proportions of Co, Cu, and Zn were emitted with stack emissions from Maritza East TEPSs (Vassilev, 1995). Another explanation for an enrichment of the above listed elements is their original high concentrations in the soils used. For instance, it was found that elements such as Ag, Be, Ga, Li, Pb, Rb and Sn were more enriched in the Maritza East host rocks (ash basis) than in the Maritza East lignite ash (Vassilev, 1994). This text is a part of a publication by Yossifova et al. (2007).

Trace elements in plant. - The contents of the elements in the plant samples is compared to the upper limit of Clarke value (according to Kabata-Pendias and Pendias, 1979), due to the fact that the samples have been taken from the recultivated mining site. The plant samples contain eight elements (Li > Be > Ga > Ti > V > Cr > Pb > Ni) with over Clarke concentrations, as Li, Be, Ga, Pb, Ti, V, and Cr have EDF significantly higher than 2.0. It should be emphasized that some of these elements (Be, Ga, Ti, Ni) also show enhanced Clarke enrichments in soils. As pointed above, elements such as Pb, Zn, Be, Ba, Rb, Sn, Ti, Ag, Mn, and Mo are more enriched in plant ashes than LAs.

A ratio between the element content in plant ash to the element content in soil was calculated to determine the "coefficient of biological consumption" (CBC) (Perelman, 1975). A CBC value >1 is informative for elements that are consumed from soils. The calculations show that elements such as Zn, Pb, Cu, Ag, Be, Mo, Cr, Mn, Ba, Sn, Co, Li, and Ni could be accumulated in plants from the soils according to the mean CBC values. However, it should be noted that the number of the elements, as well as their concentration increase compared to the bottom limit of the Clarke values. Despite the lower Clarke concentrations of Ag, Cu, Mn, and Zn in plants, these elements also show a typical biological consumption. Hence, the water-soluble modes of occurrence of Ag, Ba, Be, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Sn, Ti, and Zn in soils and/or LAs, as well as the plant affinity to these elements should have a leading role for their accumulation in plants. The quantitative elemental variations in plants are probably connected with the selective elemental capability of individual plant species. This text is a part of a publication by Yossifova et al. (2007).

Conclusions

The present data reveal that the coal industry with their mining, preparation and combustion of coal is a polluter on the environment. Various trace elements with environmental concern could be potential pollutants of surface and subsoil waters, soils and plants in the areas of coal basins, preparation plants and thermo-electric power stations. The waste products from coal industry can impact directly and indirectly on the human health. A monitoring of some heavy metals and stick emissions should be conducted.

References

Bonchev, E., 1962. On the tectonic relations between the Balkanides and South Carpathians. Travaux sur la géologie de Bulgarie. Sér. Stratigraphie et tectonique, vol. 4, 79-85 (in Bulgarian).

Bonchev, E., Karagiulev, Y., Kostadinov, V., Manolov, J., Kamenova, L., Dinkov, E., Bakalova, d., Manolova, R., 1960. Basis of the tectonic of the kraichtides and surroundings. Travaux sur la géologie de Bulgarie. Sér. Stratigraphie et tectonique, vol. 1, 7-92 (in Bulgarian).

Catelin, M., 2010. Coal. In: 2010 Survey of Energy Resources. (Eds. I. Lancu, A. Clarke and J. Trinnaman). Word Energy Council. E info@worldenergy.org; ISBN: 0946121 26 5.

Kabata-Pendias, A., Pendias, H., 1979. Trace Elements in the Biological Environment. Wydawnictwa Geologictwa, Warszawa, 299 pp. (in Polish).

Perelman, A., 1975. Landscape Geochemistry. Izdatelstvo "Vishaya Shkola", Moscow, 341 pp. (in Russian).

Kamenov, B., 1958. Geology of Bobov Dol coal basin. Annu. Dir. Gen. Rech. Geol., 8, 1-25 (in Bulgarian).

Kamenov, B., 1964. On the stratigraphy and coal-bearing sediments of Paleogene in the Pernik basin. Bull. Inst. Sci. Rech. Géol. Près Dir. Gén. Géol. 1, 233-246 (in bulgarian).

Kamenov, B., Panov, G., 1976. The geological relationship between the coal layers from Maritza West and Maritza East in the Maritza basin. Petroleum and Coal Geology 4, 60-71 (in Bulgarian)

Kamenov, B., Konstantinova, V., Gnoevaya, N., Popova, K., 1978. Petrographic composition and genesis of the bituminous rocks from the Paleogene in SW Bulgaria (Pernik and Kyustendil area). Geol. Balcanica 8, (2), 41-54.

Kalojanova, F., 1991. Healthul toxicology. Sofia, pp 256 (in Bulgarian).

Kist, A., 1987. Phenomenology, Biogeochemistry and Bioinorganic Chemistry. Tashkent, pp 236 (in Russian).

Nedyialkov, N., 1979. Maritza East lignite basin – mining and geological conditions, qualitative characteristics and features of the deposit. Coal 9, 8-12 (in Bulgarian).

Nedyialkov, N., 1985. Geological structure of the Maritza East basin and landslide phenomenon. Summary of Ph.D. theses, Bulg. Acad. of Sci., Sofia. 39 pp. (in Bulgarian).

Nedyialkov, N., Kojumdgieva, E., 1983. Stratigraphy of over coal-bearing sediments in Maritza East basin. Review of the Bulgarian Society 44, (3), 239-264 (in Bulgarian).

Minchev, D., 1961. Coal-forming phases and coal-bearing provinces. Annuaire de l'Universite de Sofia, Livre 1-Geologie 54, 319-345 (in Bulgarian).

Panov, G., 1982. The Tertiary coal-bearing sedimentation in upper Thracian graben. Summary of Ph.D.theses, Bulg. Acad. of Sci., Sofia. 32 pp. (in Bulgarian).

Regulation N3. 1979. State Newspaper 36 (in Bulgarian).

Regulation N 7. 1986. State Newspaper 96 (in Bulgarian).

Šiškov, G., Valčeva, S., Sallabasheva, V., 1982. Classification of Bulgarian coals according to the degree of the coalification. Bull. Chem. 15, 421-425 (in Russian).

Šiškov, G., Kehayova, M., Staikova, S., 1986. Coal and coal basins in Bulgaria. Sofia University "St. Kliment Ohridski", Sofia, 163 pp (in Bulgarian).

Šiškov, G., Valčeva, S., Minchev, D., Sallabasheva, V., Stefanova, Y., 1988. Petrology of coal basins and deposits in Bulgaria. Ann. Univ. Sofia Geol., 78, 122-137 (in Bulgarian).

Solodov, N. A., Semenov, E. I., Burkov, V. V., 1987. Geological handbook on heavy lithophilic trace metals. Nedra, Moskow, pp. 438 (in Russian).

Valčeva, S., 1990. Petrological characteristics of coal from Bobov Dol basin. Ann. Univ. Sofia Geol., 79, 55-70 (in Bulgarian)

Valčeva, S., Djourova, E., Stanimirova, T., Dimitrova, D., Aleksieva L., 2000. Mineralo-geochemical features of Gledachevska formation sediments in the Maritza-East lignite basin and in the technogeneous soils of the recultivated terrains. Annuare de L'Universite de Sofia, Livre 1-Geologie 92, 203-212.

Vassilev, S., 1994. Trace elements in solid waste products from coal burning at some Bulgarian thermoelectric power station. Fuel 73, (3), 367-374.

Vassilev, S., 1995. Stack emissions from coal-fired power stations: an environmental pollution with trace elements. Comtes rendus de l'Académie bulgare des sciences 48, (4), 45-47.

Vassilev, S., Yossifova, M., Vassileva, Ch., 1994. Mineralogy and geochemistry of Bobov Dol coals, Bulgaria. International Journal of Coal Geology 26, 185-213.

Vassilev, S., Eskenazy, G., Vassileva, C., 2001. Behaviour of elements and minerals during preparation and combustion of the Pernik coal, Bulgaria. Fuel Processing Tecnology 72, 103-129.

Yossifova, M., 2000a. Impact of the Waters from the Coal Dressing upon Soils and Vegetation in the Regions of "Pernik" and "Bobov dol" Central Preparation Plants. Minno Delo and Geology, 9, 9-14 (in Bulgarian, with English abstract)

Yossifova, M., 2000b. Environmental Aspects Related to the Impact of Waste Water from Coal Dressing on Human health. Geology and Mineral Resources, 3, 25-28

Yossifova, M. 2003. Characterization of the Waste Waters from “Pernik” Central Preparation Plant (Bulgaria) and Their Ecological Effects. III-rd International Conference SGEM2003: Modern Management of Mine Producing, Geology and Environmental Protection, 9-13 June, 2003, Albena resort - Bulgaria, 327-334.

Yossifova, M. 2005. Human Illness Provoked by the Use of Coal. In: CD-ROM Proceedings of ICCS&T, Oct., 9-14, 2005, Okinawa, Japan, 3P802, 1-11

Yossifova, M., 2007. Mineral and inorganic chemical composition of the Pernik coal, Bulgaria. International Journal of Coal Geology 72, 268-292.

Yossifova, M., 2009. Preliminary data for mercury and selenium in some coals and their waste products from Bulgaria and FYROM. In: R. Davidson (Ed.), CD-ROM PROCEEDINGS / 3733-539/ of Fourth Int. Conf. on Clean Coal and Technologies for our Future (CCT2009). 3rd Int. Freiberg Conf. on IGCC & XtL Technologies. Dresden, Germany, pp. 17.

Yossifova, M., S. Valčeva, E. Djourova., 2007. Mineralogy and environmental geochemistry of lagooned ashes resulted from combustion of Maritza East lignite, Bulgaria”. Int. J. of Coal Geology, 71, 287-302.

Yurovskii, A. Z., 1968. Mineral components in caustobioliths. Nedra, Moscow, 215 pp (in Russian).

ENRICHMENT OF SOME HEAVY METALS IN TOPSOILS AROUND A Pb-Zn SMELTER IN MITROVICA, KOSOVO

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Abstract

The results of a study on the spatial distribution of different elements in surface soil (0-5 cm) in the Mitrovica region, Kosovo, are reported. The investigated region (300 km^2) was covered by a sampling grid of 1.4×1.4 km and a total of 159 soil samples. Inductively coupled plasma-mass spectrometry (ICP-MS) was applied for the determination of 36 elements (Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sr, Th, Ti, Tl, U, V, W and Zn). For data evaluation, parametric and non-parametric statistics methods were used. The content of elements such as Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl and Mo in soil samples appeared as an anthropogenic association of elements due to the mining and processing activities. Thus, the average content of Pb was 19.6-fold higher than European averages; Cd 11-fold and Zn 4.5-fold higher. In the close vicinity of the city of Mitrovica, the contents of these elements were even higher than the corresponding intervention values according to the New Dutch list and were exceed in 152 km^2 of the investigated area.

Introduction

Mining and metallurgic activities in Kosovo have a long history. The Trepča Mine Limited in Mitrovica was built in 1927 and produced lead, arsenic and cadmium from the 1930s until 2000. The smelter close to Zvečan commenced work in 1939. Because of the smelter and three huge tailing dams of the factory, environmental pollution in Mitrovica increased dramatically. The smelter had worked sporadically since the 1999 conflict in Kosovo. However, an environmental audit ordered by UNMIK and conducted in March and April 2000, warned that it should be closed as an "unacceptable" source of air pollution (Palariet, 2003; Frese et al., 2004; OSCE, 2009). The amount of metal produced was 2,066,000 t Pb, 1,371,000 t Zn as well as Ag, Bi and Cd (Palariet, 2003; Frese et al., 2004; OSCE, 2009). The effect of mines and mining industries on the environment in Kosovo is difficult to ascertain as few data exist. Several reports have indicated that current levels of lead exposure are extremely high in the soil and in the air as well (di Lella et al., 2003; Jia et al., 2004; Arditsoglou and Samara, 2005; Borgna et al., 2009).

The main objectives of this investigation were to present the results of the first systematic study of spatial distribution of different chemical elements in surface soil in the K. Mitrovica region in the Republic of Kosovo, known for its long-term lead and zinc mining and metallurgical activities in the recent past and to establish the enrichment factors of some elements in soils from the broad area of K. Mitrovica and to assess the size of the area affected by the smelter plant situated nearby.

Material and methods

Study Area

The K. Mitrovica is a city located in the north of Kosovo (Fig. 1) approximately 40 km north of Prishtina (the capital of the Republic of Kosovo). The study area (301.5 km^2) is large (24 NNW-SSE km x 18 WWS-EEN km), which is limited by the coordinates (WGS 84) longitude 20.74528°-20.99235° (E) and latitude 42.78522°-42.99330° (N). About 40% of study area lies at an altitude between 480-600 m (S and SE), but only 5 % has an altitude over 1000 m, mainly in the NE of the investigated area. On the aforementioned plain are located all the major urban zones (Zvečan, Mitrovica and Vučitrn), but also the main industrial zones, particularly around Zvečan and Mitrovica.

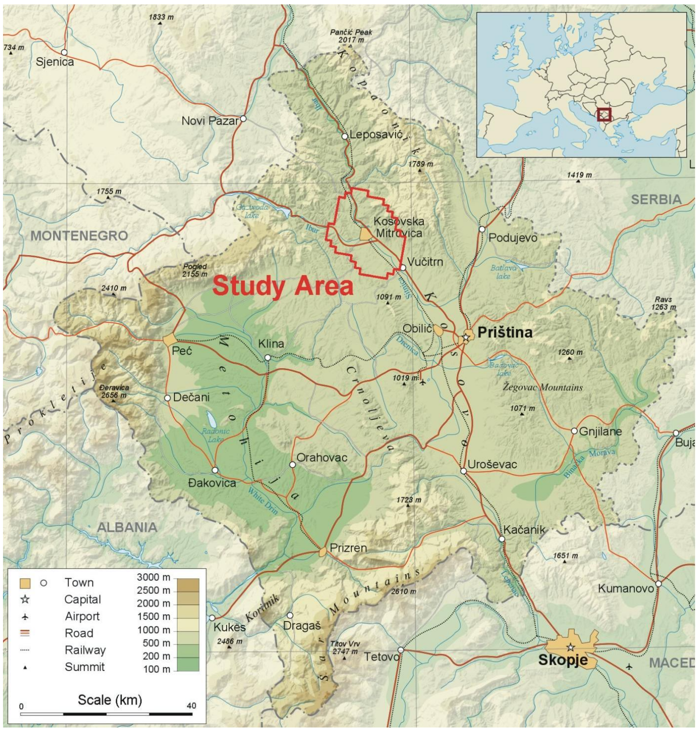

Fig. 1. Location of the study area

The investigated area belongs to the Vardar Zone (Bogdanović, 1978; Bogdanović at al., 1978). The geotectonic unit is covered by metamorphic, sedimentary and magmatic rocks of the younger Paleozoic and Triassic ages, Cretaceous flysch, Miocene volcanic rocks with pyroclastites as well as younger Pliocene and Quaternary sediments.

Sampling and sample preparation

The complete investigated region (301.5 km^2) was covered by a basic sampling grid of 2x2 km^2, but in the diagonal cross-section of each entire grid cell, one more sample was added (Fig. 2). Altogether, 156 locations were defined. In each sampling point, topsoil samples (0-5 cm) were collected. One sample represented the composite material collected at the central sample point itself and at least 4 points within a radius of 50 m around it towards N, E, S, and W. Soil samples were air dried indoors at room temperature for about two weeks. Then, they were gently crushed, cleaned of extraneous material and sifted through a plastic sieve a mesh size of 2 mm (Salminen et al., 2005). The shifted mass was quartered and milled in an agate mill to an analytical grain size less than 0.125 mm.

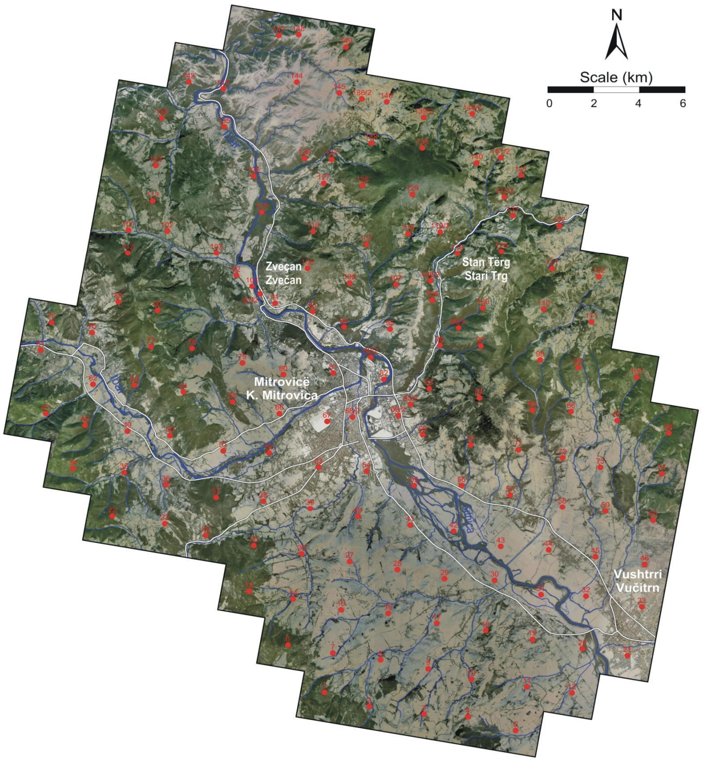

Fig. 2. Soil sample locations in the study area

Due to expected extreme contamination with heavy metals, the following zones were determined: Zone (I) – areas extremely affected by heavy metals (57 km^2); Zone (II) – areas strongly affected by heavy metals (117 km^2); Zone (III) – areas relatively little affected by heavy metals (128 km^2). The first zone included 30 sampling sites, Zone (II) included 65 sampling sites and Zone (III) included 61 sampling sites (Fig. 3). Additionally, groups of samples that covered the main urban area were defined (cca. 90% of the entire population). The wider urban area of the city of Zvečan was covered by 5 sampling sites, K. Mitrovica by 11 sampling sites, and Vučitrn by 8 sampling sites (Fig. 3).

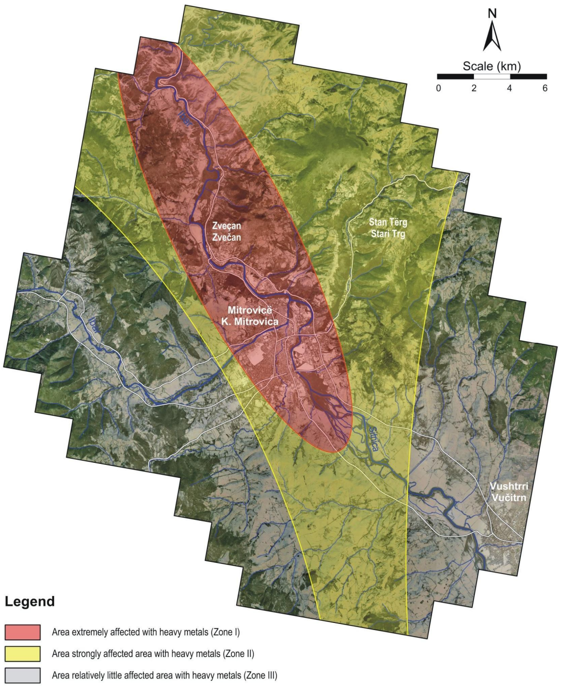

Fig. 3. Determinate polluted zones in the study area

Chemical analysis

The ICP-MS determinations of 36 elements were performed after aqua regia digestion (mixture of HCl, HNO_3 and water at 95°C - 1DX method). The following 36 elements were analysed: Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mn, Na, Mg, Mo, Ni, P, Pb, S, Sb, Sc, Se, Sr, Th, Tl, Ti, U, V, W and Zn. The sensitivity in terms of the lower limit of detection was adequate for 32 out of 36 determined chemical elements. Four elements (B, Bi, S and Se) were removed from further statistical analysis since their contents in the majority of analysed samples were below the lower detection limit of the analytical method.

Data processing

Parametric and non-parametric statistical methods were used for data processing (Snedecor and Cochran, 1967; Le Maitre, 1982). The enrichment ratio provided a much better measure for comparison. This ratio was calculated by dividing the contents of chemical elements in the topsoil of Zone I (areas extremely affected with heavy metals) by the contents in the topsoil of Zone III (areas relatively little affected with heavy metals).

Results and discussion

The distributions of elements that reflect natural processes are indicated by elements that rarely or never include industrial processes. Their contents usually change gradually across the landscape and depend on geological background. The most characteristic association is that of the high contents of Co, Cr, Fe, Ni, Mg and Sc; geochemical association consisted of Ba, La, Mo, Th, Tl and U; association of Al, Ga, K and of V and Ca and Sr. These associations represent chemical elements that are little affected by anthropogenic activities and closely dependent on the lithology. Their sources are mainly natural phenomena, such as a rock weathering and chemical processes in soil.

However, the association consists of Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl and Mo represents chemical elements that are the most probably anthropogenically distributed (Pb-Zn mining, ore processing and smelting operations). Figure 4 shows the enrichment ratio of the 31 selected elements, according to the obtained results vs. average European topsoil (Salminen et al., 2005). Figure 5 shows the enrichment of heavy metals in the topsoil of Zone I vs. Zone III.

The obtained data for the content of some elements in topsoil shows high enrichment comparing with the European values. Thus, the average content of Pb was 19.6-fold higher than European averages; Cd 11-fold and Zn 4.5-fold higher that European average values (Fig. 4). Additionally, the obtained data for the content of the anthropogenetic elements in topsoil according to the determined zones show that the highest contents were in Zone I, the extremely contaminated parts of the study area (Fig. 5). As expected, the contents decreased from Zone I to the Zone III. For these elements, the enrichment ratios were calculated between the contents of elements in the topsoil in the area of Zone I, vs. Zone III. High contents and enrichment ratios in the topsoil were noticeable. Typical enrichments were from 3.7-fold (Tl) to 10-fold (Zn), 12-fold (Cd, Bi), 16-fold (Pb), 20-fold (Sb) and 27-fold (Ag).

It was also concluded that the contents of As, Cd, Cu, Hg, Pb and Zn, set out in the New Dutch List recommendations (http://www.contaminatedland.co.uk/std-guid/dutch-l.htm). Anthropogenic pollution, the consequence of Pb-Zn mining, processing and smelting operations, was associated with high contents of As, Cd, Cu, Hg, Pb and Zn. The high contents of the abovementioned elements exceeded the optimum values in the entire study area (302 km^2). The action values of these elements were exceeded in 122 km^2 in topsoil.

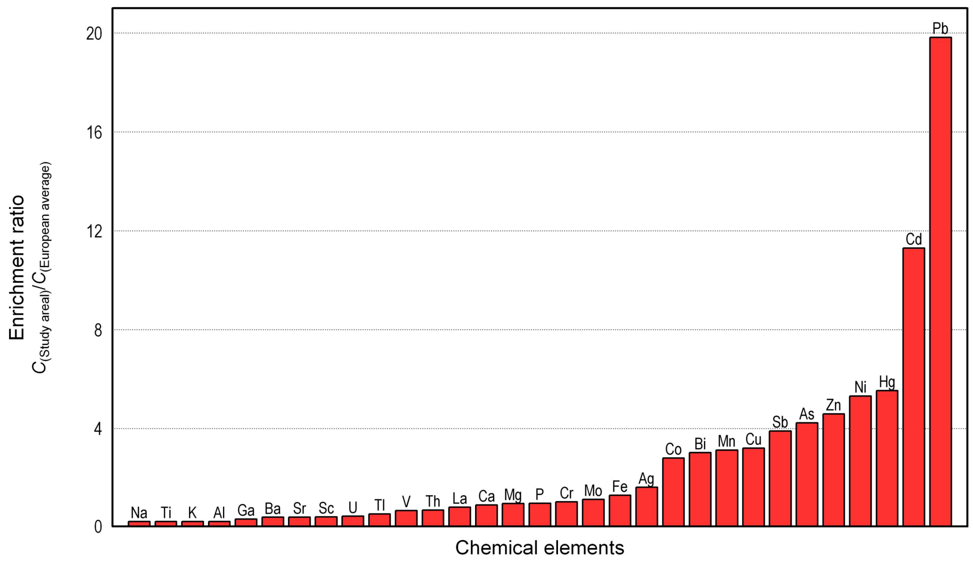

Fig. 4. Enrichment ratios of the study area topsoil vs. average European topsoil

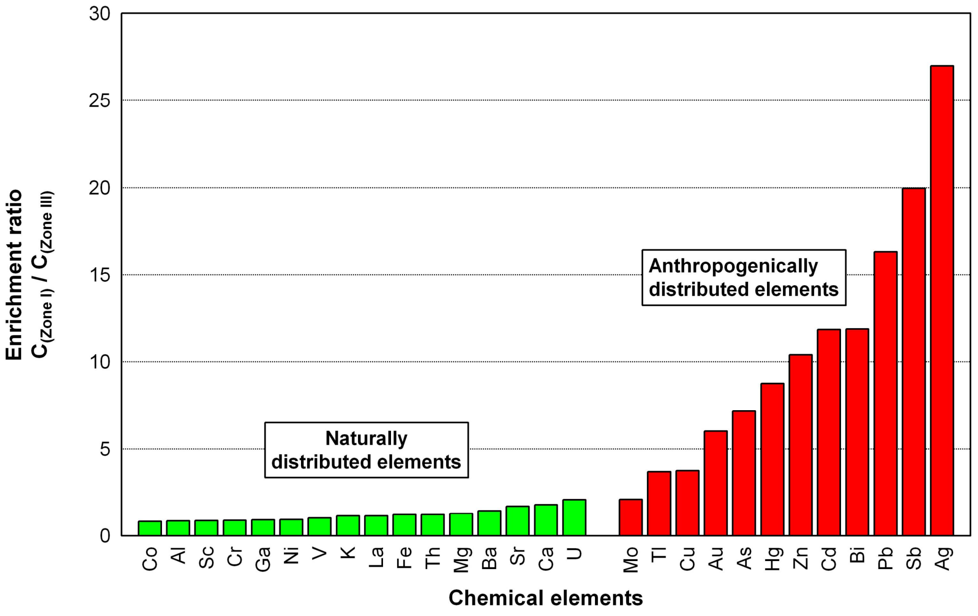

Fig. 5. Enrichment ratio of the study area topsoil comparing the results for Zone I vs. Zone III

Conclusion

The obtained results of the study of the distribution of chemical elements in the surface soil over of the Mitrovica region, Republic of Kosovo, show that the content of some elements, such as Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl and Mo, in soil samples appeared as an anthropogenic association of elements due to the mining and processing activities around the lead and zinc mines and smelter plants. Thus, the average content of Pb was 19.6-fold higher than European averages; Cd 11-fold, Hg 5.4-fold, Zn and As 4.5-fold and Cu 3.2-fold higher. In the close vicinity of the cities of Zvečan and Mitrovica, the contents of these elements were even higher than the corresponding intervention (critical) values according to Dutch standards (the New Dutch list) and were exceed in 152 km^2 of the investigated area.

References

Arditsoglou, A., Samara, C. (2005). Levels of total suspended particulate matter and major trace elements in Kosovo: a source identification and apportionment study. *Chemosphere* **59**, 669-678.

Bogdanović, P. (1978). *Basic Geological Map of SFRJ, Sheet Titova Mitrovica 1:100.000 (interpreter).* Federal Geological Survey, Beograd.

Bogdanović, P., Urošević, M., Urošević, D., Dimitrijević, M., Marković, B., Pavić, A., Menković, L., Folgić, K. (1978). *Basic Geological Map of SFRJ, Sheet Titova Mitrovica 1:100.000 (map).* Federal Geological Survey, Beograd.

Borgna, L., Di Lella, L.A., Nannoni, F., Pisani, A., Pizzetti, E., Protano, G., Riccobono, F., Rossi, S. (2009). The high contents of lead in soils of northern Kosovo. *J. Geochem. Explor*. **101**, 137-146.

Di Lella, L.A., Frati, L., Loppi, S., Protano, G., Riccobono, F. (2003). Lichens as biomonitors of uranium and other trace elements in an area of Kosovo heavily shelled with depleted uranium rounds. *Atmos. Environ*. **37**, 5445-5449.

Frese, S.D., Klitgaard, R., Pedersen, E.K., Rank, J., Klemmensen, B. (2004). *Environmental Management in Kosovo, Heavy Metal Emission from Trepca*. II DM-2003/2004, Institut for Miljø, Teknologi og Samfund, Roskilde University, Roskilde.

Jia, G., Belli, M., Sansone, U., Rosamilia, S., Gaudino, S. (2004). Concentration, distribution and characteristics of depleted uranium (DU) in the Kosovo ecosystem: A comparison with the uranium behavior in the environment uncontaminated by DU, *J. Radioanal. Nucl. Chem*. **260**, 481-494.

Le Maitre, R.W. (1982). *Numerical Petrology, Statistical Interpretation of Geochemical Data*, Elsevier, Amsterdam.

OSCE (2009). *Lead Contamination in Mitrovicë/Mitrovica Affecting the Roma Community*. Background Report, Organization for Security and Co-operation in Europe, OSCE Mission in Kosovo, Prishtina.

Palariet, M. (2003). *Kosovo’s Industrial Giant, Trepca, 1965-2000*. European Stability Initiatives, University of Edinburgh, Edinburgh, U.K.

Salminen, R., Batista, M.J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O‘Connor, P.J., Olsson, S.A., Ottesen, R.T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A., Tarvainen, T. (2005). *Geochemical Atlas of Europe, Part 1, Background Information, Mothodology and Maps*. Geological survey of Finland, Espoo.

Snedecor, G.W., Cochran, W.G. (1967). Statistical Methods, The Iowa State University Press, Ames, Iowa.

FLUID-MEDIATED ALTERATION OF MONAZITE IN GRANITOIDS OF SOUTHWESTERN BULGARIA AS PREHISTORY AND PRECONDITION FOR REE, Th AND U REDISTRIBUTION IN WEATHERING ROCKS, SOILS AND CULTIVATED AREAS

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Abstract

The report summarizes the data of the authors on the fluid-mediated alteration of monazite-(Ce) in the Igralishte granite pluton (Southwestern Bulgaria), as factor with potential to influence redistribution and dissemination of REE, Th and U in weathering profile of the granite, surrounding soils and cultivated areas. It is shown that at least three distinct types of postmagmatic alteration of monazite are carried out in the pluton: (1) partial alteration of monazite including redistribution of REE, Th and U and crystallization of new phases xenotime, thorite, huttonitic monazite, apatite occasionally associated by zircon, allanite and potassium feldspar-all related to the earliest stage of the high-temperature postmagmatic potassium metasomatism; (2) formation of porous aggregates of platy secondary Th-enriched monazite mainly as pseudomorph after the primary monazite during the latest stages of the potassium metasomatism; (3) pseudomorphic replacement of monazite by apatite aggregate resulted from the interaction of monazite with Ca-rich fluids released after albitization of plagioclase at the sodium stage of postmagmatic alkaline metasomatism.

It is shown that the all types of monazite alteration are carried out via coupled dissolution-reprecipitation mechanism. It is inferred that the high porosity of the altered monazite and its secondary products and their micrometric size are promoting factors for mechanical and chemical breakdown of these minerals in weathering profiles of the granite, especially in the presence of humic acid and microorganisms, and redistribution of REE, Th and U in the soils. The diversity of mineral bearer of REE, Th and U is most probably a factor causing uneven release of the chemical elements into exogenic solutions.

Introduction

The stability of monazite, (Ce,La,Th)PO_4, during a fluid-rock interaction is a topical problem comprehensively studied by numerous scientists during the last two decades. At least, four major fields of increased scientific interest can be defined in connection with the monazite stability. (1) Monazite is very important repository of REE, Th and U in the continental crust and the stability of the mineral in fluid-mediated processes is of crucial significance for Th-U-Pb geochronology, geothermometry and geochemistry (Poitrasson et al., 2000; Berger et al., 2008). (2) The stability of monazite is widely debated theme in connections with the perspectives of using the REE phosphate ceramics for storage of nuclear waste radioactive isotopes (Poitrasson et al., 2000; de Kerdaniel et al. 2007). (3) Fluid-mediated alteration of monazite is recognized as governing factor in the genesis of a number of uranium deposits (Hecht, Cuney, 2000). (4) Low-temperature degradation of monazite (and other REE-Th-U bearing minerals) and redistribution of REE, Th and U in weathering and pedogenetic profiles on granitoid terrains with potential role to pose a human-health and ecological risk (Read et al., 2002; Taboada et al., 2006).

Two principle types of monazite alteration during endogenic fluid-rock interaction have been recognized so far: (i) partial monazite fluid-mediated alteration (ion exchange and REE-, Ca-, Y-, Th-, U- redistribution, giving rise to specific types of zonality in the mineral disturbing the growth zonality (Poitrasson et al., 2000; Harlov et al., 2010; Hetherington et al., 2010), and (ii) complete breakdown of the mineral giving rise mainly to apatite ± allanite mineral assemblage (Finger et al., 1998; Broska et al., 2005). Much less it is known for degradation of monazite during granite weathering and soil formation, although a number of investigators emphasize a significant role of organic (humic and fulvic) acids (Taboada et al., 2006; Polyakov et al., 2010) and microorganisms (bacteria, lichens) (Tauton et al., 2000) in redistribution of REE, Th and U in weathering and pedogenetic profiles. Endogenic alteration of monazite commonly is not one-act metasomatic event but a series of fluid-mediated processes developed at variable temperature conditions and, possibly, at different geological time, and is an important factor in promoting or hindering the weathering of monazite and its products at exogenic conditions.

In the present report, the authors aim to summarize the data on the postmagmatic alteration of monazite-(Ce) in Igralishte granite pluton (Southwestern Bulgaria) and its possible influence to the further degradation of monazite and its products at exogenic conditions. The task is provoked by the facts that the pluton is with well developed weathering crust characterizing with increased content of actinide elements, and that a significant part of lands on the territory of pluton is used by the native inhabitant for pasture, hay preparing and cultivation of tobacco and vegetable cultures.

Material and methods

The Igralishte intrusive body is intruded in the Ograzhden block of the Serbo-Macedonian massif. The pluton is composed of two-mica granites belonging to the calcium-alkaline and high-calcium-alkaline series. Mineralogical and petrochemical characteristics of the pluton rocks specify them as peraluminous monzogranites. The temperatures of saturation with REE (for monazite) and with Zr (for zircon) is 820-720°C relate the granites to the so-called "cold" granites (Tarassova et al., 2008). The granite is dated at 243.28 ± 0.84 Ma by concordant zircons (ID-TIMS data) and by the in-situ LA-ICP-MS and EPMA monazite analyses (Peytcheva et al., 2009). The intrusion of the Igralishte granite at early Triassic time brackets the maximum age of the high-grade metamorphism in Ograzhden Mountain as Pre-Triassic. The initial strontium ratio of $^{87}Sr/^{86}Sri = 0.7078$ of the rocks and the inheritance of old lead components in the zircons are in agreement with crustal dominated source of the magma (Peytcheva et al., 2009). The most significant alterations of the pluton rocks are caused by postmagmatic high-temperature alkaline (K and Na) metasomatism. Besides, a tectonic and hydrothermal overprint at 36.36±0.56 Ma is recently recognized using Rb-Sr analysis of whole rock and biotite (Peytcheva et al., 2009).

Fresh granite rocks sampled during field trips in 2005-2008 years were used for the present report. The material was studied by scanning electron microscopy and electron probe microanalysis (Philips SEM515-WEDAX 3A, ZEISS EVO 25LS – EDAX Trident), transmission electron microscopy (Philips TEM420 equipped with EDAX 9100/70) and micro-Raman spectroscopy (LabRAM HR Visible with a 633 nm He-Ne laser).

Both polished massive and thin sections of granite as well as polished resin tablet with incorporated monazite grains from heavy fractions of the granite were used for the study. Specimens for TEM investigation were prepared by grinding the monazite grains in an agate mortar under alcohol and dispersing the particles onto holey carbon film supported by Cu grids.

Result and discussion

Types of monazite alteration

All examined monazite grains bring pronounced signs of alteration visible in SEM as corroded peripheries, abundance of secondary mineral inclusions and cavities, well developed porosity and secondary zonality overlapping and veiling the normal growth zonality. All this features indicate that the monazite alteration in the Igralishte pluton is not a one-act metasomatic event but a series of fluid-mediated processes everyone being related to a definite stage of evolution of magmatic-hydrothermal system of the pluton and probably to a later hydrothermal overprint.

Detailed SEM, EPMA, TEM and Raman spectroscopy investigations of the monazite and its secondary mineral products allow us to differentiate at least three types of monazite alteration.

(I) Partial alteration of monazite including redistribution of REE, Th and U and crystallization of new phases

Xenotime, YPO_4, and thorite, $ThSiO_4$, are the most typical neo-formed minerals for this stage of monazite alteration. Commonly they are grouped as veinlets crosscutting the monazite grain or occur as randomly shaped inclusions in the mineral. Beside its principle components ThO_2 and SiO_2, thorite contains also UO_2 (~8.0 wt%) and P_2O_5 (~1 wt%) (Tarassov, Tarassova, 2005). The contents of ThO_2 and UO_2 in xenotime achieve 2.0 wt% (Tarassov, Tarassova, 2005). In BSE images with enhanced contrast, it is clearly visible that the novel minerals are closely related to areas of the monazite where the primary growth zonality is disturbed and overprinted by the metasomatic one – commonly being either a patchy type of zonality with areas of variable shape and brightness, or as network-distributed dark areas in the lighter monazite matrix indicating that the alteration process developed along systems of microfissures. In all cases of metasomatic zonality, the lighter areas of the monazite are more enriched in Th and U than the darker ones. As a rule, xenotime and thorite are localized in the darker areas of the monazite thus signifying that the redistribution of REE, Y, Th and U and the crystallization of the new phases are two coupled processes.

Similar processes of metasomatic formation of thorite and uraninite inclusions in xenotime and monazite were observed by Hetherington & Harlov (2008) for granitic pegmatites of Norway. The authors inferred that the new phases were formed via dissolution-reprecipitation mechanism realized during a partial chemical alteration of xenotime and monazite including a fluid-aided redistribution of elements in the primary minerals. The same mechanism of coupled dissolution-reprecipitation

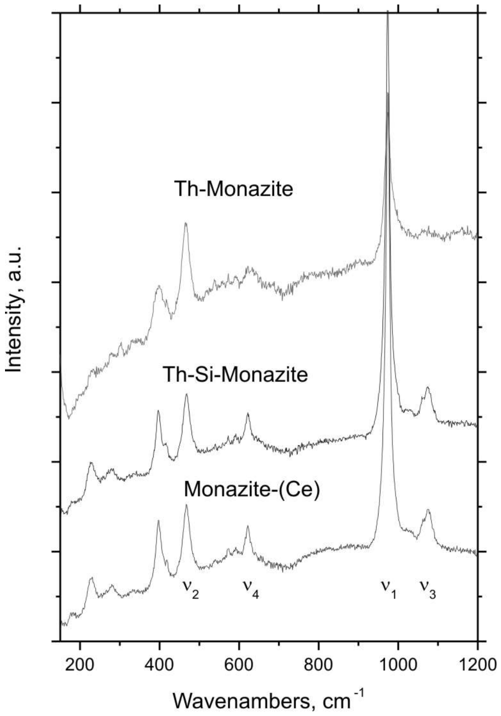

Fig. 1. Raman spectra of primary monazite and secondary Th-Si-enriched (I type of alteration) and Th-enriched (II type of alteration) monazites.

was invoked and experimentally confirmed for explanation of complex zoning in Th commonly observed in monazite from metamorphic and igneous rocks as well as for interpretation of partial replacement of monazite by Th-enriched monazite (Hetherington et al., 2010; Harlov et al., 2010). It was shown also that the described processes were carried out only in the alkaline fluids. These experimental findings as well as our data on the ages of the monazite and its secondary products in the Igralishte pluton (Tarassov, Tarassova, 2005) allows us to relate the considered partial alteration of monazite accompanied by crystallization of the new phases of Th, U, Y to the earliest stage of the high-temperature postmagmatic alkaline (potassium) metasomatism of the rocks.

Thorite is not the only mineral of thorium formed during the considered type of monazite alteration. During our examination of monazite samples, Th-U-REE-Si oxide inclusions with size of 1-2 μm and strongly prevailing content of ThO_2 were also found. The performed TEM investigations (Tarassov et al., 2008) showed that the latter material, in contrast to well-crystallized thorite, is amorphous phase.

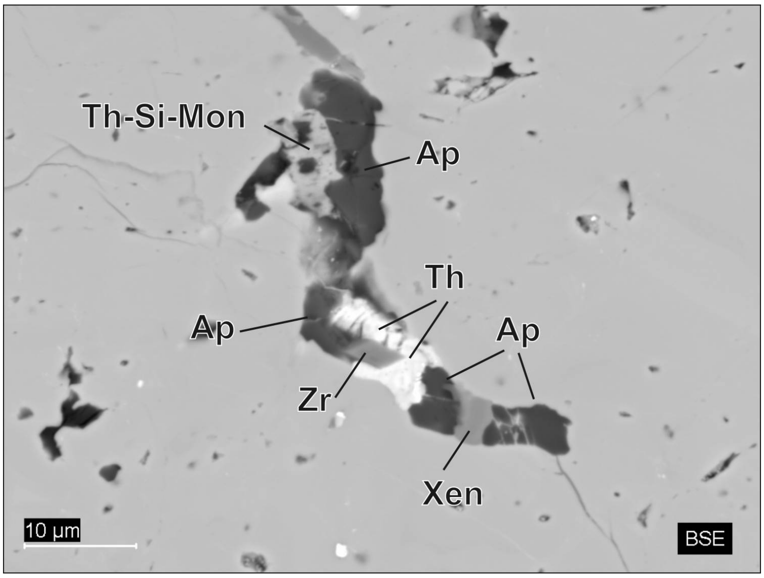

Fig. 2. Veinlet of apatite, xenotime, thorite, zircon and Th-Si-monazite cross-cutting the primary monazite.

Th-Si-enriched (huttonite-enriched) monazite (content of ThO_2 to 50 wt.%, UO_2 – to 6 wt.%) is another neo-formed mineral bearer of Th closely associated with xenotime. Unequivocal phase identification of the mineral was performed using micro-Raman spectroscopy (Fig. 1): the positions of the Raman peaks related to the internal modes of PO_4 group (symmetric stretching – ν_1, antisymmetric stretching - ν_3 and bending ν_2 and ν_4 vibrations) as well as the spectral region below 450 cm^{-1} related to the lattice vibrations, well coincide in the spectra both of primary monazite and neo-formed mineral. Besides, the obtained spectra well correspond to the Raman spectra of monazite–type rare-earth orthophosphate studied in detail by Silva et al. (2006).

Xenotime and the Th-enriched minerals are occasionally accompanied by zircon, allanite and potassium feldspar which indicates that during the high-temperature fluid-monazite (fluid-rock) interaction the fluid evolved in its chemical composition. Moreover, some complex assemblages of neo-formed minerals found by us, as that shown in Fig. 2, imply significant role of local evolution of the fluids during the monazite alteration. This finding is confirmed by the experimental works of Hetherington et al. (2010) and Harlov et al. (2010).

It should be noted that the associations of xenotime and Th mineral as inclusions in monazite have been reported elsewhere by other authors. For example, Claeson (2002) described inclusions of xenotime and Th-silicate (huttonite or thorite?) in monazite from metaaluminous leucotonalite from the Eriksberg gabbro (Sweden). Although the author supposed these minerals to be primary inclusions in the monazite, some other features as pronounced replacement of the monazite by apatite associated with allanite, allows one to suggest that the scenario of alteration of monazite in Igralishte and Eriksberg intrusives were similar.

(II) Formation of porous aggregates of platy secondary Th-enriched monazite.

As we know, till now the considered type of hydrothermal alteration of magmatic monazite has never been described in the literature. In the present report, we only briefly consider this phenomenon as the detailed investigation of the problem will be presented in our (M.T. and E.T) forthcoming paper currently being at advanced stage of preparation.

Porous aggregates of platy secondary Th-enriched monazite occur as "bay"-shaped zones in the periphery of the primary monazite (Fig. 3) or rarely as veinlets with potassium feldspar crosscutting the primary mineral. Raman spectrum of the secondary phase (Fig. 1) well resembles the spectral features typical for the monazite type compounds. At the same time, the observed differences-lower intensity and pronounced broadening of the peaks corresponding to ν_4 bending and ν_3 antisymmetric stretching vibrations as well as some changes in the low-frequency spectral range related to the lattice vibrations, most probably, are indications for a disordered or defect structure of the phase.

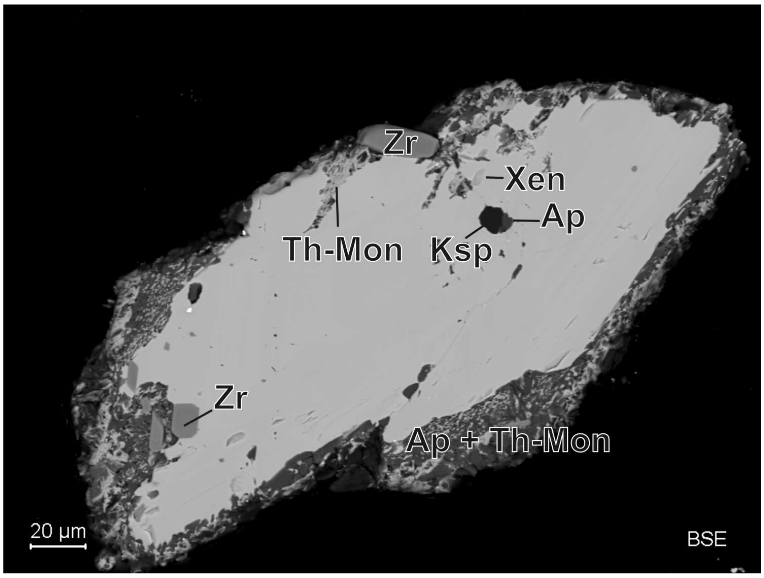

Fig. 3. Monazite grain partially metasomatically replaced by secondary Th-enriched monazite (alteration II) and by apatite aggregates (alteration III). Apatite pseudomorph contains residual forms of monazite

This suggestion is confirmed by SEM and EPMA investigations. For example, the EPMA data show that the only significant difference in the chemical composition of the primary and secondary monazites is in the increased contents of ThO_2 and UO_2 in the latter phase, achieving 15 and 2 wt%, respectively.

At the same time, in BSE images, the secondary Th-enriched monazite appears distinctly darker than the primary one (Fig. 3) and this feature should mean that the secondary phase is with lower average atomic number which is in contradiction with the data for chemical composition.

Our preliminary investigations show that the reason for the apparent discrepancy above lies in the mechanism of monazite alteration (II). TEM investigations reveal that the secondary monazite is characterized by a specific porosity making the material less dense than the primary monazite.

The mechanism of a coupled dissolution-reprecipitation does also work here, but the dissolution essentially prevails over the reprecipitation giving rise to a specific secondary mosaic microstructure of monazite with increased porosity. On the advanced stage of alterations (II and III) initially well crystallized monazite may be transformed into platy aggregates of nanometric monazite crystals as those shown in Fig. 4.

Some microtexture features as well as relationships of the secondary monazite with other metasomatic minerals allow us to associate the alteration (II) of monazite with the latest stages of the potassium metasomatism.

(III) Pseudomorphic replacement of monazite by apatite aggregates

This type of monazite alteration is reported elsewhere for metamorphic and intrusive rocks (Finger et al. 1998; Claeson, 2002; Broska et al., 2005). Corona-like development of apatite with allanite followed by epidote mantle is a typical microtexture for this type of monazite alteration (Finger et al. 1998). Pseudomorphic replacement of monazite by apatite is the most manifest type of monazite alteration in the Igralishte pluton causing anhedral (relic) outlook of the mineral (Fig. 3).

Detailed inspection of series of polished granite sections shows that the replacing apatite well preserves the outer euhedral contours of the monazite and that the degree of monazite replacement varies from almost intact monazite crystals to complete apatite pseudomorphs. Allanite is a sporadically occurred mineral associated with the apatite. At the same time, the secondary Th-enriched monazite with variable composition and degree of alteration is common inclusion in the apatite aggregates (Fig. 3).

The apatite contains significant quantities of ThO_2 to 1.3 wt%), UO_2 to 0.8 wt%, SiO_2 – to 0.9 wt% and $\Sigma(REE+Y)_2O_3$ to 9.8 wt% tentatively associated with the britholite component in the apatite composition. TEM examination shows that the pseudomorphic apatite is presented by well crystallized forms.

According to Finger et al. (1998) and Broska et al. (2005) the breakdown of monazite in the studied by them granitoids, giving rise to the pseudomorphic apatite (+allanite, +outer mantle of epidote), is caused mainly by a greenschist to amphibolite facies prograde metamorphism and the role of postmagmatic hydrothermal processes is negligible. The authors suggested that the breakdown of monazite is triggered by F-rich fluids containing Ca, Al, Si released from the alteration of anortite and biotite.

In the Igralishte pluton, the aforesaid "metamorphic model" of monazite alteration could hardly be accepted as the most important large-scale process of Ca release into fluids is the postmagmatic albitization of plagioclase (high-temperature alkaline (sodium) metasomatism). This argument as well as the textural relationships with the products of preceding stages of monazite alteration allow us to relate the pseudomorphic replacement of monazite by apatite with the sodium stage of postmagmatic alkaline metasomatism. Similarly to the considered above types of alteration, the alteration III is carried out via dissolution-reprecipitation mechanism.

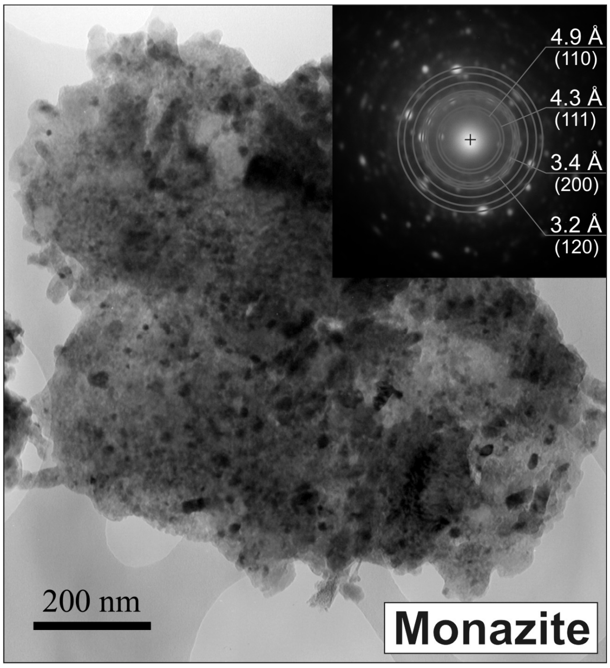

Fig. 4. Bright-field image of platy aggregate of monazite nanocrystals corresponding to an advanced stage of monazite alterations (II and III). Insert shows polycrystalline diffraction pattern of the material.

Endogenic alteration of monazite and redistribution of ree, th and u in weathering rocks, soils and cultivated areas

At least three important characteristics of the altered monazite could be emphasized as possible factors affecting the REE, Th and U redistribution in the weathering profiles of granites and in the soils:

(1) High porosity of the altered monazite and its products (pseudomorphous apatite, secondary monazite). This characteristics is a direct result of the mechanism of monazite alteration via a coupled dissolution-reprecipitation in which the porosity is an integral microstructuarl feature of fluid-induced replacement (Putnis, 2009).

(2) Diversity of mineral bearers of REE-Th-U during the monazite alteration. This characteristics binds the individual properties of the minerals during their interaction with exogenic solution and the individual geochemical behavior of the elements composing the mineral. Our data show that every one of the neo-formed after monazite minerals contains actinide and/or rear earth elements. From this group of minerals, the apatite seems to be most dissoluble mineral under exogenic conditions (Oelkers et al., 2008), especially in the presence of microorganisms (Tauton et al., 2000). Although, monazite is known as one of the less soluble phosphate minerals (Oelkers et al., 2008), its defect structure as well as the presence of organic acids can cause its degradation (Polyakov et al., 2010) and redistribution of its components in weathering and pedogenetic profiles (Taboada et al., 2006). In general, the diversity of different mineral bearer of REE, Th and U may cause uneven release of the chemical elements into exogenic solutions.

(3) Micrometric size of metasomatically formed REE-Th-U minerals and altered areas in monazite. During the weathering and pedogenetic processes, the micrometric size of mineral grains is important factor both for dissolution kinetics and for possibility the mineral to be water and airborne transported.

Conlusions

- The performed survey shows that the monazite alteration in the Igralishte pluton is not a one-act metasomatic event but a series of fluid-mediated processes related to definite stages of evolution of magmatic-hydrothermal system of the pluton.
- At least three distinct types of postmagmatic alteration of monazite are specified: (1) partial alteration of monazite including redistribution of REE, Th and U and crystallization of new REE-Th-U phases related to the earliest stage of the high-temperature postmagmatic potassium metasomatism; (2) formation of porous aggregates of platy secondary Th-enriched monazite during the latest stages of the potassium metasomatism; (3) pseudomorphic replacement of monazite by apatite aggregate resulted from the interaction of monazite with Ca-rich fluids released after albitization of plagioclase at the sodium stage of postmagmatic alkaline metasomatism.
- All types of monazite alteration are carried out via coupled dissolution-reprecipitation mechanism.
- It is inferred that the high porosity of the altered monazite and its secondary products and their micrometric size are promoting factors for mechanical and chemical breakdown of these minerals in weathering profiles of the granite, especially in the presence of humic acid and microorganisms, and redistribution of REE, Th and U in the soils. The diversity of mineral bearer of REE, Th and U is most probably a factor causing uneven release of the chemical elements into exogenic solutions.

Acknowledgements

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References

Berger, A., E. Gnos, E. Janots, A. Fernandez, J. Giese. 2008. Formation and composition of rhabdophane, bastnasite and hydrated thorium minerals during alteration: Implication for geochronology and low-temperature processes. – *Chemical Geology*, 254, Issues 3-4, 238-248.

Broska, I., C.T. Williams, M. Janak, G. Nagy. 2005. Alteration and breakdown of xenotime-(Y) and monazite-(Ce) in granitic rocks of the Western Carpathians, Slovakia. – *Lithos*, 82, 71-83.

Claeson, D.T. 2002. Stability of REE-bearing minerals in a metaaluminous leucotonalite from the Eriksberg gabbro, Transscandinavian Igneous Belt, Sweden. – *Neues Jahrbuch für Mineralogie – Abhandlungen*, 177, 3, 277-291.

de Kerdaniel, E. Du Fou, N. Clavier, N. Dacheux, O. Terra, R. Podor. 2007. Actinide solubility-controlling phases during the dissolution of phosphate ceramics. – *Journal of NuclearMaterials*, 362, 451-458.

Finger, F., I. Broska, M.P. Roberts, A. Schermaier. 1998. Replacement of primary monazite by apatite-allanite-epidote coronas in an amphibolite facies granite gneiss from the eastern Alps. – *American Mineralogist*, 83, 248-258.

Harlov, D.E., R. Wirth, C.J. Hetherington. 2007. The relative stability of monazite and huttonite at 300-900°C and 200-1000 MPa: Metasomatism and the propagation of metastable mineral phases. – *American Mineralogist*, 92, 1652-1664.

Harlov, D.E., R. Wirth, C.J. Hetherington. 2010. Fluid-mediated partial alteration in monazite: the role of coupled dissolution-reprecipitation in element redistribution and mass transfer. – *Contrib. Mineral. Petrol.* (published online: 09 December 2010, DOI 10.1007/s00410-010-0599-7)

Hecht, L., M. Cuney. 2000. Hydrothermal alteration of monazite in the Precambrian crystalline basement of the Athabasca Basin (Saskatchewan, Canada): implication for the formation of unconformity related uranium deposits.–*Mineralium Deposita*,35,791-795.

Hetherington, C.J., D.E. Harlov. 2008. Metasomatic thorite and uraninite inclusions in xenotime and monazite from granitic pegmatites, Hidra anorthosite massif, southwestern Norway: Mechanics and fluid chemistry. – *American Mineralogist*, 93, 806-820.

Hetherington, C.J., D.E. Harlov, B. Budzyń. 2010. Experimental metasomatism of monazite and xenotime: mineral stability, REE mobility and fluid composition. – *Miner. Petrol.*, 99, 165-184.

Oelkers, E.H., E. Valsami_Jones, T. Roncal-Herrero. 2008. Phosphate mineral reactivity: from global cycles to sustainable development. – *Mineralogical Magazine*, 72, 1, 337-340.

Poitrasson, F., S. Chenery, Th.J. Shepherd. 2000. Electron microprobe and LA-ICP-MS study of monazite hydrothermal alteration: Implication for U-Th-Pb geochronology and nuclear ceramics. – *Geochimica et Cosmochimica Acta*, 64, 19, 3283-3297.

Peytcheva, I., A.von Quadt, M. Tarassov, N. Zidarov, E. Tarassova, V.Andreichev. 2009. Timing and magma sources of Igralishte pluton in Ograzhden Mountain, SW Bulgaria: implications for the Permian-Triassic tectono-magmatic evolution of the region. - *Geologica Balcanica*, 38, 1-3, 5-14.

Polyakov, E.V., I.V. Volkov, V.T. Surikov, L.A. Perelyaeva. 2010. Solubility of monazite chemical components in humic acid solutions. - *J. Radioanal. Nucl. Chem.*, 286, 707-711.

Putnis, A. 2009. Mineral replacement reactions. – In: *"Reviews in Mineralogy and Geochemistry"*, Vol. 70, 87-124.

Read, D., A.G. Andreoli, M. Knoper, C.T. Williams, N. Jarvis. 2002. The degradation of monazite: Impliaction for the mobility of rare-earth and actinide elements during low-temperature alteration. - *European Journal of Mineralogy,* 14, 487-498.

Silva, E.N., A.P. Ayala, I. Guedes, C.W.A. Paschoal, R.L. Moreira, C.-K. Loong, L.A. Boatner. 2006. Vibrational spectra of monazite-type rare-earth orthophosphates. – *Optical materials*, 29, 224-230.

Taboada, T., A.M. Cortizas, C. Garcia, E. Garcia-Rodeja. 2006. Uranium and thorium in weathering and pedogenetic profiles developed on granitic rocks from NW Spain. - *Science of the Total Environment*, 356, 192-206.

Tarassov, M., E. Tarassova. 2005. Occurrence, chemical composition and electron probe dating of accessory REE-Y-Th-U minerals from Igralishte granite pluton (Ograzhden block, Serbo-Macedonian massif). – *Proceedings of Jubilee National Conference with International Participation "Bulgarian Geological Society - 80-th Anniversary"*, Sofia, Bulgaria, November 17-18, 2005, 91-94 (ISSN 1313-2377).

Tarassov, M., E. Tarassova, I. Piroeva. 2008. Alteration of monazite in the Igralishte granite pluton, Southwestern Bulgaria. – *Proceedings of National Conference with International Participation "Geoscience-2008"*, Sofia, Bulgaria, December 11-12, 2008, 45-46.

Tarassova E., Tarassov M., von Quadt A., Peycheva I. 2008. Mineralogical and geochemical characteristics of the Igralishte pluton, Southwestern Bulgaria. - *Geologica Macedonica, 2, Special issue, "First Congress of Geologists of Republic of Macedonia"*, 317-322.

Tauton, A.E., S.A. Welch, J.F. Banfield. 2000. Microbial controls on phosphates and lanthanide distributions during granite weathering and soil formation. – *Chemical Geology*, 169, 371-382.

ANTHROPOGENIC INFLUENCE OF THE BUCHIM MINE WASTE DUMP AND HYDROTAILING TO THE SURFACE AND GROUND WATERS IN THE LAKAVICA BASIN, MACEDONIA

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Abstract

Two main sources of anthropogenic influence to the running waters of Topolnica, Madenska River and Kriva Lakavica and ground waters in area od Damjan Field and Kriva Lakavica river flow were determined: Buchim mine waste dump and hydrotailling, which are in direct relation to the activity of the copper mine "Buchim"-Radovis.

By monitoring conducted it was determined that influence of hydrotailling to waters of Topolnica River is of low intensity (0.539 mg/L SO_4, 0.06 mg/L Cu and 0.1mg/L Mn), probably due to collection system constructed correctly under the hydrotailling dam.

The main influence and contamination of waters (mainly copper) originate from the Buchim mine waste dump or more precisely from JasenovDol (7.849 mg/L SO_4, 270.5 mg/L Cu and 96.9 mg/L Mn with very low pH values of 4.3) and Buchim Lake (9.092 mg/L SO_4, 142.9 mg/L Cu and 15.9mg/L Mn with very low pH values of 4.2).

Contamination of running waters in Topolnica River, Madenska River and Lakavica River may be seen by the following results: 2.875 mg/L SO_4, 98.4 mg/L Cu and 59mg/L Mn for Topolnicka River; 4.871 mg/L SO_4, 124.4 mg/L Cu and 57.4mg/L Mn for Madenska River and up to 2.6 ÷ 9.0 mg/L Cu for Lakavica River. Influence to ground waters in studied area is relatively low, mainly, within the range of 0.005 to 0.08 mg/L Cu.

Introduction

Buchim Mine has been built more than 30 years ago on the well known porphyry copper deposit Buchim. During the three decades of continuous exploitation around the Buchim Mine was created surface waste dump were have been stored more than 120 Mt of material and more than 100 Mt material within the hydrotailling dam. These secondary landfills for years have been considered as basic sources of anthropogenic influences and contamination of air, soils and especially waters. For many years those influences haven't been subject of serious scientific and practical studies, but however during last period they have been studied from few stand point according to the national and European standards for managing the secondary waste and environmental protection.

Some of the preliminary publications that have studied the issues of mine pollution at the territory of the Republic of Macedonia, including area around the Buchim Mine, can be found in works of Serafimovski et al., (2004), Alderton et al., (2005), Boev et al., (2005), Bermanec et al., (2005), Serafimovski et al., (2005a) and Serafimovski et al., (2005b). After that period studies around the Buchim Mine have been intensified and to longer distances in regards of running waters while it have been set monitoring points for particular hot spots around waste dump and hydrotailling dam with associated water drainage, ambiental dust monitoring, monitoring of soil contamination etc. Considering that issue have been completed some significant studies of soil contamination monitoring. There we think first of all to papers of Balabanova et al., (2009), Stafilov et al., (2010), Михајлов и др., (2011) etc.

Within this paper have been performed one systematization of an array of studies of running and well waters that are draining the mine waste dump, which have been separated in three segments. Within the first one were considered waters draining mine waste dump where as main drainages is stream Jasenov Dol and so called Buchim Lake. one are studies. The second one considered waters out flowing from the hydrotailling dam near the Topolnica village and their flow along the Topolnica River while the third segment closely monitored running waters of Madenska River and Kriva Lakavica. Simultaneously were studied well waters in the Damjan Field, where running waters from Jasenov Dol and Buchim Lake gravitate.

General features related with acid mine drainage waters

Mine wastes are the largest volume of materials handled in the world (ICOLD, 1996). The generation of acidic drainage and the release of water containing high concentrations of dissolved metals from these wastes is an environmental problem of international scale. Acidic drainage is caused by the oxidation of sulfide minerals exposed to atmospheric oxygen. Although acid drainage is commonly associated with the extraction and processing of sulfide-bearing metalliferous ore deposits and sulfide-rich coal, acidic drainage can occur wherever sulfide minerals are excavated and exposed to atmospheric oxygen (Turekian, 2003).

Mine workings and open pits

Minerals are typically excavated by underground mining, strip mining, or open-pit mining. The selection of the mine design is dictated by the physical structure and value of the ore body and by the characteristics of the adjacent geological materials. Although open-pit mines and underground mines are the two most common mining strategies, placer mining and solution mining also have been used for mineral extraction. The consequence of the excavation of open pits and other mining-related disturbances is that sulfide minerals previously isolated from the atmosphere are exposed to oxygen. Oxidation of sulfide minerals ensues. For example, pyrite oxidation and the factors affecting the kinetics of oxidation (O_2, Fe_3^+, temperature, pH, Eh, and presence or absence of microorganisms) have been the focus of extensive study because of their importance in formation of acid mine drainage Lowson (1982), Evangelou (1995), Evangelou and Zhang (1995), Nordstrom and Southam (1997), and Nordstrom and Alpers (1999a). The oxidation of pyrite can occur when the mineral surface is exposed to an oxidant and water, either in oxygenated or anoxic systems, depending on the oxidant. The process is complex and can involve chemical, biological, and electrochemical reactions.

Waste rock

Open-pit and underground mining result in the excavation of large volumes of rock to gain access to ore bodies. Rock of higher metal grade is processed, and rock below the cutoff grade is put to waste. The waste rock from mine operations may be used in construction activities at the mine site. Excess waste rock is deposited in waste-rock piles whose composition differs greatly from mine to mine because of variations in ore-deposit and host-rock mineralogy, and because of differences in the processing techniques and ore-grade cutoff values. Because of the large volume of rock excavated in open-pit operations, waste-rock piles may be tens of hectares in area and tens of meters in height (Ritchie, 1994).

Mill tailings

The ore extracted in most nonferrous, metalliferous mining operations is rich in base or precious metals, but the ore minerals are generally too dilute for direct processing using metallurgical techniques. Thus, most ores are processed through concentration steps that involve costs-crushing, grinding, and milling to a fine grain size-for beneficiation (differential flotation). The concentrate from the flotation step is retained for further metallurgical processing. Mill tailings as a residual material (including sulfide gangue minerals) are discharged to tailings impoundments (in form of a slurry of water and finely ground rock). The mining industry produces immense masses of mine tailings, which are typically retained in impoundments. The entry of gas-phase oxygen into the unsaturated tailings results in sulfide-mineral oxidation and the release of low-quality drainage.

Such similar situations we have monitored on the sample of the Buchim mine drainage system, as may be seen bellow.

Results and discussions related to water contamination around the Buchim Mine

In the adjacent vicinity of the Buchim Mine have been located the following hydrological structures:

- Buchim Lake, to the west from the open pit, located in its vicinity.

Draining waters from the mine waste

These waters are composed of meteoric waters flowing from upper parts above the mine waste pile (mine yard and Buchim village area) and passing through the mine waste, rain waters passing though the mine waste dump and flowing further downstream and ground waters infiltrating through the mine waste dump.

- Buchim Dol (Buchim Lake)-before the start of mine production it was built drainage system/collector with channels around the location perimeter planned for the mine waste dump. This system collects part of draining waters from the mine waste dump and guide them to the Buchim Dol (Figure 1).

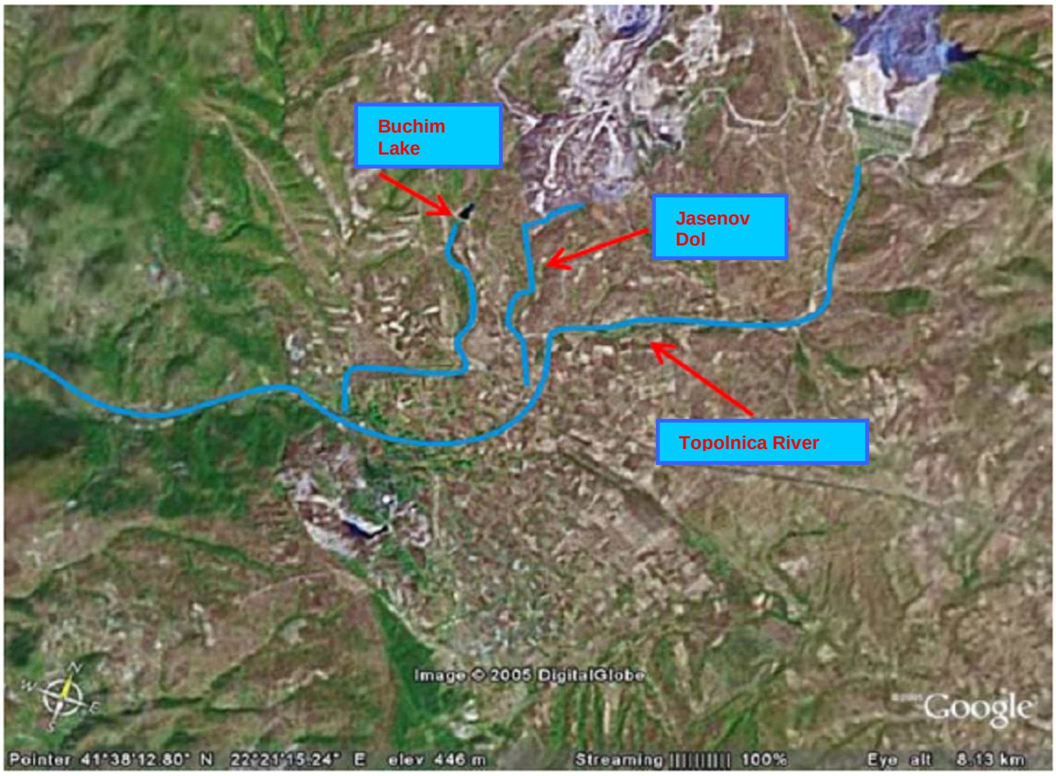

Fig. 1. Former waste waters situation, mine waste dump location

Beside these waters, this gully constitutes of atmospheric waters redirected from open pit and ground waters under the mine waste (Figure 2).

Fig. 2. Buchim Lake (left) and Buchim Dol (formation of Buchimski Dol, joining of colector and drainage waters under the mine waste dump, right)

With the latest improvements, waters at the bottom of open pit have been pumped into the pools for industrial water because they are unpolluted and can used again. They have been characterized by 30-45 mg/L), low pH value (3,6-5,5) and average flow of 15-20 l/s.

Until recently waters from Buchim and Jasenov Dol were flowing into the Madenska River. But, with implementation of activities of the UNDP project, waters from the Buchim gully are collected in an accumulation with concrete dam D1 (Figure 3), which with by pumping facility has been transferred to the accumulation into dam D2 where have been collected water from the Jasenov Dol and from there all together they have been transferred to the hydrotailling dam as temporary solution (Figure 4).

Fig. 3. Accumulation dam D1 (left) and earthen dam above the dam D1 (right)

- Jasenov Dol – part of meteoric and groundwater not covered by forementioned drainage system are flowing out into the Jasenov Dol, which passes through the main waste dump and is seeping out under the waste dump. Starting from level 650, Jasenov Dol, beside those waters encloses also meteoric and utility water from the commercial court of Buchim Mine. These waters, on its way are passing through the mine waste and running into the Topolnica river (Figure 5). This water flow has length of 900 m until into its inflow into the Topolnica river. Copper content in these waters is quite high reaching range of 450-850 mg/L Cu, with pH values in the range of 3.4-4.5 and average water flow of 5-20 l/s.

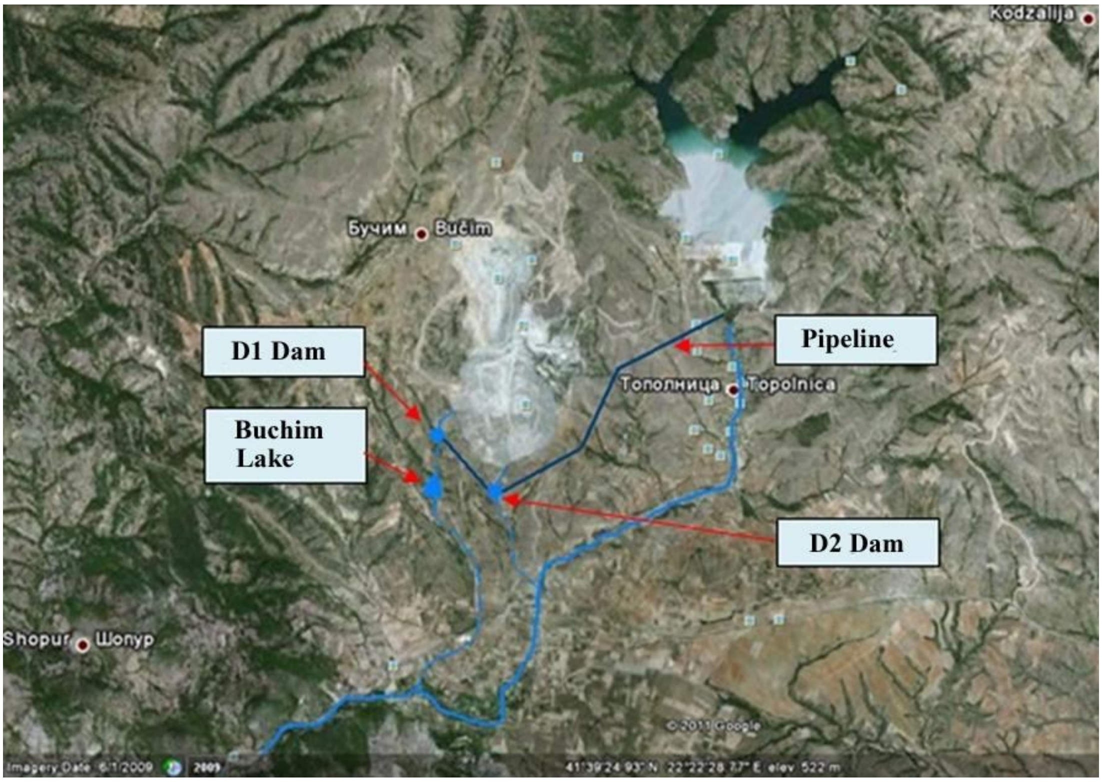

Fig. 4. Actual situation with drainage waters from the mine waste dump.

- River Topolnica, directly receives waters from the drainage system of the hydrotailling dam, as well as all other waters in the zone of mine operations. This water flow also receives waters from the Jasenov Dol (Figure 5).

Fig. 5. Jasenov Dol (left) and junction of the Jasenov Dol and Topolnica River (right)

Source of the Topolnicka River is located in the southwestern part od the Plackovica Mountain and it represents the right tributary of the Kriva Lakavica River. The river network, size of water catchment drainage basin, altitude and geological structure are determining water regime. The river water drainage basin is between altitudes of 517 and 1057 m, while the most of it lies between 700 and 800 m (Figure 6).

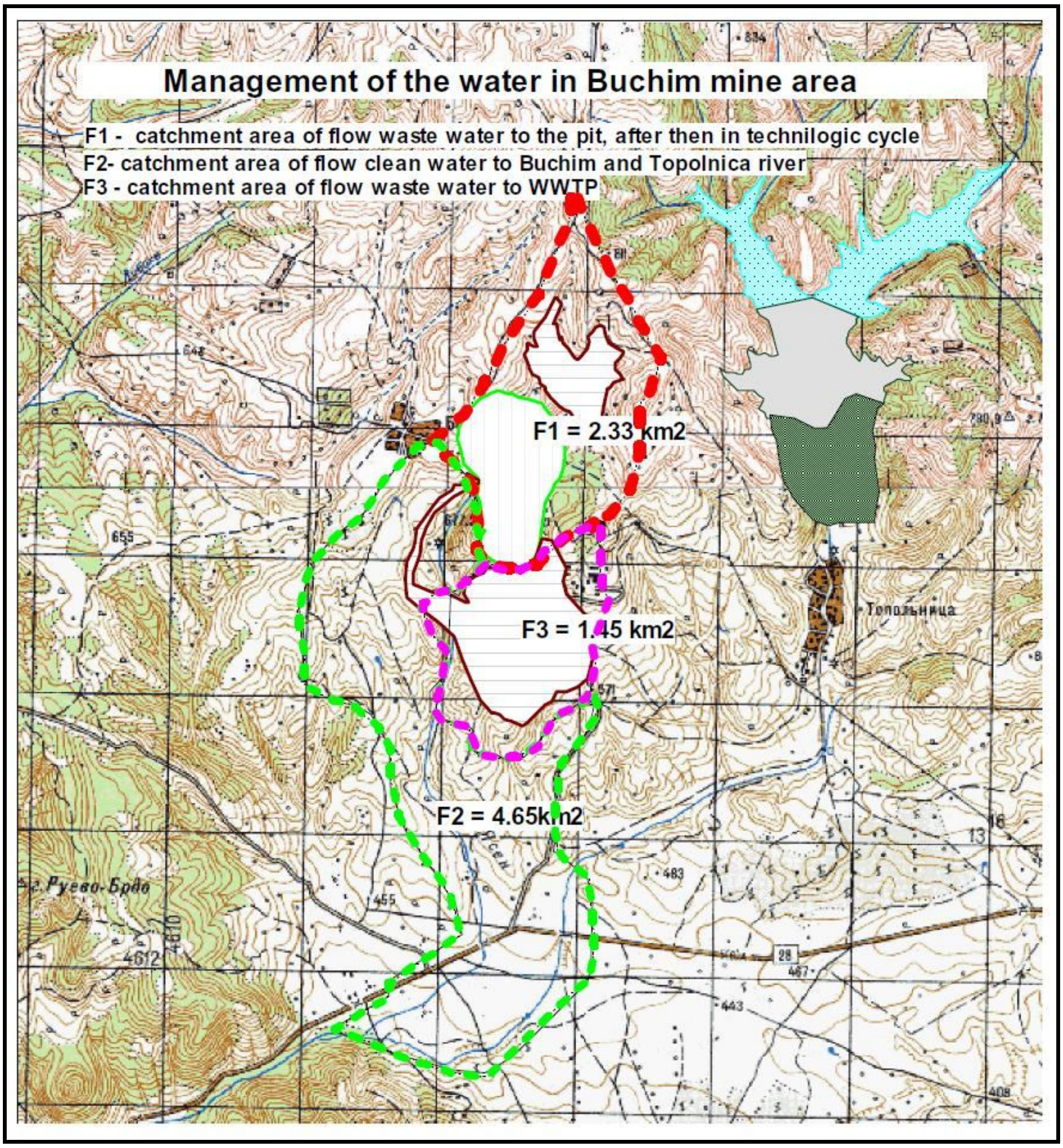

Fig. 6. Map of the Topolnica River catchment area (Buchim Dol and Jasenov Dol)

Hydrograph of the Topolnica River has been produced after one year monitoring (Figure 7).

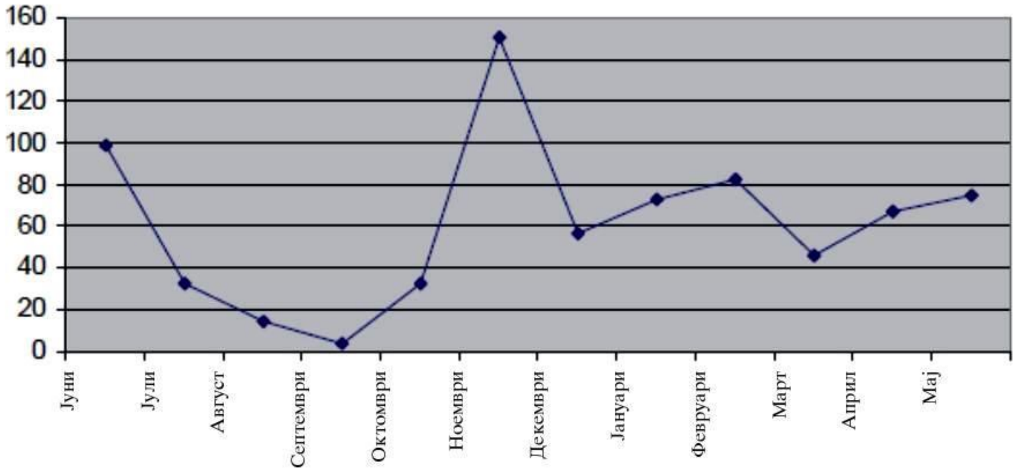

Fig. 7. Hydrograph of the Topolnica River

For this study were made measurements that have shown increased values for sulphate ions (SO_4^{2-}), which probably is due to presence of sulfide ores in mine waste dump and occurrence of so called sulphate bacteria (Thiobacilusferioxidans). This bacteria represents the most common bacteria found in mine wastes. Under certain conditions this acidophile aerobic bacteria increases the speed of oxidation of pyrite. Thiobacilusferioxidans oxidizes iron and inorganic sulfur compounds, which results in creation of sulfuric acid. This process and the presence of SO_4^{2-} point out to a possible local degardation of soil that have been in contact with waters.

- Madenska River- is forming from waters coming from Topolnica River and Jasenov Dol. The water flow of this river follows the regional road Radovis-Stip (Figure 8). It flows into the Kriva Lakavica river near the bridge on the road to Negotino. The Kriva Lakavica river is a tributary of the river Bregalnica. Waters of Topolnica river around 15 km downstream (under the name Madenska River) are flowing into the Bregalnica river, just before its mouth into the Vardar River.

Fig. 8. Madenska river

The Buchim company is monitoring the quality of these surface waters on a monthly basis, for more than 3 years (Figure 9). The analysis of water samples has been performed at the Faculty of science and mathematics in Skopje. That particular monitoring includes measurement of the following parameters: color, smell, temperature, pH, HPK, total dry residue, dissolved matter, suspended matter, $Cu^{2+,}$ Ag^+, NH_4^+, NO_3^-, NO_2^-, PO_4^{3-}.

According to the results of measurements made in 2010, significant deviations from MDK (maximal allowed values) were registered for PO_4^{3-}, pH and dissolved and suspended matters while slight deviations at incident level were registered for HPK and NO_3^-.

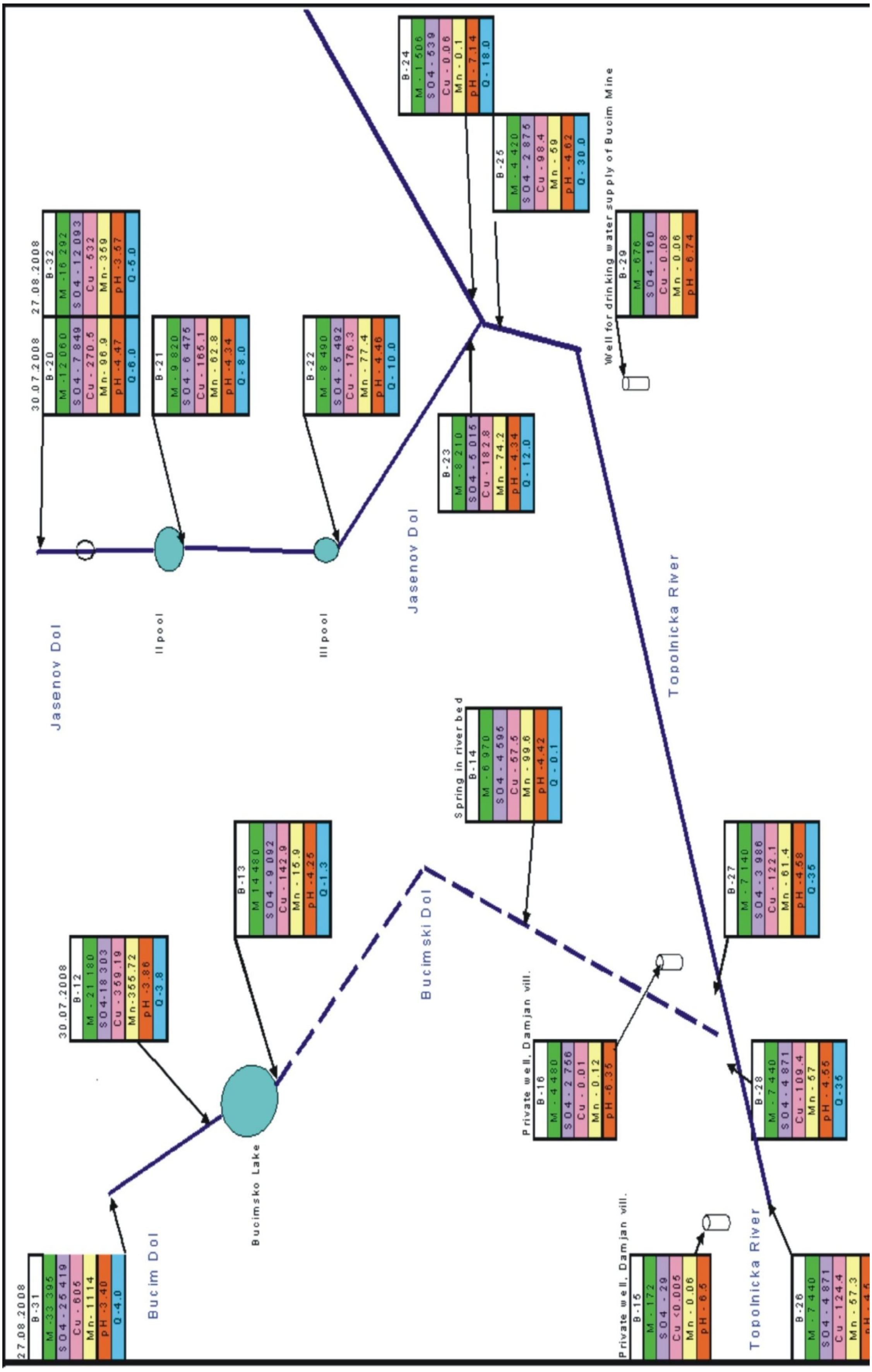

Fig. 9. Schematic review of monitoring spots of surface and ground water in the Topolnica river catchment area

In Table 1 are shown measured copper concentration values by months through 2010 in samples from the 5 sampling points.

Table 1. Copper concentrations in water samples from 5 monitoring points, around Buchim mine (in mg/L)

Month	Copper concentration (Cu^{2+}) at monitoring point (mg/l)					
	M1	**M2**	**M3**	**M4**	**M5**	**MDK**
1	0,01	45,6	61,7	364,5	0,01	0,05
2	0,01	0,96	19,4	147	0,01	0,05
3	<0,01	20,2	22,7	351,6	<0,01	0,05
4	<0,01	3,46	12,6	113,1	<0,01	0,05
5	<0,01	68,6	20,96	163	<0,01	0,05
6	<0,01	30,5	41,5	194,6	<0,01	0,05
7	<0,01	0,3	68	485	<0,01	0,05
8	<0,01	0,07	0,104	0,02	<0,01	0,05
9	<0,01	0,16	0,12	0,09	<0,01	0,05
10	<0,01	0,41	0,24	0,23	<0,01	0,05
11	<0,01	0,4	0,53	0,27	<0,01	0,05
12	<0,01	0,28	0,53	0,33	<0,01	0,05

As may be seen from the table above, the highest concentrations of copper were determined for the first seven months of 2010 (and earlier monitoring years) at monitoring points M2 (Topolnica River, under the bridge on the road Radovis-Stip, range 0.3÷68.6 mg/L Cu), M3 (Buchim Dol, outflow from Buchim Lake, range 12.6÷68 mg/L Cu), M4 (Jasenov Dol, outflow from the mine waste dump, range 113.1÷485 mg/L Cu). However, after the start of implementation of activities of the UNDP project, copper concentration values decreased almost instantly and below MDK values, which once again confirms the validity of activities applied (Figure 9).

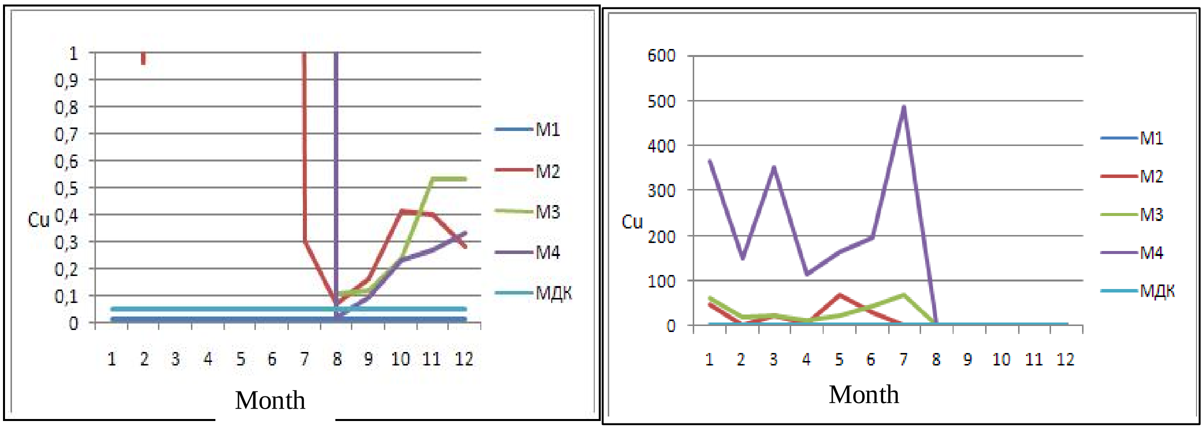

Fig. 9. Concentrations range of Cu_2^+ during the 2010 at monitoring points MM1-5, maximal (left) and minimal values (right)

Almost the same thing occurred with pH values in formerly mentioned hot spots, M2, M3 and M4, where it was noticed significant increase of values from acid ones to almost neutral ones (Figure 10).

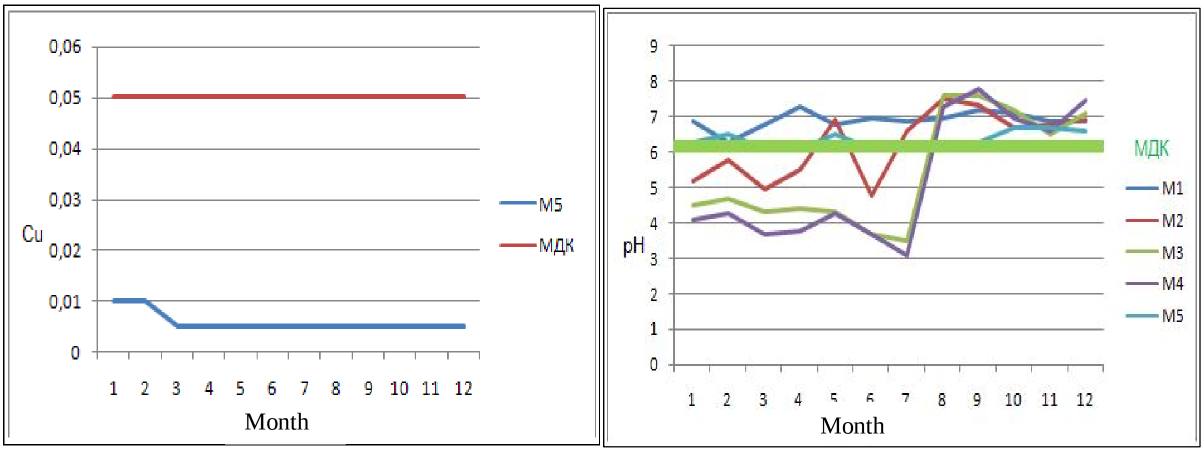

Fig. 10. Concentration range of Cu_2^+ during 2010 at monitoring point MM5 (left) and pH values at monitoring points M1-5 (right)

Also, as analyses have progressed we have noticed that copper concentrations at monitoring point M5 (water pumping station of the Buchim mine) have not experienced any significant changes in copper concentration due to UNDP project activities, which indicates that there is not any mentionable correlation between surface mine waters and waters feeding the pumping station reservoir (Figure 10).

Results and discussions related to theKrivaLakavica River

In order to monitor the impact of the work of the Buchim mine on the river Kriva Lakavica as recipient of wastewater from it, the Buchim company carries out regular monitoring of the quality of these waters (Figure 11). The monitoring is based on the monthly sampling of specimens from Kriva Lakavica river at 6 locations (VP) and specimens of groundwater at 4 locations (VI, sampling is performed from existing wells). Parameters that have been regularly monitored are: total dry residue at 105° C, total dry residue-filtrate at 105°C, suspended matter, copper, iron, HPK, SO_4, carbonate hardness and pH.

Fig. 11. Monitoring points ВП1 (left) and ВП2 (right), Kriva Lakavica river area

Copper concentrations, as part of those measurements, have been included in the Table 2, below.

Table 2. Copper values by month at each monitorig point (period 06.2010 – 12.2010)

Monitoring point	**Concentration of copper by month (mg/l)**						
	6	**7**	**8**	**9**	**10**	**11**	**12**
ВП1	1,9	0,2	0,01	0,013	0,6	2,6	0,91
ВП2	1,6	0,163	0,01	0,06	0,4	2	0,72
ВП3	0,02	0,031	0,01	0,06	0,033	0,013	0,023
ВП4	0,01	0,011	0,01	0,011	0,021	0,01	0,01
ВП5	0,046	0,011	0,01	0,007	0,013	0,01	0,012
ВП6	0,01	0,01	0,01	0,017	0,011	0,061	0,011
ВИ1	0,127	0,1	0,01	0,02	0,01	0,011	0,01
ВИ2	0,013	0,011	0,01	0,01	0,01	0,01	0,011
ВИ3	0,012	0,011	0,01	0,011	0,011	0,013	0,01
ВИ4	0,011	0,001	0,01	0,04	0,011	0,01	0,026
МДК (III)	**0,05**	**0,05**	**0,05**	**0,05**	**0,05**	**0,05**	**0,05**

As can be seen from the table above, the results

After certain period of few months, because of inadequate technical protection of the pipeline from the artificial dams (D1, D2) to the hydrotailling dam, temporary stoppage in the normal circulation of water through the system occurred. In that period, there was a water flow through the Jasenov Dol and ouflow from the Buchim Lake, which had its environmental impact to the waters of the Madenska River and Kriva Lakavica River (copper concentrtation values have "jumped sky high" once again). Those relations can be seen at Table 2 above, when during the last two months in 2010, when copper concentrations increased significantly (Figure 12).

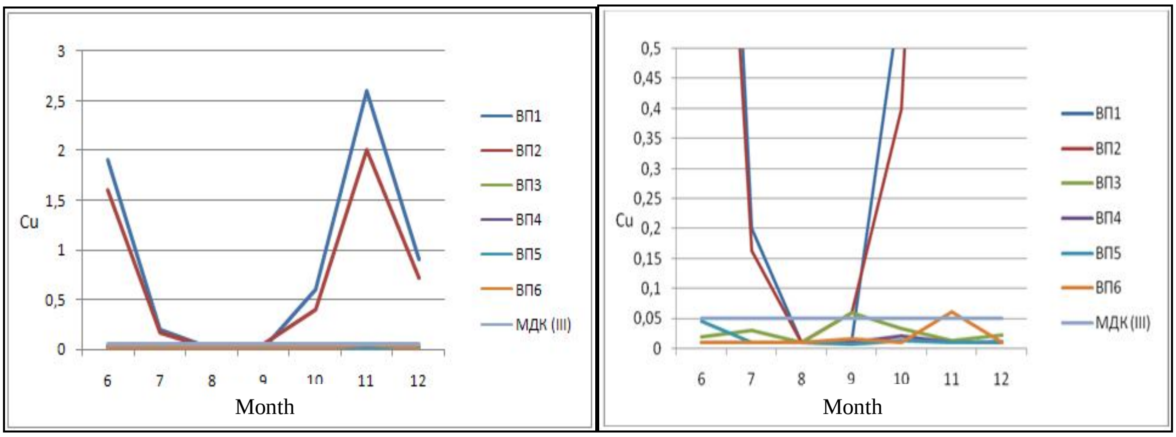

Fig. 12. Diagram of copper values in samples from surface waters, period 06.2010 – 12.2010, maximum values (left) and minimal values (right)

That very similar trend in concentrations was closely followed and matched by pH values in particular waters (running waters and ground waters), as have been shown in Table 3.

Table 3. pH values by month by monitoring point (period 06.2010 – 12.2010).

Monitoring point	pH values by month						
	6	**7**	**8**	**9**	**10**	**11**	**12**
ВП1	6,5	6,42	8,48	7,7	7,03	7,03	6,95
ВП2	6,59	6,22	8,17	7,1	8,05	7,02	6,97
ВП3	7	7,49	8,26	7,2	8,02	7,04	7,01
ВП4	7,4	7,06	8,51	7,6	8,03	6,99	7,03
ВП5	7,44	7,71	7,81	7,5	7,2	6,98	7,04
ВП6	6,99	7,88	8,05	7,4	6,05	7,01	6,99
ВИ1	6,31	6,37	7,87	6,7	7,1	6,97	7,03
ВИ2	6,1	6,41	8,08	6,9	6,2	6,99	7,99
ВИ3	6,82	6,34	7,72	6,8	7,01	6,97	6,98
ВИ4	7,03	6,38	8,15	7	7,05	7,02	7
МДК (III)	**6.0-6.3**						

As can be noticed, values of pH from range 6.1÷7.5 before the UNDP project activities went up to range 7.1÷8.5 after the initiation of the project and run back to 6.9÷7.5 during the malfunction of the system. This illustrative situation has been shown on the Figure 13, also.

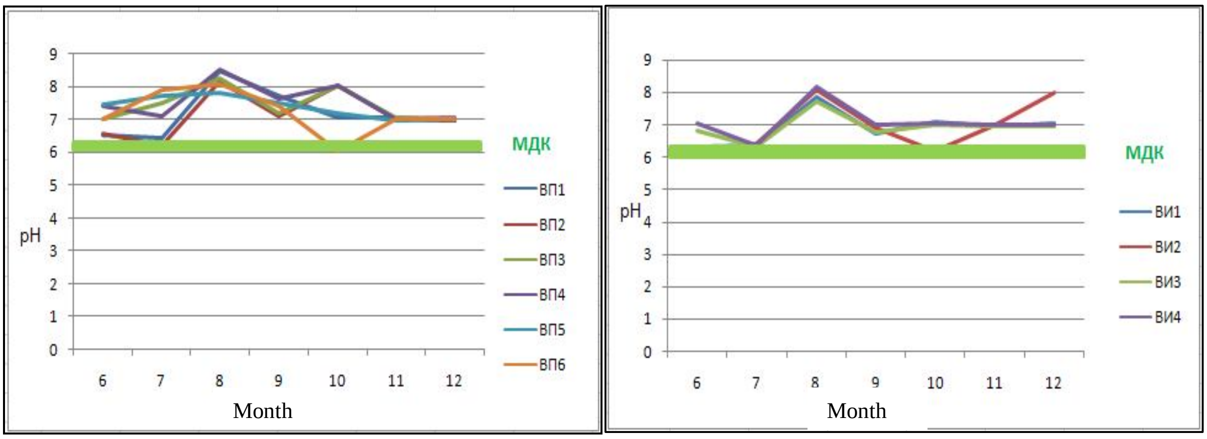

Fig. 13. Diagram of pH values by month during period 06.2010 – 12.2010, for samples from surface water (left) and groundwater (right)

However, after solving the technical difficulties of the system water transfer from the artificial dams D1, D2 to the hydrotailling was re-established, situation with waters along Kriva Lakavica River have improved significantly, which was confirmed with analyses performed in February, 2011. Present monitoring gives normal results without any deviant values in measured paramters of running and ground waters.

In general, the results of monitoring show exceeding the allowable values for the presence of copper and pH in surface water (class III) at monitoring locations closer to the mine. In accordance to the diagrams shown it has been observed trend of declining values in terms of time with high probability due to implementation of UNDP project activities for collection and diversion of contaminated waters into the hydrotailling dam.

Conclusion

According to the results from measurements, it is obvious that there is a significant decrease of values of measured parameters, starting from July, 2010, which came as a result of the getting into function of the system for capturing drainage water from the existing dump and disposal into the tailing dam. The decrease trend has been confirmed by results from measurements in February 2011, also. That means improvement of the quality of surface waters or more precisely increase of absorption capacity of the recipient water flows.

On the other side, data for the ground water quality (regular measurements of water from mine pump station and measurements within the UNDP Project) are pointing out to an insignificant or minimal influence of contaminated drainage waters from mine waste dump to ground water.

References

Alderton, D.H.M., Serafimovski, T., Mullen, B., Fairall, K.,James, S., 2005: The chemistry of waters associated withmetal mining in Macedonia, *Mine Water Environ.*,24,139-149.

Boev, B. and Lepitkova, S., 2005. Trace Elements in the Soils of Some Regions in the Republic of Macedonia.2nd Inter. Workshop on UNESCO-IGCP Project Anthropogenic effects on the human environment in Tertiary basins in the Mediterranean, Ljubljana 2005 pp. 11-15.

Balabanova, B., Stafilov, T., Bačeva, K. andŠajn, R., 2009. Atmospheric pollution with copper around the copper mine and flotation, Bučim, Republic of Macedonia, using biomonitoring moss and lichen technique. GeologicaMacedonica, Vol. 23, pp. 35–41

Bermanec, V., Žigovečki, Ž.,Tomašić, N., Palinkaš, L. A., Kniewald, G.and Serafimovski, T., (2005). Stream sediment mineralogy as indicator of environmental impact of copper deposits exploitation in Buchim, Macedonia. 3rd International Workshop on the UNESCO-IGCP Project: Anthropogenic effects on the human environment in Tertiary basins in the Mediterranean, Stip, 21st October 2005, pp. 87-90.

Evangelou V. P. (1995) Pyrite Oxidation and its Control: Solution Chemistry, Surface Chemistry, Acid Mine Drainage (AMD), Molecular Oxidation Mechanisms, Microbial Role, Kinetics, Control, Ameliorates and Limitations, Microencapsulation. CRC Press, Boca Raton, FL.

Evangelou V. P. and Zhang Y. L. (1995) A review: pyrite oxidation mechanisms and acid mine drainage prevention. Crit. Rev. Environ. Sci. Technol. 25(2), 141–199.

ICOLD (1996) A Guide to Tailings Dams and Impoundments: Design, Construction, Use and Rehabilitation. International Commission on Large Dams, Bulletin (United Nations Environment Programme) no. 106, 239pp.

Lowson R. T. (1982) Aqueous oxidation of pyrite by molecular oxygen. Chem. Rev. 82, 461–497.

Михајлов, М., Сидеровски, К., Стафилов, Т и Серафимовски, Т., 2011. Студија за оцена на влијанието врз животната средина. Стручен фонд на ДПТУ Бучим – Радовиш. 171 стр.

Nordstrom D. K. and Southam G. (1997) Geomicrobiology of sulfide mineral oxidation. In Geomicrobiology: Interactions between Microbes and Minerals (eds. J. F. Banfield and

K. H. Nealson). Mineralogical Society of America, Washington, DC, vol. 35, pp. 361–385.

Nordstrom D. K. and Alpers C. N. (1999a) Geochemistry of acid mine waters. In The Environmental Geochemistry of Mineral Deposits (eds. G. S. Plumlee and M. J. Logsdon). Society of Economic Geologists Inc., Littleton, DC, vol. 6A, pp. 133–157.

Ritchie A. I. M. (1994) Sulfide oxidation mechanisms: controls and rates of oxygen transport. In The Environmental Geochemistry of Sulfide Mine-wastes (eds. J. L. Jambor, and D. W. Blowes). Mineralogical Association of Canada, Nepean, ON, vol. 22, pp. 201–246.

Serafimovski, T., Alderton, D.H.M., Mullen, B., and Fairall, K., 2004: Pollution Associated With Metal Mining in Macedonia. 32nd International Geological Congress, Florence, Italy, Scientific Sessions: abstracts (part 1) - 362.

Serafimovski, T., Alderton, H. M. D., Dolenec, T., Tasev, G.,Dolenec, M., 2005a: Metal pollution around the BučimMine; 3rd International Workshop on the UNESCO-IGCPProject: Anthropogenic effects on the human environmentin tertiary basins in the Mediterranean, Štip, 36–56.

Serafimovski, T., Alderton, H. M. D., Dolenec, T., Tasev, G., and Dolenec. M., 2005b: Heavy metals in sediments and soils around the Bucim copper mine area.*Geologica Macedonica,* Stip. Volume 19, pp. 69-81.

Stafilov, T., Balabanova, B., Šajn, R.,Bačeva, K. and Boev, B., 2010.Geochemical Atlas of Radoviš and the environs and the distribution of heavy metals in the air.Facullty of Natural Sciences and Mathematics-Skopje; Faculty of Natural and Technical Sciences-Štip and Faculty of Agriculture-Štip.88 p.

Turekian, K.K., (ex.ed.) 2003. Treatise on Geochemistry, Ten Volume Set, Volume 1-10, 5155 p.

SPATIAL DISTRIBUTION OF K,Th AND U ELEMENTAL CONCENTRATION IN SOILS OF THE REPUBLIC OF MACEDONIA

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Abstract

In order to establish a startup database of the natural radioactivity in the Republic of Macedonia (area of 25713 km^2), the elemental concentrations of K, U and Th in the surface soil were determined using high-resolution gamma spectrometry. A total number of 213 soil samples were collected during the period 2008-2009 from the entire territory of the country. The K elemental concentrations were found to be normally distributed with arithmetic mean value of 1.87 %, ranging from 0.26 to 4.44 %. The results for U and Th elemental concentrations were found to be log-normally distributed with geometric mean values 3.08 and 9.29 ppm, and arithmetic means 3.36 (varying from 0.74 to 8.99 ppm) and 10.16 ppm (from 1.6 to 35.77 ppm), respectively. The geometric mean values of the ratios Th/U, K/U and K/Th were found to be: 3.12, 0.61 and 0.20, respectively. The results were compared to the results of the studies from other countries.

Key words: Soil, Potassium, Uranium, Thorium, Gamma spectrometry

Introduction

Radionuclides have been an essential constituent of the Earth since its creation. It has been observed that most of the natural radioactive elements in the soil are primordial radionuclides from the uranium series, thorium series and ^{40}K. The activity concentration of these radionuclides is related to the composition of each lithologically separated area, as well as to the content of the rocks from which the soils originate[1]. However, the differences in the natural radioactivity of soil are closely correlated to their geological origin[2,3]. It has been reported that the higher levels of natural radiation in any area in the world could be associated with volcanic rock, whereas the lower levels to sedimentary rock, with some exceptions [4,5]. On the other hand, the human exposure to natural radiation and the impact of the radiation on the human health are very important issues for any country, since the primordial radionuclides present in soil significantly affect the terrestrial gamma radiation levels. Therefore, measurements of the natural radioactivity in the soil have been performed worldwide, such as the up-to-date investigations in Turkey[6,8], India[7] and Rep. of Srpska[9].

There are no systematic data on this subject available for the Republic of Macedonia. The three previous studies that were found in the open literature were: the first and the second being local studies, pertaining to small parts of the country[10,11], and the third one covering the entire territory, but based on a limited number of samples[12]. In this paper, we present the results of the first systematic study of the K, Th and U elemental concentrations in the surface soil samples taken from all over the country. The study focuses on identification of the differences among the diverse regions. The outcome will be used to establish a baseline map for that area as a reference data to assess any possible changes in

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radioactivity background level due to nuclear, industrial and other human activities in the future.

Study Area

The Republic of Macedonia is a South Eastern European country which is situated in the central Balkan Peninsula on 25713 km^2 area. From geological point of view, the country consists of four geotectonic zones: Western Macedonian zone, Pelagonian massif, Vardar zone and Serbo-Macedonian massif. Between the Vardar zone and the Serbo-Macedonian massif there is a separate area of volcanic rocks, named Kratovsko-Zletovska area [13]. All the aforementioned zones are represented in Fig. 1.

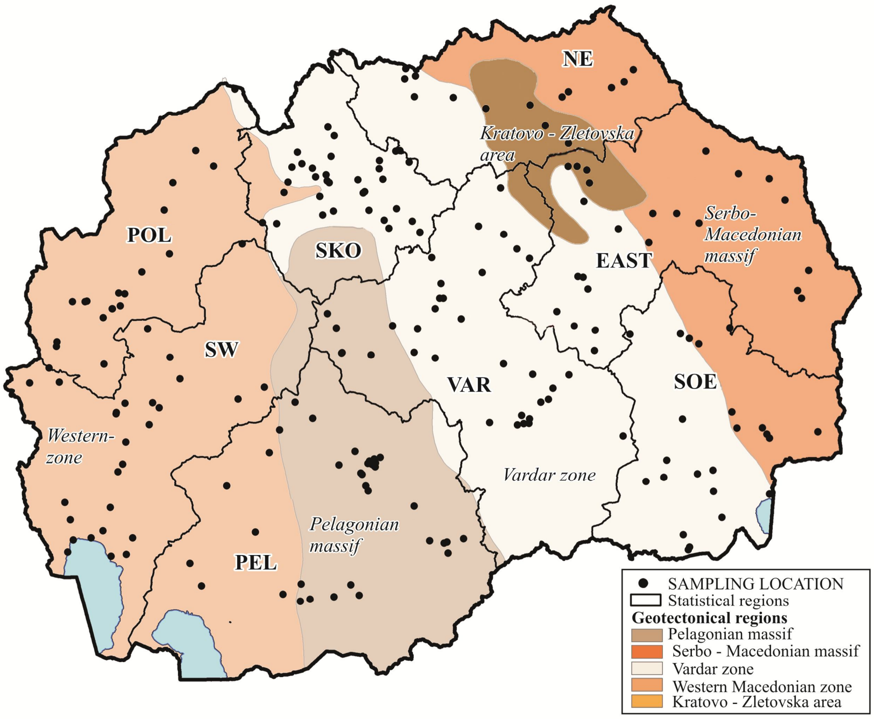


Fig. 1. Map of the sampling spots (dots); 8 Statistical regions (divided by black borderlines); 4 geotectonic zones and one geotectonic area (presented by different shading tones).

The geotectonic zones are characterized by their own geological evolution. The bedrock complexes (magmatic, sedimentary and metamorphic rocks) are different due to the various ages of genesis: from Precambrian to Cenozoic. For the convenience of the data and results presentation, as well as for the needs of future estimation of population exposure and epidemiological studies, a division of the country in 8 statistical regions has been adopted. The statistical regions are: Polog (POL), Southwest (SOW), Pelagonia (PEL), Skopje (SKO), Vardar (VAR), Northeast (NOE), East (EAS) and Southeast (SOE), as presented with black dividing borders in Fig. 1.

Experimental procedure

Sampling and Sample Preparation

A total number of 213 surface soils on 20 cm depth[14] were collected from the sampling locations within the study areas shown in Figure 1, during the period of 2008-2010. The greater part of the impurities, such as stones, pebbles and organic materials was removed from the samples. The samples were than dried, sieved and set in a standard Marinelli beaker of 500 cm^3 to be ready for gamma spectrometry measurements.

Radioactivity Measurements

The gamma spectrometry measurements were carried out with a p-type HPGe detector (Canberra Inc.; 25% relative efficiency, resolution of 1.79 keV at 1.33 MeV, 8192 ch. digital analyser) and software GENIE 2000 for the spectrum evaluation. The efficiency calibration was done with a mixed calibration source (MBSS 2) from the Czech Metrological Institute with same geometry as the one used for the soil samples.

The purpose of the gamma spectrometry measurements was to determine the activity of each of the following radionucleides: ^{40}K, ^{232}Th, ^{238}U. The activity of ^{40}K was determined from the 1460 keV line, whereas the activity of ^{232}Th from the gamma lines of ^{228}Ac (338.32 keV, 911.2 keV, 968.97 keV), ^{208}Tl (583.19 keV) and finally, the activity of ^{238}U was determined from the gamma lines of ^{234}Th (63.28 keV) and ^{234m}Pa (1001.03 keV) [15]. The analysis procedure included subtraction of the background spectrum, correction for interfering lines and correction for self absorption. The verification of the method was performed with two reference materials from the International Atomic Energy Agency, IAEA-385 and PT IAEA-CU-2009-03 proficiency test. The total relative combined uncertainty of each nuclide was: for ^{238}U (≈ 15%) and for ^{232}Th and ^{40}K < 5%, at the 68% confidence level.

The specific activities of ^{238}U, ^{232}Th and ^{40}K (in Bq kg^{-1}) were converted to potassium, uranium and thorium elemental concentrations, respectively, according to the following equations[16]:

$$\begin{aligned} &1\%\ (\mathrm{K}) = 313\ \mathrm{Bq\ kg^{-1}}\ (^{40}\mathrm{K}) \\ &1\mathrm{ppm}\ (\mathrm{U}) = 12{,}35\ \mathrm{Bq\ kg^{-1}}\ (^{238}\mathrm{U}),\ \text{and} \\ &1\mathrm{ppm}\ (\mathrm{Th}) = 4{,}06\ \mathrm{Bq\ kg^{-1}}\ (^{232}\mathrm{Th}) \end{aligned} \qquad (1)$$

The results of U and Th are reported in ppm (parts per million), whereas the activity of potassium is reported in % K because of its presence in the environment along with its stable counterparts.

Results and discussion

Utilizing the specific activity of the gamma spectrometry measurements, the K, U, and Th elemental concentrations were determined using equation (1) for all the 213 soil samples from the study area. The statistics of these results is presented in Table 1, whereas the histograms are shown in Fig.2.

Table 1. Statistical data for elemental concentrations in all 213 analyzed soil samples

Statistical data	K(%)	U(ppm)	Th(ppm)
No. of observations	213	213	213
Minimum concentration	0.26	0.74	1.60
Maximum concentration	4.44	8.99	35.8
Median concentration	1.87	3.18	9.54
Arithmetic mean concentration	1.87	3.36	10.2
Standard deviation	0.61	1.38	4.42
Standard error of the mean	0.04	0.09	0.30
Geometric mean concentration	1.76	3.08	9.29
Geometric standard deviation	1.47	1.53	1.55

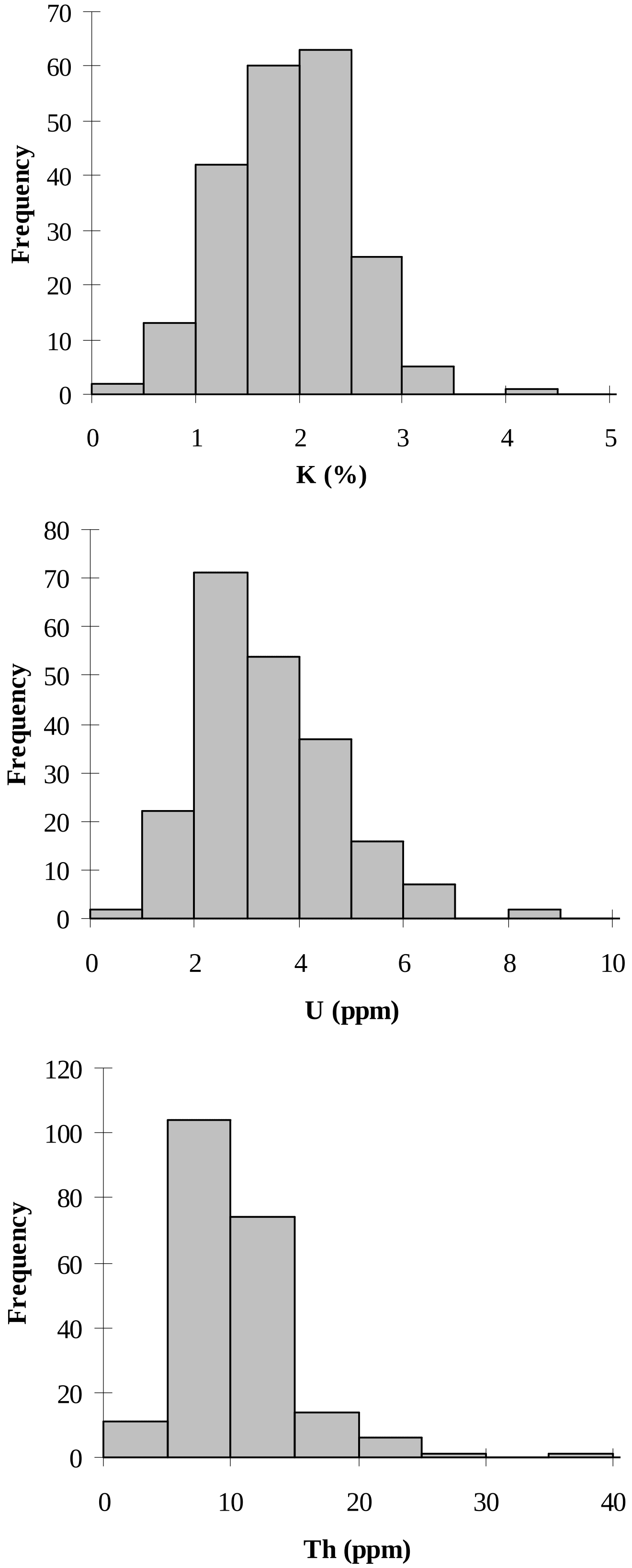


Fig. 2. Frequency distribution of K, U and Th elemental concentrations in the surface soil

The frequency distributions were found to be normal for the K elemental concentrations, though the results for U and Th were found to follow the log-normal distribution (χ^2, Kolmogorov-Smirnov test, $p<0.05$). The statistical analyses for U and Th were performed only for the log transformed values, since the log transformation reduces the influence of extreme values[17].

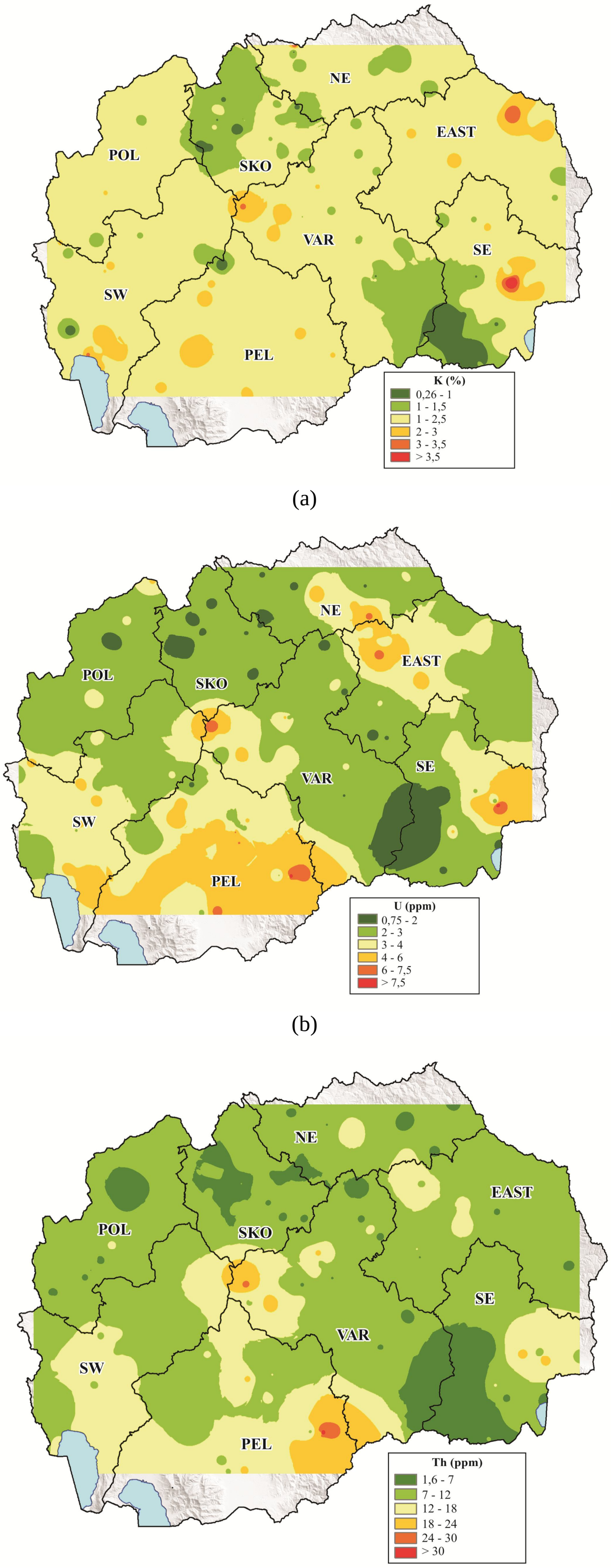
Taking into account the geological diversity of the area and the fact that the K, U and Th elemental concentrations depend on the composition of each lithologically separated area, as well as from their content in the rocks from which the soils originate, differences between regions were expected to occur. Table 2 shows a summary of the arithmetic mean values and the standard deviation of the K (%), U (ppm), Th (ppm), as well as the geometric mean and geometric standard deviation of the U (ppm), Th (ppm) concentrations for each of the eight statistical regions.

Table 2. K, U and Th elemental concentrations in soils from different statistical regions

		K (%)		U (ppm)				Th (ppm)			
Region	No.	AM	SD	AM	SD	GM	GSD	AM	SD	GM	GSD
SW	34	2.07	0.61	3.78	0.91	3.66	1.30	11.3	2.60	11.0	1.27
SE	20	1.75	0.94	3.22	2.05	2.58	2.04	8.81	5.96	6.69	2.26
VAR	26	1.88	0.57	3.25	1.13	3.09	1.38	11.3	5.19	10.3	1.52
EAST	30	1.94	0.48	3.28	1.11	3.10	1.42	9.62	2.79	9.21	1.36
PEL	38	2.07	0.46	4.43	1.44	4.20	1.40	13.5	5.27	12.8	1.38
POL	19	1.97	0.42	2.84	0.79	2.73	1.35	7.87	2.19	7.58	1.32
NE	14	1.78	0.65	3.14	1.41	2.87	1.54	8.97	3.05	8.52	1.39
SKO	32	1.41	0.44	2.28	0.56	2.20	1.33	7.34	1.77	7.13	1.29

The analysis of variance showed that the differences among the mean values of K, U and Th elemental concentrations for the eight statistical regions are statistically significant (ANOVA, $p = 0.0002$). In addition, the Fisher's LSD-test applied for evaluation of the differences among the mean values, showed that the lowest arithmetic mean value of the K elemental concentration (1.41 %) was found for the Skopje statistical region (LSD, $p < 0.0001$). The later result could be related to the fact that Skopje region belongs to the geotectonic Vardar zone, which is composed of different geological units. But, the area of Skopje is mainly composed of Neogene–Quaternary sediments, mainly by clay and sandstone[18].

On the other hand, the highest arithmetic mean value (4.43ppm) and geometric mean value (4.20 ppm) of U elemental concentration were found for Pelagonija (PEL) statistical region (LSD, $p < 0.0001$). This result was expected, since this region belongs to the Pelagonija Massif which is dominantly composed of granite and metamorphic rocks of the Precambrian period [19].The results of the Fisher's LSD test showed that the lowest U concentration (GM = 2.20 ppm) was found for Skopje region (LSD, $p < 0.0001$). Similar distribution among the statistical regions was found for the Th elemental concentration. The highest average elemental concentration (GM=12.77 ppm) was found for Pelagonija and the lower elemental concentrations: 6.69 ppm, 7.13 ppm and 7.58 ppm were found for Southeast, Skopje and Polog statistical regions, respectively. To visualize the differences among the statistical regions, the interpolated maps of the K, U, Th elemental concentrations were created (Fig. 3). Furthermore, as the K, U and Th elemental concentrations were grouped by geotectonic zones, the differences revealed to be statistically significant (ANOVA, $p<0.0001$).



(a)

(b)

(c)

Fig. 3. Interpolated map of: (a) K, (b) U and (c) Th elemental concentration.

Hence, the lowest K elemental concentration was found for the Vardar zone (LSD, $p<0.0001$), whilst the values for the other zones comprised one single group. The results showed that the U and Th elemental concentrations in the Pelagonija massif and the Kratovsko-Zletovska area are significantly higher in comparison to other geotectonic zones (LSD, $p<0.0001$). The results of the arithmetic mean values of U and Th elemental concentrations in the soils from Kratovsko-Zletovska area (4.65ppm and 13.06ppm, respectively) turned to be very similar to those of the Pelagonija Massif (4.45ppm and 14.63ppm, respectively) but significantly higher than those of other geotectonic zones.

According to the UNSCEAR 2000 report[4]., the world mean value of U and Th elemental concentrations in soils ranges from 1.3 to 8.9ppm and from 2.7 to 15.8ppm, with average global value of 2.8 ppm and 7.4 ppm, respectively. If we compare the FYR of Macedonia's average values of U (3.36ppm) and Th (10.16ppm) elemental concentrations to the average world values, one would conclude that the values are somewhat higher than the world mean, but at the same time, they are in the reported range of values. The same document reports that the global average K elemental concentration is 1.3%, which is lower than the average value obtained in this study (1.87%). Additionally, the idea was to compare the obtained results with the results of studies of some other countries. For example, from the investigations made in Cyprus, for 115 soil samples taken from the different lithological units, the arithmetic mean values of K, U and Th elemental concentrations are found to be: 0.4%, 0.6 ppm and 1.2 ppm respectively[1]. For Provincia dell Aquila (Central Italy), the corresponding values are: 0.88%, 1.97ppm and 10.1ppm for K, U and Th respectively[20]. There is a great similarity between the results of this study and the results from the Republic of Serbia, where the K, U and Th elemental concentrations were reported to be: 1.98 (0.88-2.99) %, 2.76 (1.2-6.24) ppm and 10.4 (4.45-21) ppm, respectively [21]. The comparison of the results is presented in Table 3.

Table 3 Comparison of the results of K, U and Th elemental concentrations in soils of R of Macedonia with results of some other countries

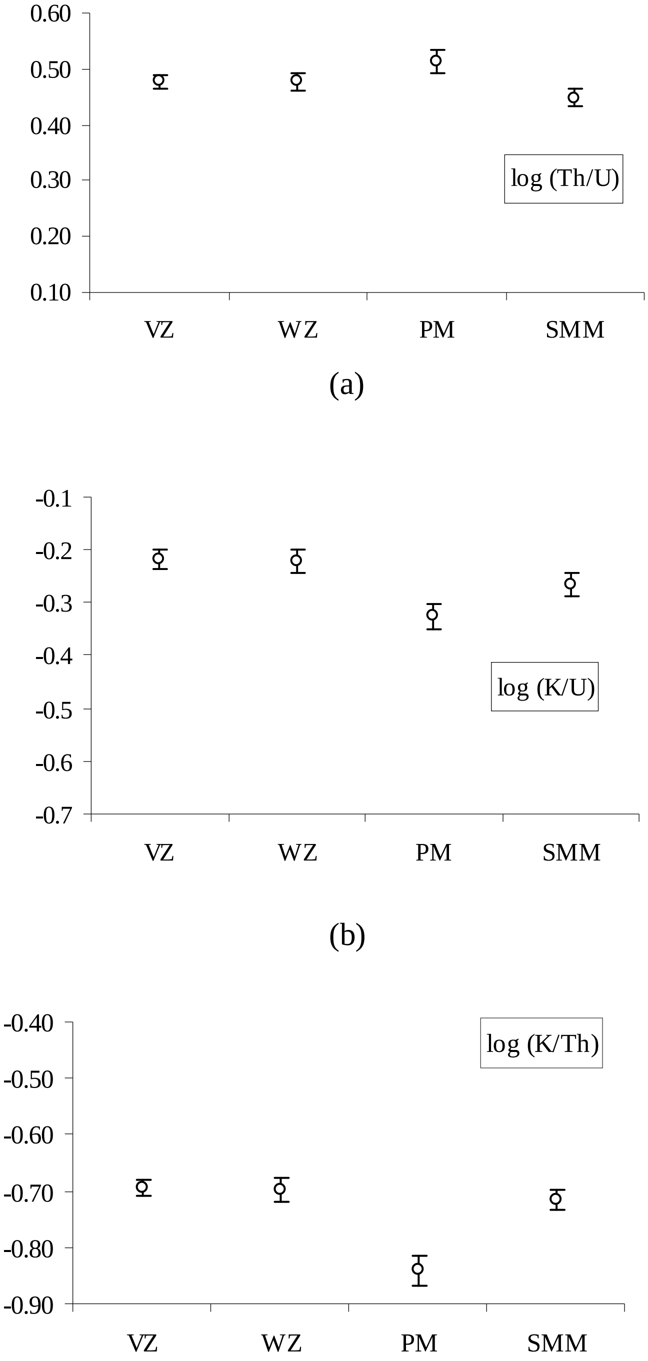
Region/country	K(%)	U(ppm)	Th(ppm)	Reference
FYR of Macedonia	1.87 (0.26-4.44)	3.08 (0.74-8.99)	9.29 (1.6-35.8)	Present study
Provincia dell Aquila (Central Italy),	0.88 (0.047-1.86)	1.97(0.41-5.7)	10.1 (0.36-58)	[20]
Sebia and Montenegro	1.98 (0.88-2.99)	2.76(1.2-6.24)	10.4 (1.45-21.0)	[21]
Cyprus	0.4 (0.0001-1.9)	0.6 (0.0008-3.2)	1.2 (0.003-9.8)	[1]
World average	1.34 (0.45-2.72)	2.80 (1.30 -8.91)	7.39 (2.71-15.8)	[4]

In order to identify the relative depletion or enrichment of the investigated radionuclides in the surface soil, the correlations between K, U and Th elemental concentrations were studied by means of Pearson correlation coefficient as a measure of the linear dependence. The highest correlation, $R = 0.78$, was found between the Th and U elemental concentrations. Lower correlations appeared for K versus U ($R = 0.56$) and for K versus Th ($R = 0.59$). Furthermore, the following ratios between the concentrations: Th/U, K/U, K/Th in the surface soil were determined. The results for the ratios in this study were distributed within a wide interval of values which followed the log normal distribution (χ^2 and Kolmogorov-Smirnov test, $p < 0.05$).

The geometric mean value of the ratio Th/U was 3.01 (with geometric standard deviation of 1.30), with individual values distributed in the interval from 1.38 to 7.75. Hence, the obtained mean value is matching the theoretical value for normal continental soils (3.0)[1]. This ratio is comparable to the values of 2.93 and 2.88 reported for Jordan, obtained for soil of sediment and volcanic origin, respectively [21] and 3.89 reported for Serbia and Montenegro[21]. For the ratios K/U and K/Th elemental concentrations it was derived: 0.57 (0.16–1.44) and

0.19 (0.05–0.59), respectively. The values for the aforementioned ratios for Serbia were 0.76 and 0.50, respectively[21].

For further elucidation, the ratios Th/U, K/U and K/Th, grouped in 4 different geotectonic zones, were analyzed and compared. The ANOVA test indicated that Th/U ratio was not significantly different among the zones (p = 0.115) (Fig. 4a).



(a)

(b)

(c)

Fig. 4. Arithmetic mean values and 95 % LSD intervals of the (a) log (Th/U), (b) log (K/U) (c) log (K/Th) within the geotectonic zones: Vardar zone (VZ), Western zone (WZ), Pelagonian massif (PM) and Serbo-Macedonian Massif (SMM).

However it indicated significant differences for the K/U and K/Th ratios ($p < 0.05$). The K/U and K/Th ratios in the Pelagonian Massif (PM) were significantly lower in comparison to those of the other three geological groups (LSD, $p = 0.006$ and $p < 0.0001$, respectively), which is presented in Fig. 4b and 4c. For comparison, lower K/U and K/Th ratios in soils from volcanic origin have also been reported for soils in Jordan[22].

Conclusion

The K, U and Th elemental concentrations were determined for 213 samples of surface soil taken from the entire area, subject to this research (Republic of Macedonia). After the statistical processing of the results, the arithmetic mean values (± standard deviation) of the elemental concentrations for all samples were found to be (1.87 ± 0.61) % for K, (3.4 ± 1.4) ppm for U and (10.2 ± 4.4) ppm for Th. Taking into account the log-normal distribution of the U and Th results, the corresponding geometric mean values were found to be 3.1 ppm and 9.3 ppm, respectively.

From the statistical analysis, significant differences among the values for different regions and geotectonic zones were found. The higher values for U and Th elemental concentrations were related to soils of volcanic origin, whereas the lower values were associated to soils of sedimentary origin. From the analysis of the Th/U, K/U and K/Th ratios, it was evident that only the values for K/U and K/Th are correlated to the geology, whereas their statistically significant lower values were related to the soils of volcanic origin.

References

[1] Tzortzis, M., Tsertos, H. Determination of thorium, uranium and potassium elemental concentrations in surface soils in Cyprus. J. Environ. Radioact., **2004,** 77, 325-338.

[2] UNSCEAR Report. Sources and effects of ionizing radiation. United Nations Scientific Committee on the New York. **1993.**

[3] Chiozzi, P., Pascale, V., Verdoya, M. Naturally occurring radioactivity at the Alps-Apennines transition. Radiat. Meas. **2002,** 35, 147-154.

[4] UNSCEAR Report. Sources and effects of ionizing radiation. United Nations Scientific Committee on the New York. **2000.**

[5] Rani, A., and Singh, S. Natural radioactivity levels in soil samples from some areas of Himachal Pradesh, India using γ-ray spectrometry. Atmospheric Environment **2005,** 39(34), 6306-6314.

[6] Baykara, O., Doğru, M. Determination of terrestrial gamma, ^{238}U, ^{232}Th and ^{40}K in soil along fracture zones. Radiat. Meas. **2009,** 44,116-121.

[7] Singh, J., Singh H., Singh S., Bajwa B.S., Sonkawade R.G. Comparative study of natural radioactivity levels in soil samples from the Upper Siwaliks and Punjab, India using gamma-ray spectrometry. J. Environ. Radioact. **2009,** 100(1), 94-98.

[8] Taskin, H., Karavus, M., Ay, P., Topuzoglu, A., Hidiroglu, S., Karahan, G. Radionuclide concentrations in soil and lifetime cancer risk due to gamma radioactivity in Kirklareli, Turkey .J. Environ. Radioact. **2009,** 100, 49-53.

[9] Janković, M., Todorović, D., Savanović, M. Radioactivity measurements in soil samples collected in the Republic of Srpska Radiat. Meas. **2008,** 43(8), 1448-1452.

[10] Dimovska, S., Stafilov, T., Šajn, R., Frontasyeva, M. Distribution of some natural and man-made radionuclides in soil from the city of Veles (Republic of Macedonia) and its environs. Radiat Prot Dosimetry, **2010,** 138(2): 144-157.

[11] Dimovska, S., Stafilov, T., Šajn, R. Radioactivity in soil from the city of Kavadarci (Republic of Macedonia) and its environs. Radiat Prot Dosimetry, **2011,** doi:10.1093/rpd/ncq601.

[12] Stojanovska, Z., and Nedelkovski, D. Initial investigation of the natural radioactivity in the soil in some locations in Macedonia from radiation protection point of view. Physica Macedonica, **2008,** 58, 67-74.

[13] Arsovski, M., Dumurdžanov, N. Alpine Tectonic Evolution of the Vardar Zone and its Place in the Balkan Region. Geologica. Macedonica, **2005,** 9, 15–22.

[14] ISO 18589-3. Measurement of radioactivity in the environment-Soil-Measurement of gamma-emitting radionuclides. **2007.**

[15] ISO 18589-2. Measurement of radioactivity in the environment-Soil-Guidance for the selection of the sampling strategy, sampling and pre-treatment of samples. **2007.**

[16] IAEA-TECDOC-1363. Guidelines for radioelement mapping using gamma ray spectrometry data. IAEA. **2003.**

[17] Bossew, P., Lettner H. Investigations on indoor radon in Austria, Part 2: Geological classes as categorical external drift for spatial modeling of Radon potential. J. Environ. Radioact. **2008,** 99, 81-97.

[18] Karamata, S. Geological Evolution of Our Area Since Triassic Until Quaternary. Institute for Geologic Investigations of Nuclear and Other Mineral Resources, Belgrade, Proceedings, **1975,** 10, 1–15.

[19] Dimitrijević, M. The Serbo-Macedonian Massif. Tectonic of the Carpathian-Balkan Regions, Geological Institute Dyoniz Stur. **1974,** 291–296.

[20] Bellotti, E., Di Carlo, G., Di Sabatino, D., Ferrari, N., Laubenstein, M., Pandolaand, L., Tomei, C. γ-ray spectrometry of soil samples from the Provincia dell'Aquila (Central Italy). Appl. Radiat. Isot. **2007,** 65(7), 858-86.

[21] Dragović, S., Janković, Lj., Onjia, A., Bačić, G. Distribution of primordial radionuclides in surface soils from Serbia and Montenegro. Radiat. Meas. **2006,** 41(5), 611-616.

[22] Al-Hamarneh, F.I., Awadallah I.M. Soil radioactivity levels and radiation hazard assessment in the highlands of northern Jordan. Radiat. Meas. **2009,** 44, 102-110.

AIR POLLUTANTS EMISSION ESTIMATION FROM MINING INDUSTRY IN MACEDONIA

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Abstract

This paper presents air pollutants (particles and gaseous) emissions estimation from extraction and concentration processes of raw mineral materials (commonly referred as mining industry). Emissions estimations are based on extensive analysis of each specific site including production rates, equipment and processes used as much as type of material processed. Data for national mining industry are based on 2010 unofficial reports (obtained through authors direct research), and are compiled as per CORINAIR (CLRTAP) reporting requirements. Methodologies and results are discussed below.

Introduction

Emission estimations and creation of polluters inventory is first step for proper planning of protection measures, as much as requirements from international agreements signed by our government. Having this in mind and as a part of wider National reporting activities taken by MOEPP and different subcontractors of the specific project, an extensive efforts for inventory of mining operations and estimation of associated emissions were taken during the 2010.

Due to each mine/quarry unique characteristics and based on intensity and type of activities/processes involved, a different methodologies for emission estimations are applied, including:

- ✓ Guidelines for CLRTAP Emission Inventories 2001 - ETC ACC (Group 05).
- ✓ US EPA (1998), Compilation of Air Pollutant Emission Factors, AP-42, Fourth Edition, United States Environmental Protection Agency.
- ✓ NATIONAL POLLUTANT INVENTORY GUIDE, 2004 Version 3.1, Australian Government, Department of Environment and Heritage.

Based on methodologies requirements, the emission inventory compiled includes all operations (active in 2010) at the national level, involved in some form of extraction and primary processing of raw mineral materials. Based on type of minerals involved, and according to industry standards all operation are classified in four major groups, as follow:

- Extraction and processing of energy minerals
- Extraction and processing of hard rock metallic minerals
- Extraction and processing of aggregates
- Extraction and processing industrial minerals

The inventory does not include sand and gravel operations as much as dimensioned stone quarries, where due to specific technologies and usual low intensity of activities, air pollutants emission are quite limited and of now importance at local or national level. Due to similar reasons underground mining operations are also omitted.

Emission sources and air pollutants of interest

Using the same approach, common emission sources could be divided in two distinctive groups, emissions from raw mineral extraction processes and emissions from primary processing activities.

During the extraction processes common air pollutants include particulate matters (TSP and PM 10) and following gaseous substances CO, NO_x, SO_x and VOC_s, usually associated with following activities;

- blasting,
- material transportation and handling,
- vehicle exhaust emissions.

Pollutants of interest from primary processing activities are dominated by particulate matters (TSP and PM 10) and in many smaller rates gaseous substances including CO, NO_x, SO_x and VOC_s, associated with following activities;

- crushing
- grinding
- classification
- material transportation and handling

Processes of material destruction and natural disintegration, especially for energy minerals (oxidation, self-burning…) could result with greenhouse gasses emissions including methane, ethane and propane.

Largest part of this emissions could are fugitive emissions (>90%) and cannot be associated with specific location or process, while small part (<10%) comes from point or line sources.

Emission factors

As basis for estimation in the inventory creating processes, default emission factors recommended by US and Australian (USEPA, SPCC and NERDDC) reports were used. The emission factors used were drafted as a compilation of systematic measurements in real operating conditions in Australian and US mines.

Based on certainty expected, for each emission factor an appropriate rating (EFR) is defined. The EFR system is as follows:

A - Excellent
B - Above Average
C - Average
D - Below Average
E - Poor
U - Unrated

It must be noted that those ratings does not imply emission factors absolute precession. The main criterion affecting the uncertainty of an emission factor remains the degree of similarity between the equipment/process selected in applying the factor, and the target equipment/process from which the factor was derived. This means that if properly selected and applied factors could provide satisfactory precession and could be used with great certainty.

Emission factors for specific operations and associated activities are given bellow.

Table1. Default emission factors - coal extraction and processing

Activity	**TSP**	**PM$_{10}$**	**Units**	**EFR**
Draglines	0.06	0.026	kg/m^3	B
Excavators/Loaders	0.029	0.014	kg/t	C
Buldozers	102	32.5	kg/h	B
Bucket wheel	minimal	minimal		
Screpers	1.64	0.53	kg/VKT	A
Stockpiling	0.004	0.0017	kg/t	U
Reclaiming	0.03	0.013	kg/t	U
Transfer points	0.00032	0.00015	kg/t	U
Conveyor (runoff mine)	0.005	0.002	kg/t	C
Conveyor (dry material)	0.06	0.5	kg/t	C

Table 2. Default emission factors - extraction d processing of aggregates, construction materials and industrial minerals

Activity	**TSP**	**PM$_{10}$**	**Units**	**EFR**
Excavators/ loaders	0.025	0.012	kg/t	C
Bulldozers	17	4	kg/h	B
Mine roads, fugitive dusts	3.88	0.96	kg/VKT	U
Trucks	0.012	0.0043	kg/t	
Draglines	0.06	0.026	kg/m^3	B
Scrapers	1.64	0.53	kg/VKT	A

Table 3. Default emission factors - extraction of metallic ores

Activity	**TSP**	**PM$_{10}$**	**Units**	**EFR**
Excavators/ loaders	0.025	0.012	kg/t	C
Bulldozers	17	4	kg/h	B
Mine roads, fugitive dusts	3.88	0.96	kg/VKT	U
Trucks	0.012	0.0043	kg/t	
Draglines	0.06	0.026	kg/m^3	B
Scrapers	1.64	0.53	kg/VKT	A

Table 4. Common emission factors for gaseous substances

Activity	**Emission factors (kg/1000 l diesel)**					
	PM_{10}	**CO**	**NO_x**	**SO_x**	**VOC_s**	**EFR**
Buldozer	3.03	9.4	34.16	1.7	3.31	C
Excavator	17.7	14.73	34.29	1.7	1.58	C
Screper	3.27	10.16	30.99	1.7	2.28	C
Trucks	17.7	14.73	34.29	1.7	1.58	C
Loader	3.51	11.79	38.5	1.7	5.17	C

Table 5. Common emission factors - processing activities

Activity	**TSP**	**PM_{10}**	**Units**	**EFR**
Primary crushing	0.2	0.02	kg/t	C
Secondary crushing	0.6	ND	kg/t	D
Tertiary crushing	1.4	0.08	kg/t	E
Material transport and handling	0.06	0.03	kg/t	C

Results obtained

Data collected for each site are used for construction of specific flow charts, in order to identify material flow and processes involved. Based on those flow charts, emissions are estimated and results are compiled in a format as per CLRTAP emission inventories requirements. Emission data compiled in tables for each of the major groups of national mining industry are presented below.

Table 6. Fugitive emissions - industrial minerals

Sites	**(kg/year)**					
	TSP	**PM 10**	**CO**	**NOx**	**SOx**	**VOCs**
Govrlevo	205.950	60.408	2.304	5.944	284	452
Usje	365.140	82.645	3.599	8.960	433	591
Mikrogranulati-Gostivar	140.165	19.646	1.735	4.616	218	390
Hamzali	128.278	16.720	247	615	30	40
Memisli	291.516	33.031	502	1.264	61	88
Opalit	365.305	58.336	848	2.060	100	121
Strmos	154.648	39.161	970	2.427	117	164
Silika Mineral	235.696	31.606	1.723	4.603	217	394
Group Total	1.886.699	341.554	11.929	30.489	1.460	2.240

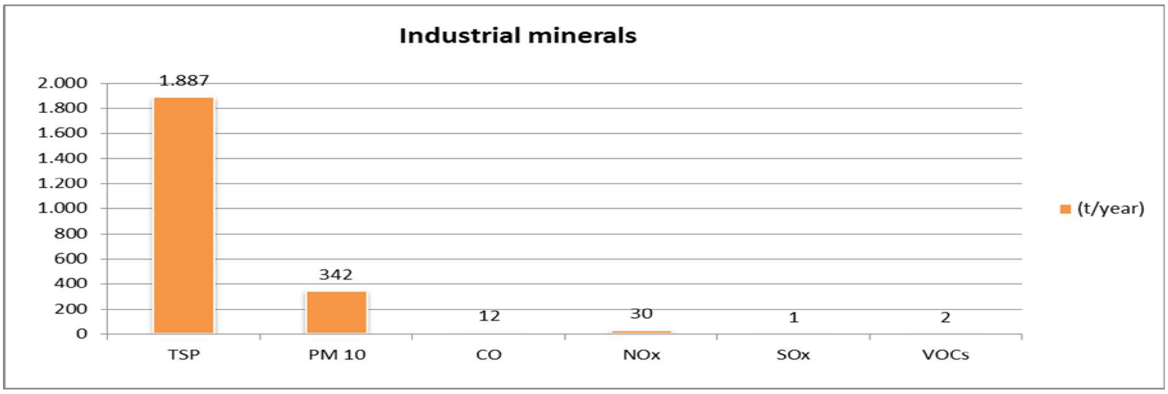

Fig. 1. Total emission - industrial minerals group

Table 7. Fugitive emissions - energy minerals group

Sites	**(kg/year)**		**m^3/year**			
	TSP	**PM 10**	**Mhetane**	**Ethane**	**Propane**	**CO**
REK Bitola	1.814.021	1.222.461	14.146.000	1.028.800	514.400	771.600
REK Oslomej	671.277	417.677	1.903.000	138.400	69.200	103.800
BRIK Berovo	7.965	3.840	26.250	2.100	1.050	1.575
Piskupstina-Struga	9.215	4.443	27.000	2.160	1.080	1.620
Group Total	2.502.479	1.648.420	16.102.250	1.171.460	585.730	878.595

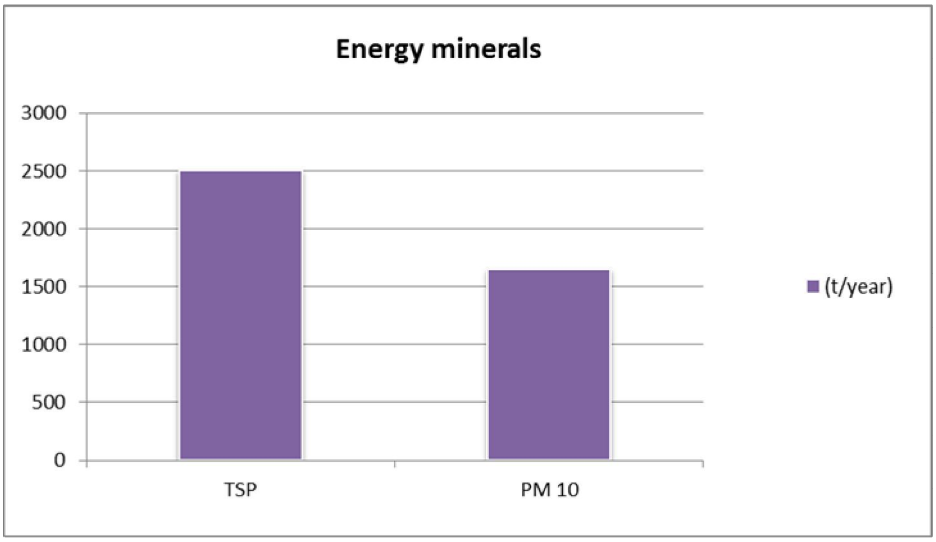

Fig. 2. Total particulate emission - energy minerals group

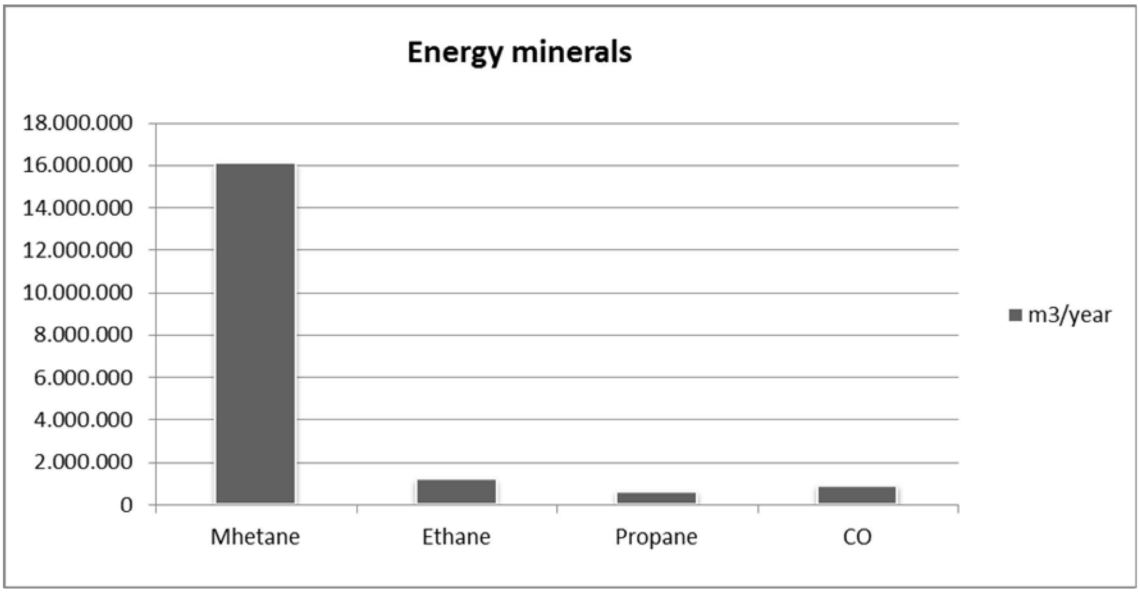

Fig. 3. Total gaseous emission - energy minerals group

Table 8. Fugitive emissions – construction materials/aggregates group

Sites	**(kg/year)**					
	TSP	**PM 10**	**CO**	**NOx**	**SOx**	**VOCs**
Banjani	232.776	39.628	921	2.315	112	159
Cajle	573.493	77.049	1.069	2.649	128	171
FHL Sivec	1.231.208	176.954	13.449	36.914	1.724	3.424
Brazda	133.050	34.827	2.516	6.477	309	489
Zebrenjak	202.055	24.904	1.362	3.516	168	268
Grupcin	16.772	5.514	1.835	4.947	232	435
Prevalec	389.835	43.430	818	2.022	98	129
Krasta	200.788	24.679	1.872	5.050	237	445
Gopceli	138.040	19.298	2.021	5.399	255	462
Tatarli-Cuka	108.271	14.501	1.925	5.157	243	445
Trojaci	184.184	22.400	1.704	4.659	218	428
Pelagonija-Gostivar	202.905	24.357	901	2.437	114	216
Pelagonija Kavadarci	151.822	18.504	790	2.026	97	151
Progres Gostivar	192.512	24.503	707	1.757	85	115
Sopotnica	299.923	42.078	853	2.184	105	161
Tajmiste	235.560	32.480	633	1.641	78	127
Urban Invest	97.381	11.317	448	1.131	54	79
Vratnica	187.344	23.929	781	2.024	96	156
Zelenikovec	136.121	16.752	309	803	38	62
Group Total	4.914.040	677.103	34.914	93.106	4.393	7.925

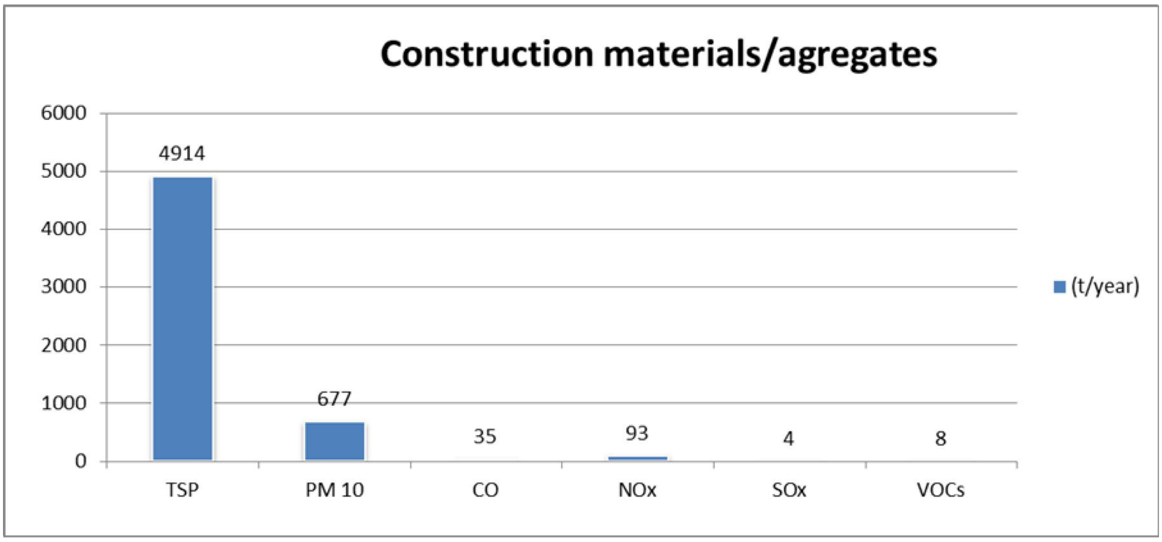

Fig. 4. Total fugitive emissions - construction materials/aggregates group

Table 9. Fugitive emissions – metallic minerals group

	(kg/year)					
	TSP	**PM 10**	**CO**	**NOx**	**SOx**	**VOCs**
Feni	1.531.230	183.643	2.926	7.674	364	619
Buchim	9.884.902	1.167.752	15.505	40.275	1.918	3.140
Group Total	11.416.132	1.351.395	18.431	47.948	2.282	3.759

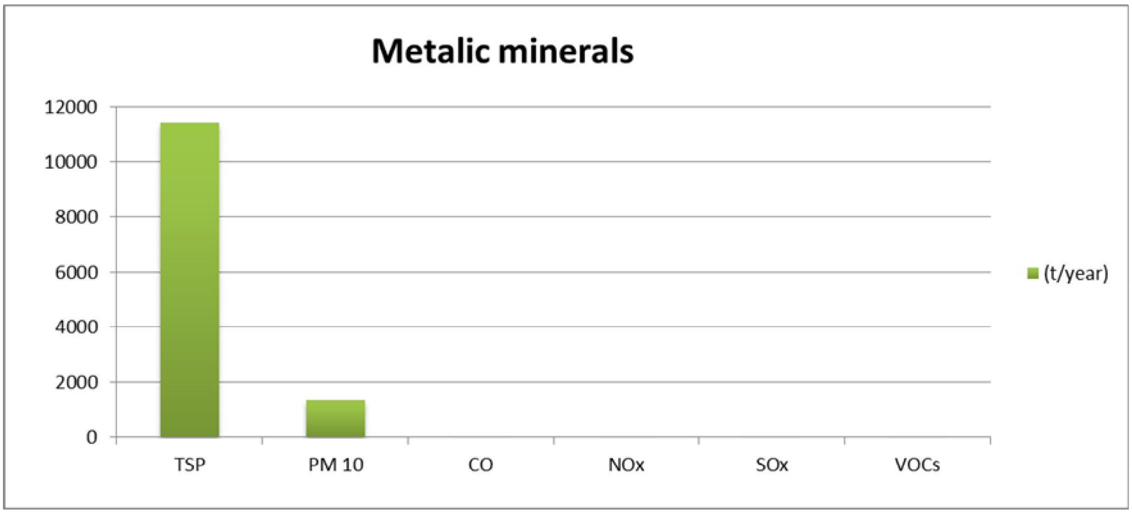

Fig. 5. Total fugitive emissions – metallic minerals group

Instead of conclusion

It must be noted that the results presented are indicative and for reporting/planning purposes only, and total values does not have any significance as an air pollution indicators for national level.

Of course parameters obtained for each specific sites or agglomeration operation located in close proximity could be a solid base for planning and licensing purposes.

REFERENCES:

Bouncier A J & Davis W T (1992), Air Pollution Engineering Manual, Air & Waste Management Association (US), Van Nostrand Reinhold, New York.

Holmes Air Sciences (1998), "Review of Load Based Licensing Requirements and Exploration of Alternative Approaches". Report to the Minerals' Council of NSW, April 1998.

New South Wales Environment Protection Authority [NSWEPA] (1997), Metropolitan Air Quality Study: Air Emissions Inventory, NSWEPA, Sydney.

NERDDC (1988), Air Pollution from Surface Coal Mining: Volume 2 Emission Factors and Model Refinement, National Energy Research and Demonstration Council, Project 921.

Pitt, O. Fugitive PM10 Emission Factors, 15th International Clean Air and Environment Conference, Sydney, 27-30 November 2000, p303-306.

SPCC (1986), Air Pollution from Coal Mining and Related Developments, ISBN 0 7240 59369.

US EPA (1985), Compilation of Air Pollutant Emission Factors, AP-42, Fourth Edition United States Environmental Protection Agency, Office of Air and Radiation, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, 27711.

SURFACE SPRINGS OF LAKE OHRID - ACCESS OF PHYSICOCHEMICAL COMPOSITION

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Abstract

The goal of the paper is to point out specific characteristics of karst springs of Lake Ohrid as they contribute substantially to the lake's inflow. Supplying with nutrients, dissolved oxygen and constant living conditions surface springs are beneficial for lakes extraordinarity as a special boundary for many endemic species. It was shown that Lake Ohrid undergoes eutrophication, so another goal of our protection is monitoring of sensitive parameters regularly following the tributaries that feed this basin. Of interest was the quantification of basic physico-chemical spring properties in order to better understand how and what kind of groundwater is delivered to Lake Ohrid. As karst systems show heterogeneity and variability of many hydrogeological, ecological and other parameters, seven individual surface springs belonging to a larger spring area were monitored during three years. All of them are used as a source of drinking water. Categorization of the water samples is according to OECD regulations, positive by law regulations of Republic of Macedonia. Investigations are done according to standard limnological methods. It was found that there were no major changes with springs intrusion and runoff.

Key words: Lake Ohrid, surface springs, physico-chemical investigations, drinking water

Introduction

Lake Ohrid is located on the central Balkan with approximately two-third of its surface area belonging to Macedonia and about one-third belonging of Albania. Mediterranean climate and the small drainage basin of 2600 km² (catchment/lake surface ratio of ~7) of Lake Ohrid results in a long hydraulic residence time scale of ~70 years (Albrecht, 2008). The water balance of the lake is characterized by average in- and output rates of approximately 37.9 $m^3 s^{-1}$ (Albrecht, 2008), about two-third of the output occurs via River Crni Drim and one-third through evaporation. Relative to its surface, the catchment area is small. Excluding Lake Prespa, it is even smaller with 1,002 km^2 (Popovska and Bonacci, 2007). Today's water input from tributaries is a minor water source, whereas a significant ratio of inflow is delivered by inflows from karstic aquifers (~53%), direct precipitation on the lake surface (~23%), and river inflow (~23%) (Albrecht, 2008). There are around 40 tributaries which flow into the Lake Ohrid (23 on the Albanian side and 17 on Macedonian side). Most of them carry very poor amounts of water during the dry summer period. The hydrography above all reveals the karstic character of Lake Ohrid. Lakes. Many sub-lacustrine and surface springs, particularly on the South-eastern and Southern side of Lake Ohrid, are charged by neighbouring Lake Prespa as well as by mountain range precipitation seeping through the karstic rocks and mixing with the waters originating in Lake Prespa (Anovski *et al.*, 1980; Eftimi and Zoto, 1997; Matzinger *et al.*, 2006a; Amataj *et al.*, 2007; Popovska and Bonacci, 2007).

The karstic springs are the most interesting phenomenon from a hydrogeological point of view, as they present heterogeneity and variability of many hydrogeological, ecological and other parameters. The aim of this article is to present few important surface spring groups by characterizing some physico-chemical parameters, such as temperature (T), electroconductivity, pH, ionic composition, and concentration of dissolved oxygen and some trace elements. These springs are large enough to supply the amount of freshwater needed for human requirements for the city of Ohrid. Inputs *via* springs provide nutrient-rich waters generating areas of enhanced biological activity (Stankovic, 1960; Gilbert *et al*., 1984; Naumoski, 1990; Sywula *et al*., 2003). Different authors determined unique life-forms with impressive percentages of diversity and endemism. The planaria species *Dendrocoelum sanctinaumi*, which is found in the St. Naum surface spring area shows clear genetic difference from littoral forms (Sywula *et al*., 2006) and many other species like freshwater sponge (Hadžišče, 1956; Gilbert and Hadžišče, 1984), forms of *gastropoda* and many others. Because of the crucial effects of springs on Lake Ohrid, they were included in this monitoring program. In this article, we present the temporal variability of spring water properties and show differences of those properties among different sites.

Materials and methods

Samples were taken from seven individual springs: three belonging to the larger spring complex at St. Naum (Capture – Spring 1, Church and St. Petka); two spring sites are located on higher elevations relative to Lake Prespa (849 m a.s.l.) named Elšani and Korita; Kališta spring in the North-western part of the Lake and Biljana's springs in the North-eastern part. A map with summary of all monitored surface springs is presented on the Fig. 1. Monitoring was done between June 2005 and September 2008.

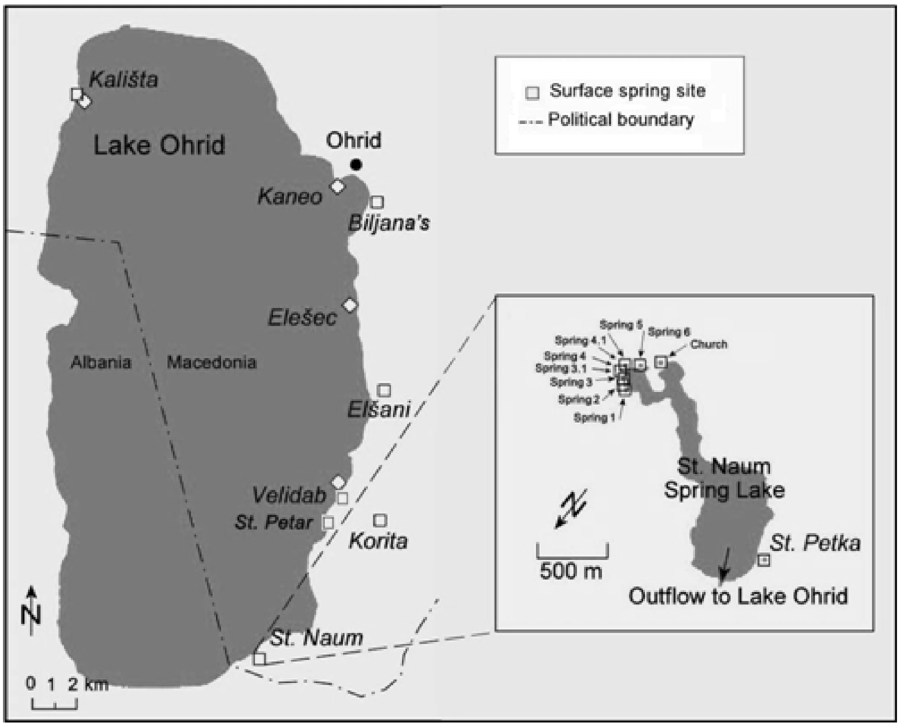

Fig. 1. Locations of surface springs of Lake Ohrid

Water temperature (*T*), specific conductance (κ_T), and pH were measured in-situ on a monthly basis from September 2005 to December 2006, after that quarterly until September 2008 at all sampling sites using hand-held instrument. The instruments' accuracies were 0.2°C, 5% of the measured conductance value, and 0.01 for pH. Values κ_T were transformed to specific conductance at 20 °C (expressed with κ_{20}) based on ionic composition (Wüest *et al.* 1996).

Water samples were taken at Spring 1, Church and St. Petka, Korita, Elšani, Biljana's spring and Kališta on a monthly basis from September 2005 to December 2006, after that quarterly until August, 2008. Samples were stored in clean plastic bottles for analysis of ions and trace elements, in glass vials for analysis of stable isotopes, and in glass bottles for analysis of dissolved oxygen. The bottles were cooled immediately after sampling. Phosphate was measured using a Procon flow analyzer (DEW, 1996) at Eawag, Kastanienbaum and photometrically (Strickland and Parsons, 1968) at the Hydrobolological Institute, Ohrid. Cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (Cl^-, SO_4^{2-}, NO_3^-) were measured with ion chromatography with an accuracy of <5% of measurement (Weiss, 2004) at Eawag, Kastanienbaum and by atomic absorption spectrometry (Varian, SpectrAA 220). Analysis of dissolved oxygen (DO) and oxygen saturation ($O_{2,sat}$) was carried out following the Winkler method (Clesceri *et al.*, 1989). For trace elements analysis water samples were concentrated with solid phase extraction and after that determined with electrothermal atomic absorption spectrometry (ETAAS). All other lab work was accomplished at Hydrobiological Institute, Ohrid and Faculty of Natural Science and Mathematics, Skopje.

Results and discussion

Average spring water temperature in the study area ranged from 8.2 °C at Spring Korita to 11.9 °C at Spring St. Petka. Average values for temperature, pH and conductivity are given in the Table 1. The regular annual climate conditions, as well as mountain site explains very low temperature of the Korita spring. Depending of the season its water temperature varies from 7.2 °C to 10 °C. At St. Naum spring area, *in-situ* measurements of the temperature from the individual springs were in a narrow range of 0.6 °C. Hence, water temperatures in the entire study area seemed to be constant during the entire year.

Average conductivity lied between 261-385 μS cm^{-1} (Table 1). Springs pH ranges between 7.5-7.9. Temporal constancy of the spring water could be noticed at St. Naum spring area (Table 1). At Kališta and Korita, pH values were 7.4 and 7.8. Alkalinity was determined as a concentration of $CaCO_3$ (in mg l^{-1}) and results were lower than 187 mg l^{-1} at all sampling sites. Only at Kalšita, seasonal changes could be noticed with variations from 160 to 220 mg l^{-1} $CaCO_3$ during the summer periods.

During the present study values of content of free CO_2 fluctuated in high range and pattern of variations were irregular, due to the rate of decomposition. Determined values at all investigated localities demonstrate continued presence in all seasonal periods in all three years. According to the seasonal dynamic there is higher trend in summer than in winter period. DO concentrations were from 6 to 13 mg l^{-1} (Table 1). Variations in DO occur seasonally where lower values were determined in the summer period. Springs at St. Naum area at the East side of the lake showed geographical trend. Starting from the most northern spring at the HBI yard, Biljana's water becomes more under-saturated with DO towards St. Naum spring area. Average values for the amount of biodegradable organic matter all years don't exceed higher value than 2.25 mg l^{-1} O_2 during the whole monitoring.

Table 1. General physico-chemical parameters of the surface spring of the Lake Ohrid

Parameter	Kališta	St. Naum -Spring 1	Church	St. Petka	Korita	Elšani	Biljana's
T (°C), mean	11,47	10,65	11,18	11,88	8,17	10,30	10,93
Range	11-11,9	10,3-11,2	10,3-11,40	10,3-13,60	7,2-10,20	10,01-11	10-15,30
CV	0,02	0,03	0,03	0,09	0,12	0,03	0,15
k_{20}/µS cm^{-1}, mean	316,45	237,82	256,73	261,09	221,96	242,18	234,35
Range	260-365	205-277	208-287	229-286	173,5-255	199,8-293	191,8-263
CV	0,12	0,13	0,13	0,10	0,15	0,14	0,11
pH, mean	7,32	7,52	7,53	7,55	7,78	7,62	7,63
Range	6,84-7,58	6,75-7,87	6,8-7,84	6,85-7,93	6,63-8,28	7,13-7,93	7,22-7,92
CV	0,03	0,05	0,05	0,04	0,06	0,04	0,03
Total alk., mg l^{-1} CaCO$_3$, mean	3,76	3,19	3,19	3,20	2,83	2,99	2,92
Range	3,2-4,44	2,96-3,48	2,8-3,5	2,12-3,44	2,58-3,10	2,78-3,12	2,69-3,2
CV	0,12	0,06	0,07	0,12	0,06	0,04	0,06
DO/mg l^{-1}, mean	8,43	7,75	6,64	6,11	10,20	9,82	10,07
Range	6,68-9,54	6,35-9,21	5,07-8,49	4,55-7,20	8,62-12,96	9,31-10,79	9,79-10,82
CV	0,09	0,10	0,15	0,12	0,12	0,05	0,03
Total P/µg l^{-1}, mean	87,65	34,49	10,78	31,20	10,56	19,00	23,03
Range	0,46- 719	0,41-301	0,45-20,41	0,45-52,4	0,58-22,83	0,24-78,6	2,85-9,05
CV	2,53	2,57	0,49	0,52	0,66	1,17	1,23
Total N/g l^{-1} Mean	446,69	543,40	360,87	388,60	262,38	379,50	379,87
Range	32,8-1203	32,8-1457	38,6-596	0-1192	0-450,06	121,7-706	152,5-671
CV	0,77	0,71	0,45	0,91	0,61	0,42	0,44
Cl^{-1}/µM, mean	107,54	95,17	90,04	108,50	85,92	95,16	72,34
Range	69,5-123	68,2-112	62,3-111	44,5-196	68,5-110	55,6-195,9	44,2-119,0
CV	0,18	0,16	0,21	0,61	0,19	0,55	0,50
Ca^{2+}/µM, mean	1027	919,93	901,89	887,13	900,60	842,25	758,0
Range	868 -1397	511-1454	423-1425	723-1009	679 -1057	499-1132	357 -1021
CV	0,19	0,35	0,38	0,14	0,15	0,22	0,37
Mg^{2+}/µM, mean	128,6	159,96	197,12	163,56	59,81	80,25	64,27
Range	73,6- 205	83,7-225	111-288	35,5-260	19,86-132	40,8-159,2	22,1-139,8
CV	0,33	0,27	0,30	0,48	0,84	0,55	0,71
Na^{+}/µM, mean	71,9	76,01	85,33	82,61	30,88	43,07	49,2
Range	39,5-120,8	42,3-120	35,0-144	24,4-152	14,36-51,9	24,54-55,6	15,8-62,0
CV	0,50	0,38	0,41	0,48	0,52	0,20	0,27
K^{+}/µM, mean	12,63	20,79	22,42	27,03	3,73	10,99	7,40
Range	9,15-16,7	18,3-22,5	18,22-25,15	22,6-32,1	2,8-4,20	9,8-13,46	5,9-8,87
CV	0,21	0,07	0,08	0,10	0,14	0,10	0,12

CV- Coefficient of variation

Average cationic composition is given in the Table 1. The highest value for calcium is detected at Kališta. Average values for (SO_4^{2-}) exceeded from 0.4 mg l^{-1} at Elšani, 0.32 mg l^{-1} at St. Petka surface and lowest value of 0.12 at Kališta, St. Naum and Korita. Concentrations of NO_3-N exceed 0.04-0.8 mg l^{-1} for NO_3-N (Fig 2). Nitrite concentrations in these freshwaters were usually very low, 0.001 mg l^{-1} for NO_2-N. Generally, the determined concentrations of organic nitrogen content in the entire study area spanned a large range resulting in large relative differences (e.g. average concentration of organic nitrogen at springs Elšani and Korita was at least three fold the value measured for spring St. Petka and almost five fold measured at St. Naum Spring 1). Surface springs contained less than 0.03 mg l^{-1} phosphorus except Kališta surface spring which showed seasonal fluctuations and had average phosphorus values of 0.08 mg l^{-1} (Fig 3). Consequently, increase was usually in the summer period when is the tourist season with highest values at spring Kališta measured in august, 2006 of 0.7 mg l^{-1} and St. Naum spring area of 0.3 mg l^{-1}.

The method of solid face extraction (Karadjova, 1999; Stafilov, 2002) was used for concentrating and determination of eight trace elements: Pb, Cd, Cr, Cu, Fe, Hg, Ni, Co, Mn, As. The concentration of different metals in waters varies over a wide range: from 11 μg l^{-1} for iron till 0.02 μg l^{-1} for Cd, generally very small concentrations, below permissible limits. As and Co were under detection limits for all gathered samples.

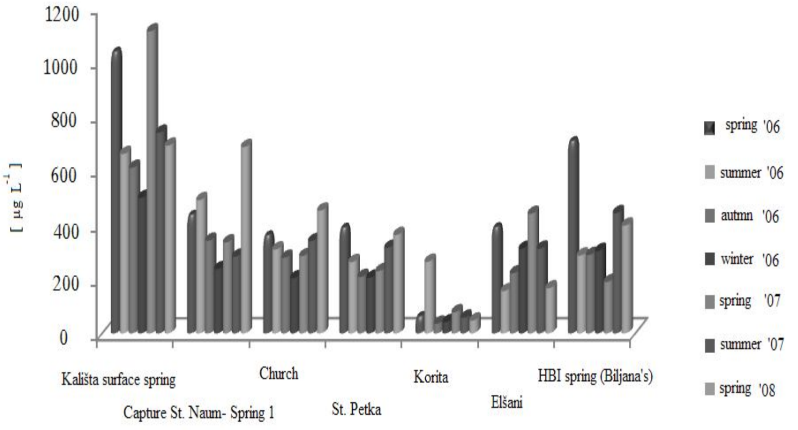

Fig. 2. The NO_3-N and concentration in surface springs, seasonal dynamic in µg l^{-1}

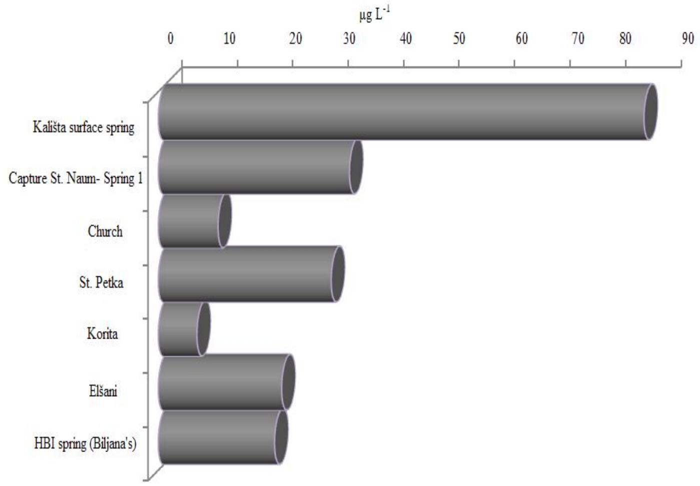

Fig. 3. Seasonal changes in TP for subaquatic springs in µg l^{-1}

Conclusions

Data gathered in this study indicate general stability of spring water characteristics. Measured parameters showed only little seasonal variation, as demonstrated most distinctly by records of water temperature. However, springs were found to be individually characterized by physico-chemical signatures. Similarly, other measurement parameters do not seem to vary in time. In the case of conductivity, pH, DO, variability was minor as indicated by small standard deviations of the averaged values. Variations of ion concentrations were relatively high but not systematic. At St. Naum spring area beside the fact that sources of spring water vary in their physical and chemical properties over time, the temporal stability of these properties measured in spring water is surprising. Neither signals from precipitation events nor seasonal changes in Lake Prespa's outflow are detected at spring outflows at this area. The most likely explanation for temporal stability to this remarkable extent is the existence of large reservoirs within the karsts system in which groundwater is stored for long periods. Owing to the high amount of spring water draining into Lake Ohrid, the groundwater reservoirs feeding the springs must be huge. Large underground lakes may exist inside the mountains between Lake Ohrid and Lake Prespa. Alternatively, large porous channels may be present through which groundwater flows slowly towards Lake Ohrid. The greater the scale of such reservoirs the longer groundwater will be stored. Naturally, residence time has to be longer than one year that temperature can be balanced. Biljana's and St. Naum general characteristics of the spring regime are the direct correlation between precipitation and spring discharge.

Water from all surface springs was usually remarkably clear. The quality of spring water represents the general water quality of the ground-water system. Most spring water was of excellent quality. The specific conductance of all subaquatic and surface springs water generally is less than 400 μS cm^{-1}, indicating that small amounts of minerals are dissolved in the water. Chloride and sulphate concentrations generally are less than 0.3 and 5 mg l^{-1}, respectively. Spring-water temperatures range from 8 to 12 °C. Higher water temperatures in spring Church indicate that the water originates from deeper parts of the karstic aquifer system, or due seismic activities. Fluctuations of temperature and nutrients at Korita and Elšani are regarding the mountain area, thus, variations were explainable.
Even though general conclusions, anthropogenic influence is still presented with higher amounts of phosphorus measured at Kališta spring area.

References

Anovski, T., Naumovski, J., Kacurkov, D., Kirkov P. (1980). A study of the origin of water of St. Naum Springs, Lake Ohrid. *Fizika*, **12**, 76–86.

Albrecht, C., Wilke, T. (2008). Ancient Lake Ohrid: biodiversity and evolution *Hydrobiologia*, **615**, 103–140.

Amataj, S., Anovski, T., Benischke, R., Eftimi, R., Gourcy, L.L., Kola, L., Leontiadis, I., Micevski, E., Stamos, A., Zoto, J. (2007). Tracer methods used to verify the hypothesis of Cvijić about the underground connection between Prespa and Ohrid Lake. *Environmental Geology*, **51**, 749–753.

Clesceri, L., Greenberg, A., Eaton, A. (Eds.) (1998). Standard Methods for the Examination of Water and Wastewater (20th ed.), pp. 4–129–130. Washington DC, USA: APHA, AWWA, WEF.

DEW (1996). German Standard Methods for Water Analysis, Volume II. Weinheim, Germany: VCH.

Karadjova, I. (1999). Determination of Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb in natural waters, alkali and alkaline earth salts by electrothermal atomic absorption spectrometry after preconcentration by column solid phase extraction *Mikrochimica Acta*, **130**, 185-190.

Eftimi, R., Zoto, J. (1997). Isotope study of the connection of Ohrid and Prespa lakes. International Symposium "*Towards Integrated Conservation and Sustainable Development of Transboundary Macro and Micro Prespa Lakes*", Korcha, Albania.

Gilbert, J.J., Hadzisce, S. (1984). Taxonomic notes on the shallow-water endemic sponges of Lake Ohrid, Yugoslavia, with a description of two new species and a redescription of *Spongilla stankovici*. *Archiv für Hydrobiologie*, **99**, 331-339.

Hadžišče, S. (1956). III. Beitrag zur Kenntnis der Gastropodenfauna des Ohridsees.–Beschreibungen der bis jetzt unbekannten Schnecken und Beispiele der Speciation bei den Gastropoden des Ohridsees. *Zbornik na rabotite, Hidrobioloski Zavod-Ohrid*, 4.

Matzinger, A., Jordanoski, M., Veljanoska-Sarafiloska, E., Sturm, M., Wüest, A. (2006a). Is Lake Prespa jeopardizing the ecosystem of ancient Lake Ohrid? *Hydrobiologia* 553, 89–109.

Moore S. (2006). Submarine groundwater discharge with special reference swoam, Willard - Department of Geological Sciences University of South Carolina Columbia, SC 29208.

Naumoski, T. (1990). Phosphorus supply in Lake Ohrid, Macedonia, Yugoslavia. *International Verein Limnology*, 24, 253-257.

Popovska, C., Bonacci, O. (2007). Basic data on the hydrology of Lakes Ohrid and Prespa. Hydrological Processes, 21, 658-664.

Stafilov, T., Pavlovska, G., Čundeva, K. (2002). Lead(II) and cobalt(III) heptyldithiocarbamates as new coflotation reagents for preconcentration of cadmium before its ETAAS determination, *Journal of Institute of Sciience and Technology* **-** *Balikesir University*, 4, 85-89.

Stankovic, S. (1960). The Balkan Lake Ohrid and its Living World, Volume IX of Monographiae Biologicae. Den Haag, Netherlands: Uitgeverij Dr. W. Junk.

Strickland, J., Parsons, T. (1968). A Practical Handbook of Seawater Analysis (Second ed.)., pp. 71–76. Ottawa, Canada: Fisheries Research Board of Canada.

Sywula, T., Krstanovski, Z., Tasevska, O., Sell, J., Kretowicz, T. (2003). Genetic differences among several species of tricladida from the relict Lake Ohrid as revealed byenzyme electrophoresis. *Folia biologica*, **51**, 105–109.

Sywula, T., Krstanovski, Z., Biała, A., Wysocka, A., Kilikowska, A. Sell, J. (2006). Phylogenetic position of *Dendrocoelum lacteum* (Tricladida) from the Balkan Lake Ohrid evidenced by allozyme data. *Biochemical Systematics and Ecology*, **34**, 212-218.

Weiss, J. (2004). Handbook of Ion Chromatography. Weinheim, Germany: Wiley-VCH.

Wüest, A., Piepke, G., Halfman, J.D. (1996). Combined effects of dissolved solids and temperatue on the density stratification of Lake Malawi, in: Johnson, T.C., Odada, E.O. (Eds.), The Limnology, clymatology and paleoclymatology of the East African Lakes, Toronto, p. 183-202.

PROTECTION OF POLLUTION OF THE ARTESIAN AQUIFER AT RAOTINCE SITE-POLOG BASIN, WESTERN MACEDONIA

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Abstract

This paper shows protective measures should be taken to carry out preventive protection of groundwater from the artesian aquifer in locality Raotince. Based on research by two hydrogeological exploitation investigative boreholes artesian aquifer with poorly mineralized water is noticed in Kvarter - Pleistocene lake sediments with two aquifer layers.

Introduction

Raotince is located in the western part of Macedonia, 20 km north-east of the city of Tetovo (Fig. 1) the emergence of mineral waters and mineral waters poor in this area appear in the left and the right bank of the river Vardar from village Kopance Raotince to the village. In the immediate vicinity of the site Raotince passes the river Vardar. Mineral waters from the wider environment Raotince be examined by several authors: (Bajic, 1929, Kekic, 1971-1972, Kotevski, 1973-1976).

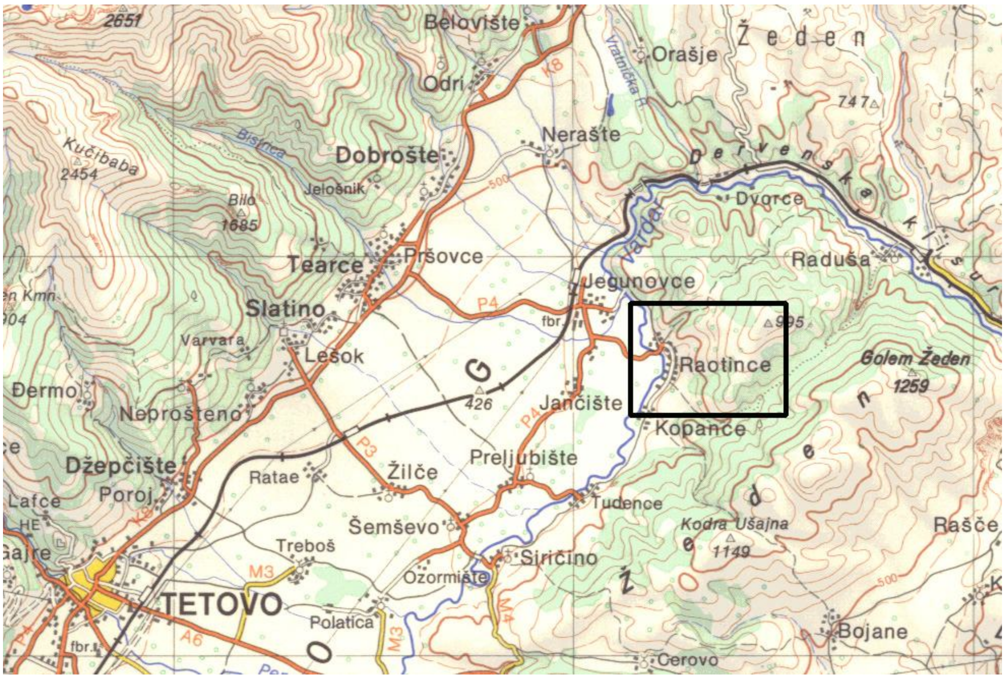

Fig. 1. Geographical position of the investigated area.

Geological composition of the wider region

The geology of the region is made up of Paleozoic, Permotriasic, Mezozoic, Tertiary and Quarternary rocks (Petkovski, Karovic, 1977) (Fig. 2).

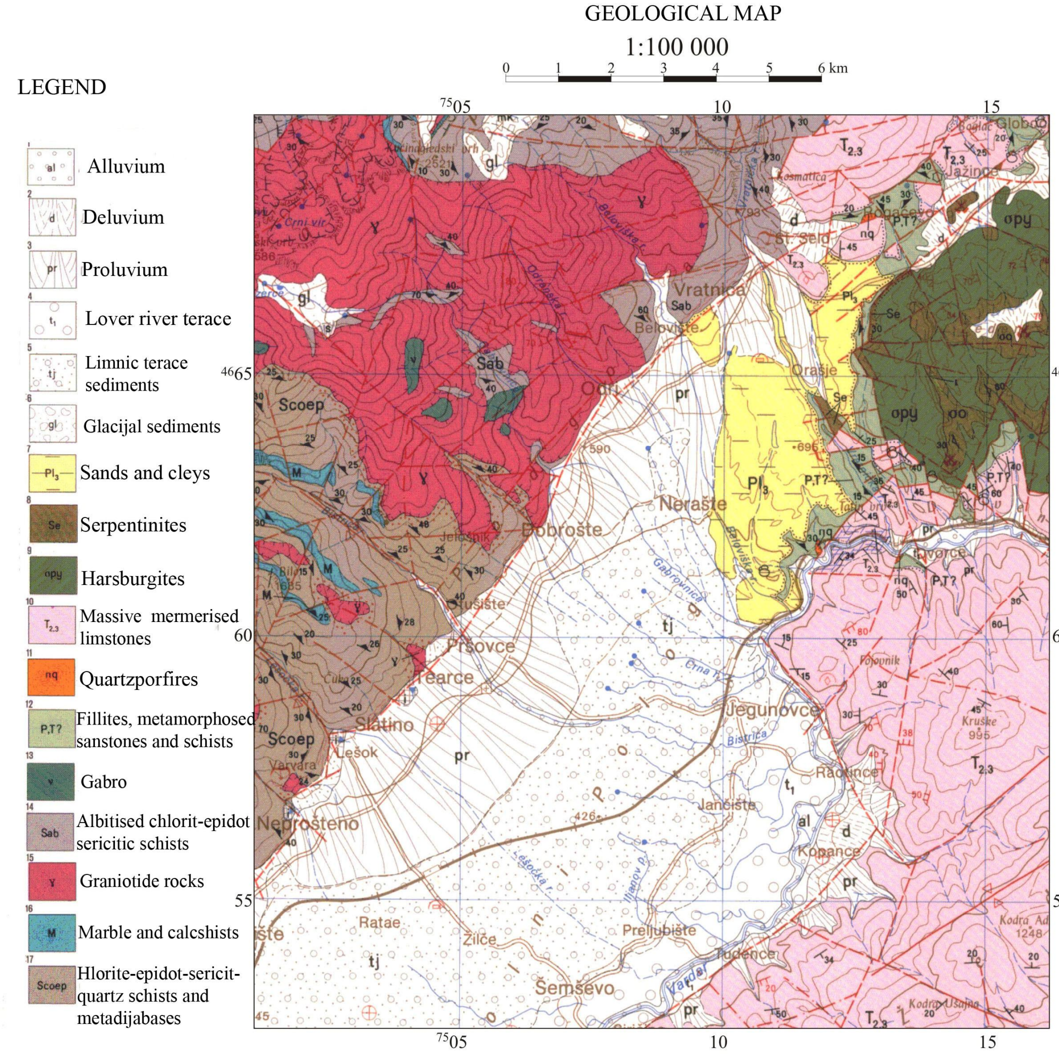

Fig. 2. Geological map of the investigated area. (Petkovski and Karovic 1977).

The oldest rocks are represented of Paleozoic rocks present of: epidote - chlorite-sericite- quartz schist and metadijabases (Scoep), marbles and kalkshists (M), granite rocks (γ), albitized – chlorite - epidiot - quartz schist, and gabbros (ν). Permotriasic rocks are represented by: filites, metamorphosed cleystones, sandsstones and schists (P, T) and quartz porphyry **(π q).**

Mezozoic is present of Trijasic massive marble (T 2.3), jurasic harcburgites **(σpy)** and serpentinites (Se).

Tertiary is made up of only Pliocene sediments.

Quarterly rocks are represented of: moraine material (gl), limnic terace sediments (tj), lower river terraces (t1), proluvijal (pr), deluvijal (d) and alluvial sediments (al). The investigated area by geotectonic regional aspect belongs to the Western Macedonian zone (Arsovski, 1997).

Hydrogeological features of artesian aquifer

Hydrogeological features of the artesian aquifer from Roaotince locality is according to data obtained from two investigative exploitation boreholes that are performed to a depth of D1 = 50 m and D3 = 70 m.

Based on data obtained by investigative drilling hydrogeological profile is designed of which is represented litological members and their mutual relationship (Fig. 3). From the hydrogeological profile can be seen that the topmost parts of the terrain is built from quarter alluvial - terraces sediments whose thickness ranges up to 11 meters. These alluvial terraces sediments which are built of gravel and sand have formed aquifer with free level. Under the alluvial-terraces sediments until the final depth of drillholes is determined Quarter - Pleistocene lake sediments, presented with gravel, sand and clay as well as their mutual shifts.

Artesian aquifer was founded by two aquifers layers with various granular gravels and sands with a small percentage of clay. Artesian aquifer layers in D-1 well is found at a depth of 24-35 m and 38-49 m, and in D-3 well on the depth of 35-43 m and 55-67 m. Above and below the aquifers there are clay sediments which are sandy in individual places.

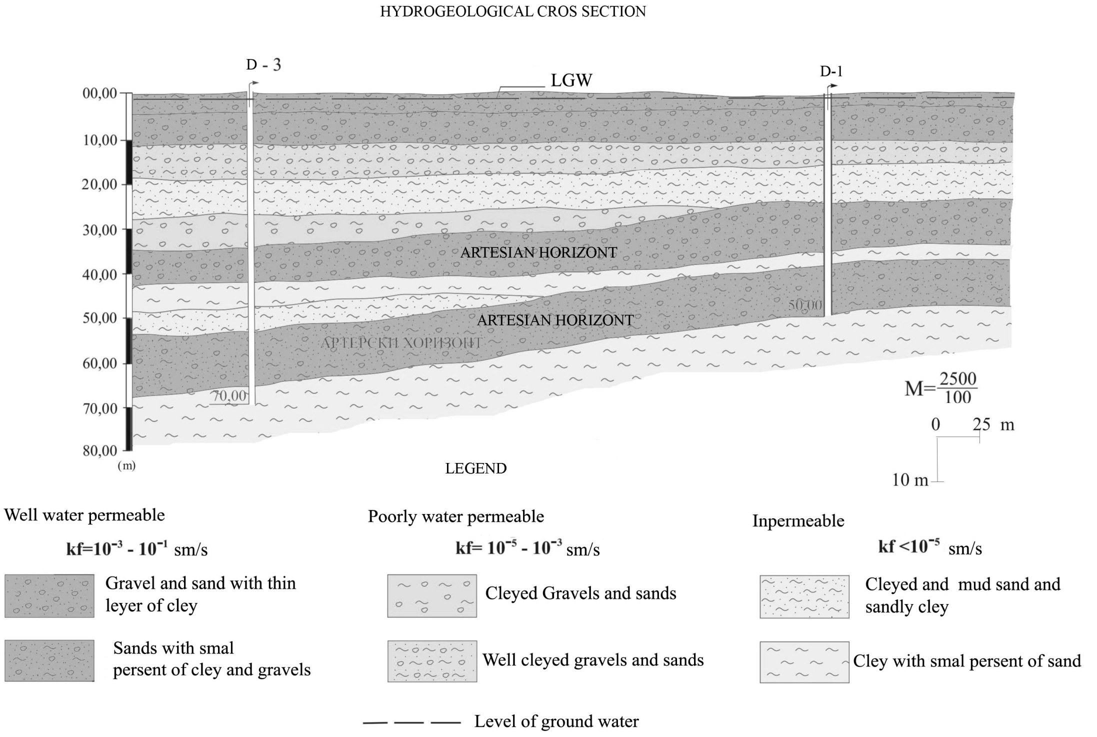

Fig. 3. Hydrogeological profile.

Quality of the water

Quality ot the mineral water was analized by the National Institute for Health Protection in Skopje have been made two chemical analysis. According to the chemical composition the water belongs to the group of hydrocarbonate, calcic- magnesian water.

It is characterized by a pleasant tartness, no smell and has increased mineralization ranging from 708-895 mg / l, according to which it belongs to the group of low mineralized water. According to the pH value (pH = 6.32) water belongs to the group of weakly acidic waters.

Opportunites for pollution of artesian water

In order to protect groundwater from artesian aquifer will be discussed some opportunities where it can be contamination occur .
Like most prospective areas in which can lead to contamination of groundwater in artesian aquifer can be:

- Active water intake facilities (wells)
- Excluded and abandoned wells and piezometers
- Zones of feeding - underground flow of aquifer
- Roof sediments with vertical infiltration of pollutants

Critical areas for contamination of groundwater from the aquifer with free level which is formed in alluvial sediments can be:

- shallow, dug wells, septic tanks, farms
- underground facilities (sewage)
- agriculture, breakdown outbursts, traffic accidents and more.
- petrol pumps
- the waters of the river Vardar, which are in hydraulic connection with aquifers that formed in alluvial sediments

Suggested measures for protection of artesian waters

Artesian aquifer in Raotince locality is located in urbanized and populated area in which space has a higher number of potential contaminants such as fecal sewage, septic tanks, intensive agriculture where farms use pesticides, herbicides, fungicites, etc. To make preventive protection of groundwater in aquifer, one of the most important measures for protection is to conduct continuous monitoring that should be systematically follow certain parameters in the function of the quality of groundwater. To this aim it should be formed piezometric surveillance network which has to be deployed at sites that are sensitive to pollution in the vicinity of Raotince and the wider in Lower Polog valley .

With a group of piezometers should be monitor the groundwater quality from artesian aquifer and the second group of piezometeres should be monitor groundwater quality in alluvial sediment in which is formed an open type of aquifer by a free level which is very susceptible to pollution. Piezometeres should be made so that water does not impoundment both of aquifer in order to be follow environmental pollution especially in every aquifer areas. The location of piezometres should be choose according to local conditions on the terraine, in order to get first the information about the possible contamination of groundwater. Based on this information would be take appropriate measures would not be led to pollution of water from deep artesian horizonts.

Since there are no availabile of sufficient data from which can accurately determine the feeding zones od atresian aquifer which are most sensitive areas through which may come from water pollution on aquifer, it is necessary to make detailed hydrogeological investigations combined with tracer tests. These studies should define the direction of movement of groundwater and to define zones of feeding atresian aquifer.

Some extraction wells which will draw the water from atresian aquifer and from the aquifer with free level should be defined sanitary protection zones that should be given proposed measures to make preventive protection of groundwater.

Conclusion

To make preventive protection of artesian waters from in atresian aquifer from Raotince locality, should be carried out continuous monitoring piezometaric network to be deployed at sites that are sensitive to pollution in the vicinity of Raotince and the wider Lower Polog valley.

Around extraction wells which will draw water from atresian aquifer and from the artesian with free level should be defined sanitary protection zones that should be given a proposal for preventive measures protecting groundwater.

References

Арсовски М., 1997: Тектоника на Македонија. РГФ- Штип.

Бајиќ Б., 1929: Минералне и лековите воде у јужној Србии. Гласник Скопског научног друштва, књ. VI – Скопје.

Котевски Ѓ. 1987: Хидрогеологија на минералните, термалните и термоминералните води на територијата на Р. Македонија. Самоуправна практика Скопје.

Котевски Г., 1980: Извештај за хидрогеолошките истражувања на минералните и термоминералните води на локалитетот Бањиче на реката Пена. Геолошки завод Скопје. ООЗТ Институт за геотехника и хидрогеологија. Скопје.

Кекиќ А. 1986: Геологија и хидрологија на Полошката котлина и потеклото на водата од изворот Рашче. Самоуправна практика Скопје.

Кекиќ А. 1973: Хидрогеолошке одлике Полошке котлине. (докторска дисертација).

Мирчовски В. Мајер Д. 2011: Заштита на подземни води. Учебник. Факултет за природни и технички науки, Универзитет Гоце Делчев Штип.

Лончар И., 1996: Елаборат за резерви и квалитетот на минералните води на локалитетот Раотинце-Тетовско. Градежен институт Македонија, Скопје.

Петковски П., Каровиќ, Ј., 1977: Толкувач на основната геолошка карта на Р. М. 1: 100 000 на листот Качаник. Геолошки завод Скопје.

Петковски П., Каровиќ, Ј., 1977: Основна геолошка карта на Р.М. 1:100 000 лист Качаник. Геолошки завод Скопје.

HEAVY METAL CONTAMINATION OF PADDY SOILS FROM KOČANI FIELD (REPUBLIC OF MACEDONIA)

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Abstract

The research focuses on the heavy metals contamination of paddy soils from Kočani Field (Republic of Macedonia). Very high concentrations of Ag, As, Cd, Cu, Mo, Ni, Pb, Sb and Zn were found in the paddy soils samples from the vicinity of the Zletovska River (western part of Kočani Field). This river drains the untreated effluents from the Pb-Zn mine in Zletovo-Kratovo region and it is used for irrigation of the surrounding paddy fields. Heavy metal contamination of Kočani paddy soils was evaluated by an index of geoaccumulation (I_{geo}), which confirmed high heavy metal contamination status for Kočani paddy soils, especially around Zletovska River area. Taking into account the results of this research the area around the Zletovska River is considered as the most anthropogenically impacted part of Kočani Field.

Key words: Contamination, heavy metals, paddy soil, Kočani Field, Republic of Macedonia.

Introduction

Base-metal mining activities together with milling and grinding operations, concentrating ore and the disposal of tailings, acid mine and mill wastewater provide important sources of heavy metals entering into the environment (ADRIANO, 1986). Consequently, very high concentrations of heavy metals can be found in and around abandoned and active mines, which can affect nearby agricultural soils, food crops, riverine water and stream sediments (ADRIANO, 1986; JUNG, 2001; JUNG & THORNTON, 1997; KORRE et al., 2002; LEE et al., 2001; LIU et al., 2005; LU & ZHANG, 2005; SIMMONS et al., 2005; WITTE et al., 2004, WONG et al., 2002; YANG et al., 2004).

Numerous studies worldwide have investigated the heavy metal concentrations in soils (KABATA-PENDIAS & PENDIAS, 2001). Although mining is one of the most important industries in the Republic of Macedonia, studies about heavy metal concentrations in soils originating from historical or current base-metal mining activities are scarce, especially in the area of Kočani region (DOLENEC et al., 2007; ROGAN et al., 2009; ROGAN et al., 2010). In this context, the major aims of the presented study are:

- to detect the total heavy metal concentrations and distribution in paddy soil samples from Kočani Field and compare these results with permissible levels of heavy metals in arable soils;
- to assess the soil contamination by index of geoaccumulation (I_{geo}) (MULLER 1969, 1979), and;
- to evaluate the overall environmental risk of the soil system in the Kočani Field area.

Materials and methods

Study area

Kočani Field is located in eastern Macedonia, about 32 km from the city of Štip and 115 km from the capital city Skopje. With an average length of 35 km and width of 5 km, Kočani Field lies in the valley of the Bregalnica River between the Osogovo Mountains in the north and Plačkovica Mountains in the south (Fig. 1).

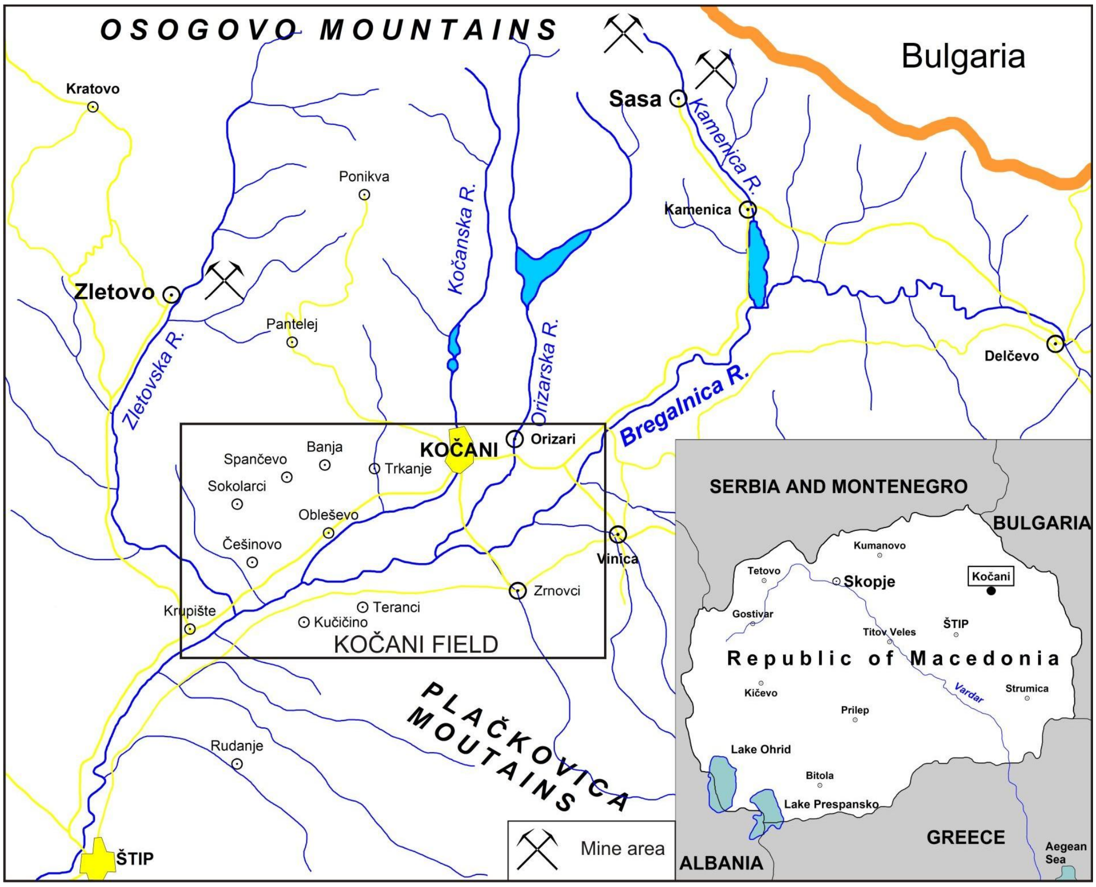


Fig. 1. Study area, Kočani Field, R. Macedonia

The broader region is well known as an agricultural and mining province, with significant thermal activity. The municipality of the Kočani area comprises 28 settlements with 38,092 inhabitants.

The Bregalnica River, together with its tributaries, represents the principal drainage system in the investigated area and is, therefore, an important water supply for the irrigation of the surrounding paddy fields. The main tributaries of the Bregalnica River are the Kamenica River in the northeastern part of the study area and the Zletovska River in the western side of Kočani Field (Fig. 1). The Zletovska River originally drained the central part of the Zletovo-Kratovo volcanic complex as well as the untreated mine effluents from the Pb-Zn Zletovo mine and its ore processing facilities. Both rivers are used by local farmers for the irrigation of the nearby paddy fields.

The Kočanska and Orizarska Rivers are two small tributaries of the Bregalnica River (Fig. 1) that drain the southern part of the Osogovo Mountains, as well as the untreated municipal wastes and domestic sewage of the cities of Kočani and Orizari. The riverine water of the Kočanska and Orizarska Rivers is also used for the irrigation of the paddy fields located in the northeastern part of Kočani Field.

The paddy soil of Kočani Field was estimated to originate from the composite material of the sediment derived from igneous, metamorphic and sedimentary rocks located in the wider area of Kočani. The sediment material was transported by the Bregalnica River and its tributaries and deposited in the Kočani depression (DOLENEC et al., 2007). The soil mineralogy and elemental composition are closely related to the acidic and intermediate rocks of the Kočani region (DOLENEC et al., 2007).

Zletovo-Kratovo ore district

The Zletovo-Kratovo Pb-Zn ore district is situated 5 km northwest of the Zletovo village and about 7 km from the city of Probistip (Fig. 1). It is located in the central part of the Zletovo-Kratovo volcanic complex. The mineral association comprises galena (principal ore mineral) and sphalerite, with subordinate pyrite, lesser amounts of siderite and chalcopyrite and occasionally pyrrhotine, marcasite and magnetite. Minor occurrences of U-mineralisation have also been discovered (pitchblende).

The Zletovo mine has an annual capacity of 350,000 tons of Pb-Zn concentrate (8% Pb and Zn) and significant concentrations of Ag, Bi, Cd and Cu. Ore is concentrated at the flotation processes at Probistip, and tailings material is stored in two impoundments in the adjacent valleys (ALDERTON et al., 2005).

Paddy soil sampling and analysis

The sampling of the paddy soils was carried out in autumn 2005. The sampling locations are shown in Fig. 2. Paddy soil samples were assembled at 38 locations from seven profiles across Kočani Field (Sections I–VII).

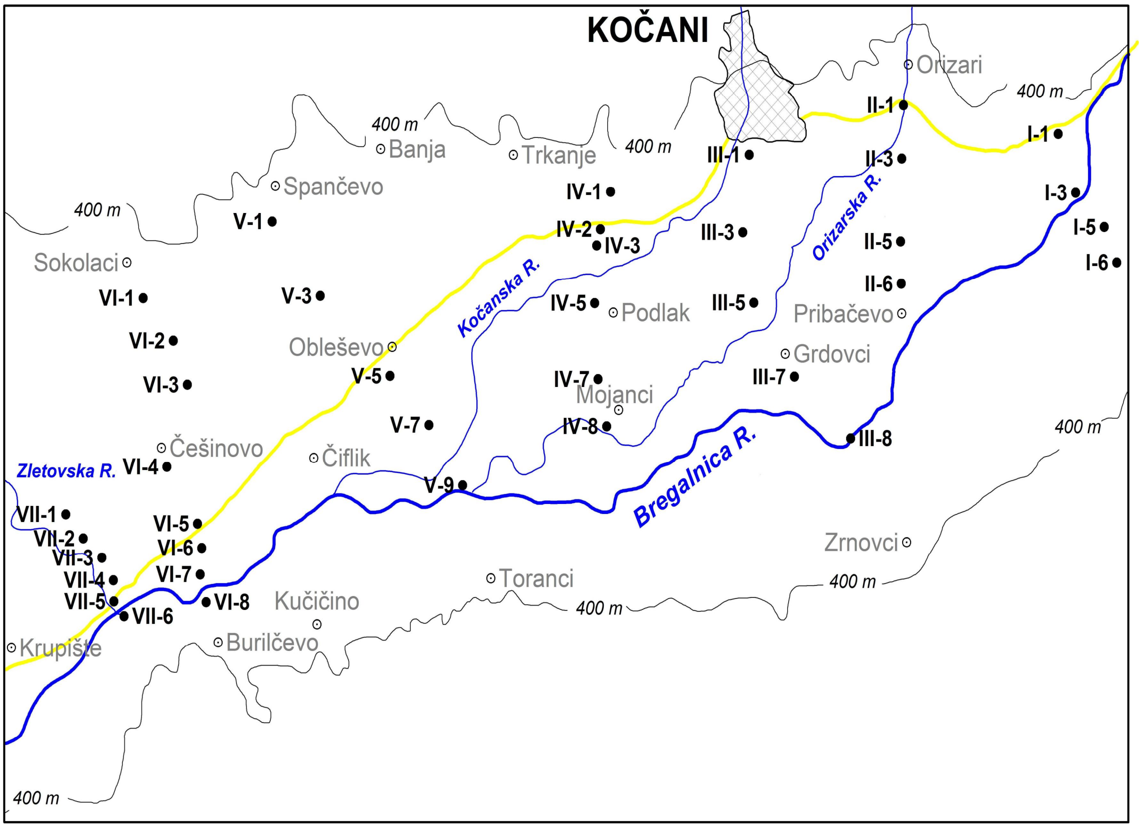


Fig. 2. Paddy soil sampling locations map.

Near surface paddy soils (0–20 cm in depth) were collected because it is impossible to distinguish the A, B and C horizons in the agricultural soil. The paddy soils were sampled using a plastic spade to avoid any heavy metal contamination. Each paddy soil sample comprised a composite of five sub-samples taken within a 1×1 m^2 square.

The paddy soil samples were air dried at 25°C for one week and sieved through a 2 mm polyethylene sieve to remove plant debris, pebbles and stones. Afterwards they were ground in a mechanical agate grinder into a fine powder for subsequent physicochemical parameters and geochemical analysis.

All paddy soil samples were analysed for heavy metal concentrations in a certified commercial Canadian laboratory (Acme Analytical Laboratories, Vancouver, B.C., Canada) by extraction for 1 h with 2-2-2-HCl-HNO_3-H_2O at 95°C with ICP-MS.

The accuracy and precision of the paddy soil analysis were assessed using an international reference material such as Canadian Certified Reference Material Project (CCRMP) SO-1 (soil) and United States Geological Survey (USGS) G-1 (granite).

The analytical precision and accuracy were better than ±5% for the investigated elements. This was indicated by the results of the duplicate measurements in 10 soil samples as well as duplicate measurements of the G-1 and SO-1 standards.

Results and discussion

Heavy metal concentration in the paddy soil

Table 1 shows the concentrations of Ag, As, Cd, Cu, Mo, Ni, Pb, Sb and Zn determined in the paddy soil samples from Kočani Field together with the assumed permissible level (1st limiting level) of heavy metals adopted by the National Environmental Protection Agency of Slovenia (EPA-Slovenia URADNI LIST RS, 1996), typical heavy metal contents of comparable soils around the world (BOWEN, 1979) and the maximum allowable concentrations (MAC) of trace elements in agricultural soil proposed by the GERMAN FEDERAL MINISTRY OF ENVIRONMENT (1992).

The permissible level of heavy metals and the MAC of trace metals signify the values above which toxicity is considered possible.

Table 2 displays the descriptive statistical parameters (mean, median, range and standard deviation (SD)).

The Ag, Mo, Ni, Sb concentrations defined in the paddy soil samples from Kočani Field were corresponding to the average worldwide values for Ag (WEDEPOHL, 1974) and Sb (BOWEN, 1979) and did not exceed the limit values for Mo and Ni reported by the Environmental Protection Agency of Slovenia (Table 1).

Very high concentrations of As, Cd, Cu, Pb and Zn (Table 1) were found in the paddy soils samples from Section VII. The determined values significantly exceeded the typical As content within comparable soils around the world (BOWEN, 1979), as well as the limit values for As, Cd, Cu, Pb and Zn suggested by the environmental protection agencies of Slovenia and Germany (Table 1).

Table 1. Total heavy metal concentrations in the paddy soil of Kočani Field: (1) typical contents of Ag, As, Cd, Cu, Mo, Ni, Sb, Pb and Zn in comparable soils around the world; (2) limits for elemental concentrations in soil (EPA-Slovenia, URADNI LIST RS, 1996); (3) maximum allowable concentrations (MAC) of trace elements in agricultural soils proposed by the GERMAN FEDERAL MINISTRY OF THE ENVIRONMENT (1992).

Element (μg/g) **Location**	**Ag**	**As**	**Cd**	**Cu**	**Mo**	**Ni**	**Pb**	**Sb**	**Zn**
I-1	0.7	3.4	0.1	14.9	0.5	15.6	19.1	0.2	53
I-3	0.2	18.7	0.5	40.3	1	31.1	81.3	0.6	162
I-5	0.1	5.6	0.2	32	0.5	29.7	18.8	0.2	85
I-6	0.7	5.1	0.1	25.9	0.5	25.7	13.1	0.2	70
II-1	0.1	6.1	0.2	26.7	0.5	29.4	26.6	0.2	93
II-3	0.1	5	0.1	29.1	0.4	28.2	21	0.2	81
II-5	0.1	5.3	0.2	24.9	0.5	22	20.8	0.3	80
II-6	0.1	11.8	0.3	25.7	0.6	20.8	32.1	0.8	100
III-1	0.1	6.1	0.2	27.2	0.6	27.5	18.1	0.2	89
III-3	0.1	3.1	0.4	32.6	0.3	25.4	20.4	0.2	95
III-5	0.1	8.3	0.2	32.7	0.5	36.8	23.9	0.2	102
III-7	0.7	8.2	0.2	16.8	0.3	13.9	22.1	0.4	64
III-8	0.7	4.2	0.1	21.8	0.5	20.8	10.5	0.1	64
IV-1	0.1	3.8	0.1	28.5	0.7	21.7	13.9	0.2	74
IV-2	0.7	3.5	0.2	17.1	0.6	17.3	17.9	0.2	68
IV-3	0.7	4.3	0.3	23.4	0.5	24.1	19.1	0.2	102
IV-5	0.1	6.3	0.2	25.7	0.6	25.5	15.4	0.2	94
IV-7	0.1	8.1	0.2	26.2	0.7	26.1	17	0.2	83
IV-8	0.1	5.9	0.2	28.9	0.6	28.6	18.1	0.2	96
V-1	0.1	10	0.2	19	0.7	9.1	30.8	0.3	85
V-3	0.1	7.8	0.2	20	0.6	9.5	26.9	0.2	73
V-5	0.1	6.5	0.2	25	0.6	22.8	22.1	0.2	98
V-7	0.1	6.4	0.2	22.8	0.4	17.2	17.8	0.3	67
V-9	0.1	4.5	0.2	20.8	0.3	16.7	19.2	0.3	69
VI-1	0.1	5	0.2	21.4	0.3	17.1	24.1	0.3	71
VI-2	0.1	6.8	0.3	24.5	0.6	9.9	39.4	0.2	76
VI-3	0.1	10.1	0.3	34.1	0.6	22.3	35.4	0.3	86
VI-4	0.1	9.9	0.3	28.6	0.5	25.2	41.4	0.4	105
VI-5	0.1	10.5	0.3	25	0.5	21.7	39.6	0.4	94
VI-6	0.1	11.5	0.3	28.3	0.6	22	45.1	0.5	107
VI-7	0.7	7.7	0.1	19.3	0.5	16.4	20	0.4	66
VI-8	0.7	6.2	0.2	29.5	0.5	30.5	16.3	0.2	72
VII-1	0.9	22.2	2.7	48.8	1.3	10.9	411.9	1.8	531
VII-2	2	42	5.6	99.4	1.8	15.4	892.4	2.5	1134
VII-3	1.4	35.1	4.5	89.4	1.4	15.5	726.7	2	893
VII-4	2.1	47.6	6.4	80.1	1.8	11.9	983.1	3	1245
VII-5	1.6	39.6	5	68.3	1.6	14.1	745.1	2.2	928
VII-6	0.6	20.7	2	47.1	0.9	19.8	295.7	1	384
1	0.1-8	6	0.35	30	/	/	35	1	90
2	/	20	1	60	10	50	85	/	200
3	/	/	1.5	60	/	/	100	/	200

Table 2. Descriptive basic statistic parameters for heavy metals in the paddy soils of Kočani Field.

Elements (μg/g)	Ag	As	Cd	Cu	Mo	Ni	Sb	Pb	Zn
Mean	0.306	11.4	0.9	33	0.682	21.0	0.57	128	206
Median	0.100	6.7	0.2	26	0.600	21.7	0.25	22	88
Minimum	0.066	3.1	0.1	15	0.300	9.1	0.10	11	53
Maximum	2.100	47.6	6.4	99	1.800	36.8	3.00	983	1245
S.D.	0.541	11.3	1.7	20	0.389	6.8	0.72	260	310

To compare the distribution of each heavy metal in the paddy soil samples between Sections I–VII, whisker plots were employed (Fig. 3).

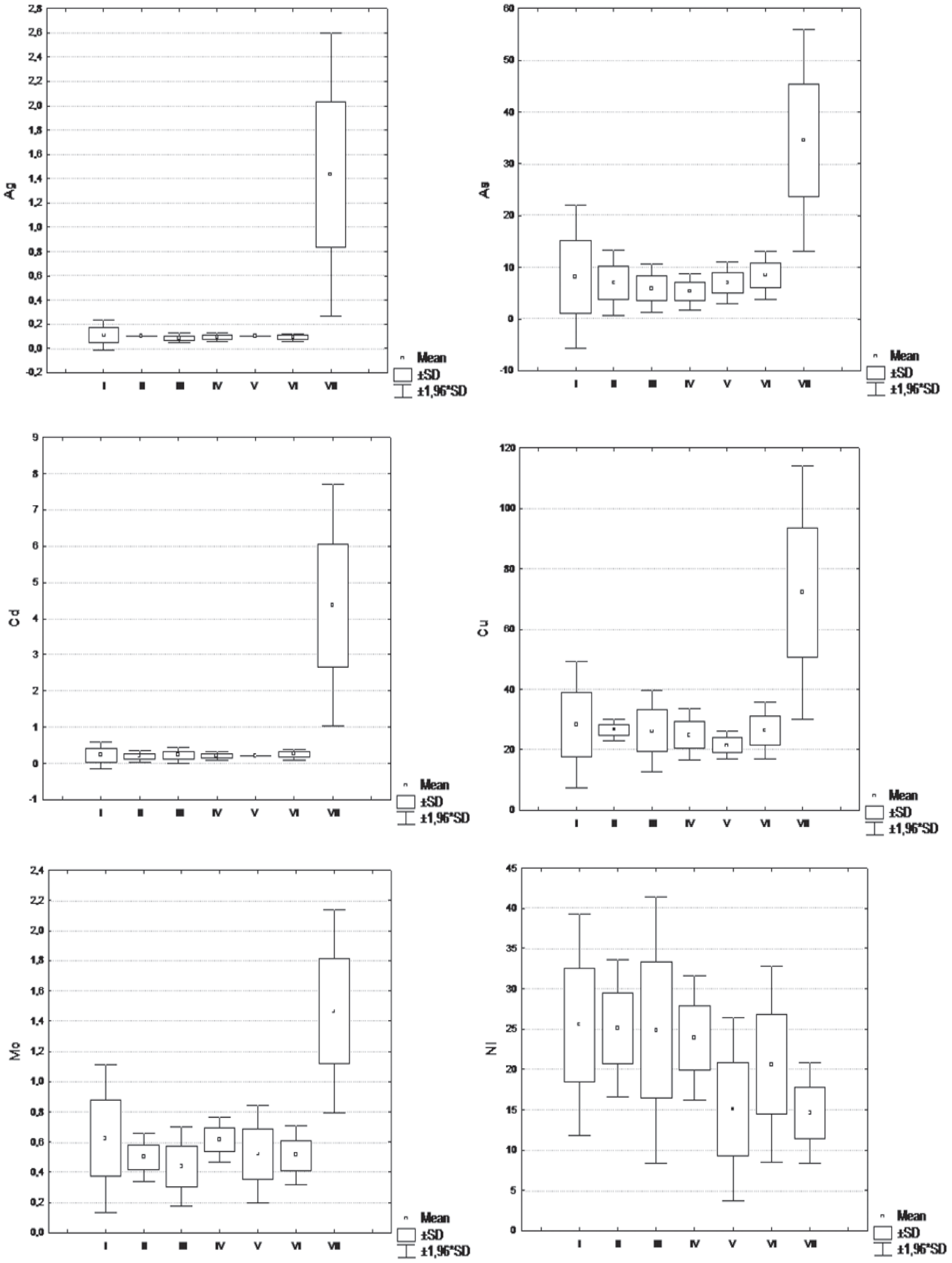


Fig. 3. Whisker plots of Ag, As, Cd, Cu, Mo, Ni, Pb, Sb and Zn for paddy soil samples.

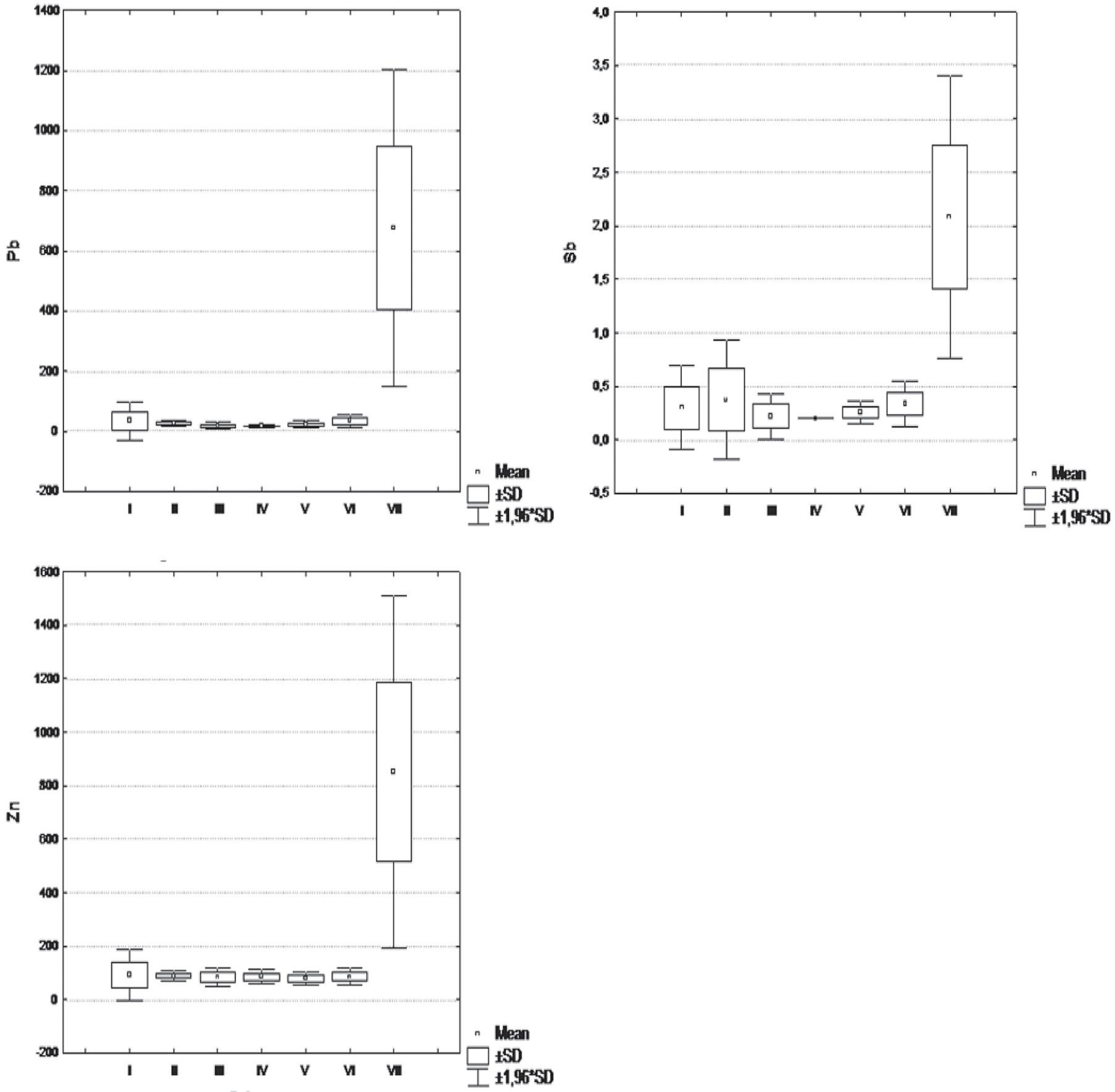


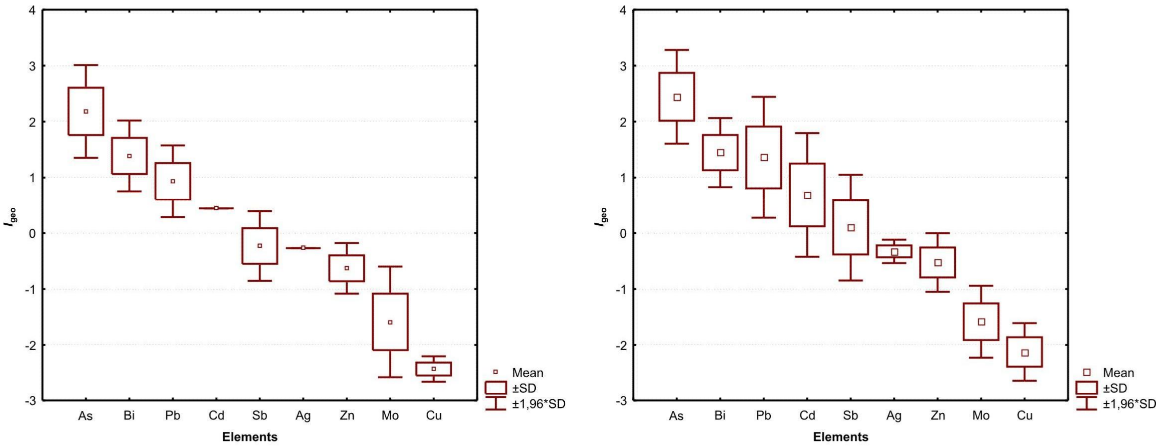
Fig. 3. ***(continued)*** Whisker plots of Ag, As, Cd, Cu, Mo, Ni, Pb, Sb and Zn for paddy soil samples.

All soil samples in Sections I–VI had similar levels of median values, suggesting that their intersection differences were not substantial, whereas significant variations existed only between Section VII and the other sections. The only exception and consequently difference was is the distribution of the Ni values in the paddy soil samples.

Index of geoaccumulation (I_{geo})

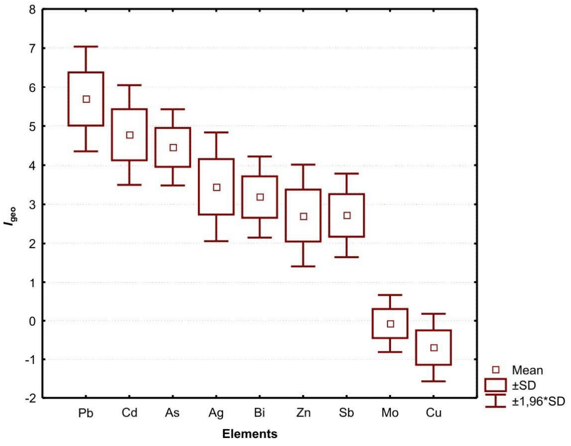
The I_{geo} values for Ag, As, Bi, Cd, Cu, Mo, Pb, Sb and Zn in the studied soils are showed in Fig. 4. The I_{geo} and contamination level results for soil samples from profile A ranging from –2.6 (Cu) to 2.74 (As) indicated the disposition of metals as: As > Bi > Pb > Cd > Sb > Ag > Zn > Mo > Cu.

The obtained I_{geo} values for profile B revealed the range from –2.4 (Cu) to 2.94 (As). The results showed that the examined soils were moderately to highly polluted with As (I_{geo} classes 3, 4), uncontaminated to moderately polluted with Bi, Pb, Cd and Sb (I_{geo} classes 1, 2, 3) and uncontaminated with Ag, Zn, Mo, and Cu (I_{geo} class 1). According to the I_{geo} and the contamination level, the degree of contamination from strong to weak in studied soils from profile B was (equally like in profile A): As > Bi > Pb > Cd > Sb > Ag > Zn > Mo > Cu.



PROFILE A

PROFILE B



PROFILE C

Fig. 4. Box plots of I_{geo} values for paddy soils (profile A, B and C)

The calculated I_{geo} values for samples from profile C ranged from –0.74 (Mo) to 6.36 (Pb). The paddy soils from profile C are categorized as highly to very seriously polluted with Pb, moderately to very highly polluted with Ag, As, Bi and Cd (I_{geo} classes 4, 5, 6), moderately to highly polluted with Sb and Zn (I_{geo} classes 3, 4, 5) and uncontaminated Cu and Mo (I_{geo} class 1). Based on I_{geo} clasification, the magnitude of metal pollution of paddy soils in profile C was in the following order: Pb > Cd > As > Ag > Bi > Zn > Sb > Mo > Cu.

The paddy soil samples from Section VII, located in the vicinity of the Zletovska River and Zletovo-Kratovo ore district, received a comparatively higher input of anthropogenically derived heavy metals than other parts of the Kočani area. The As, Cd, Cu, Pb and Zn concentrations determined in the paddy soils from Section VII significantly exceeded maximum permissible levels. The distinction between heavy metal contents in Section VII and the other sections was also confirmed by statistical analysis. The pollution in Section VII is undoubtedly related to the irrigation of the paddy fields with the riverine water from the Zletovska River, which drains acidic mine waters and untreated mining waste effluents from the Zletovo-Kratovo mine (ALDERTON et al., 2005).

Elevated concentrations of As, Cd, Cu, Pb and Zn were observed in other paddy soil sections (especially Sections V and VI). This elevation originates from the discharges of the untreated municipal and domestic waste from the city of Kočani and the village of Orizari into the riverine systems of the Kočanska and Orizarska Rivers, which are both used for irrigation purposes. The increased concentrations of the investigated heavy metals could also be explained by the agricultural application of various fertilisers and pesticides, urban and traffic sources and atmospheric deposition.

Although the concentrations of Ag, Mo, Ni and Sb were below the mentioned threshold values, their enrichment in the paddy soil samples near the Zletovska River was also noticeable. This situation confirms the higher input of heavy metals in the area around the Zletovska River.

The high anthropogenic impact on the paddy soils in Section VII was as well demonstrated by the calculation of the Index of geoaccumulation (I_{geo}). The elevation of the heavy metals present in the paddy soil samples from the other parts of Kočani Field was similarly verified with the results of the environmental indexes. From an environmental point of view, it is evident that the paddy soil samples from Section VII represent a serious risk to the surrounding ecosystems (DOLENEC et al., 2007; ROGAN et al., 2009, ROGAN et l., 2010).

Conclusions

As, Cd, Cu, Pb and Zn concentrations determined in the paddy soils from Section VII significantly exceeded the permissible maximum levels. Although the concentrations of Ag, Mo, Ni and Sb were below the mentioned threshold values, their enrichment in the paddy soil samples near the Zletovska River was noticeable, consequently confirming the higher input of heavy metals in the area around the Zletovska River.

The high anthropogenic impact on the paddy soils in Section VII was demonstrated by the calculation of the index of geoaccumulation. The elevation of the heavy metals present in the paddy soil samples from other parts of Kočani Field was similarly verified with the results of the environmental index.

According to the results of the heavy metal concentrations present in the paddy soil the area around the Zletovska River is considered as the most anthropogenically impacted part of Kočani Field. The highly elevated concentrations of the analysed heavy metals were undoubtedly related to past and present mining activities, especially in the Zletovo-Kratovo ore district.

Acknowledgements

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References

ADRIANO, D.C. (1986). *Trace Elements in the Terrestrial Environment (1st ed.)*. New York : Springer-Verlag.

ALDERTON, D.H.M., SERAFIMOVSKI, T., MULLEN, B., FAIRALL, K., JAMES, S. (2005): The chemistry of waters associated with Metal Mining in Macedonia. *Mine water and the Environment*, 24, 139-149.

BOWEN, H.J.M. (1979): *Environmental Chemistry of the Elements* (1st ed.). New York : Academic Press.

DOLENEC, T., SERAFIMOVSKI, T., TASEV, G., DOBNIKAR, M., DOLENEC, M., ROGAN, N. (2007): Major and trace elements in paddy soil contaminated by Pb–Zn mining: a case study of Kočani Field, Macedonia. *Environmental Geochemistry and Health*, 29, 21-32.

GERMAN FEDERAL MINISTRY OF THE ENVIRONMENT (1992): Novelle zur Verordnung über das Aufringen von Klärschlamm (Bundesgesetzblatt).

HAKANSON, L. (1980): An ecological risk index for aquatic pollution control: a sedimentological approach. *Water Resources*, 14, 975-1001.

JUNG, M.C. (2001): Heavy metal contamination of soils and waters in and around the Imcheon Au-Ag mine, Korea. *Applied Geochemistry*, 16, 1369-1375.

JUNG, M.C. & THORNTON, I. (1997): Environmental contamination and seasonal variation of metals in soils, plants and waters in the paddy fields around a Pb-Zn mine in Korea. *Science of the Total Environment*, 198, 105-121.

KABATA-PENDIAS, A. & PENDIAS, H. (2001): *Trace Elements in Soils and Plants (3rd ed.)*. Boca Raton : CRC Press.

KORRE, A., DURUCAN, S., KOUTROUMANI, A. (2002): Quantitative-spatial assessment of the risks associated with high Pb loads in soils around Lavrio, Greece. *Applied Geochemistry*, 17, 1029-1045.

LEE, C.G., CHON, H.T., JUNG, M.C. (2001): Heavy metal contamination in the vicinity of the Daduk Au-Ag-Pb-Zn mine in Korea. *Applied Geochemistry*, 16, 1377-1386.

LI, X.D., COLES, B.J., RAMSEY, M.H., THORNTON, I. (1995): Sequential extraction of soils for multielement analysis by ICP-AES. *Chemical Geology*, 124, 109-123.

LIU, H., PROBST, A., LIAO, B. (2005): Metal contamination of soils and crops affected by the Chenzhou lead/zinc mine spill (Hunan, China). *Science of the Total Environment*, 339, 153-166.

LOSKA, K., WIECHULA, D., KORUS, I. (2004): Metal contamination of farming soils affected by industry. *Environment International*, 30, 159-165.

LU, X., ZHANG, X. (2005): Environmental geochemistry study of arsenic in Western Hunan mining area, P.R. China. *Environmental Geochemistry and Health*, 27, 313-320.

ROGAN, N., SERAFIMOVSKI, T., DOLENEC, M., TASEV, G., DOLENEC, T. (2009): Heavy metal contamination of paddy soils and rice (*Oryza sativa* L.) from Kočani field (Macedonia). *Environmental Geochemistry and Health*, 31, 439-451.

ROGAN ŠMUC, N., DOLENEC, T., SERAFIMOVSKI, T., TASEV, G., DOLENEC, M. (2010): Distribution and mobility of heavy metals in paddy soils of the Kočani Field in Macedonia. *Environmental earth sciences*, 61, 899-907.

SIMMONS, R.W., PONGSAKUL, P., SAIYASITPANICH, D., KLINPHOKLAP, S. (2005): Elevated Levels of Cadmium and Zinc in Paddy Soils and Elevated Levels of Cadmium in Rice Grain Downstream of a Zinc Mineralized Area in Thailand: Implications for Public Health. *Environmental Geochemistry and Health*, 27, 501-511.

TESSIER, A., CAMPBELL, P.G.C., BISSON, M. (1979): Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, 51, 844-851.

URADNI LIST RS (1996): Uredba o mejnih opozorilnih in kritičnih emisijskih vrednostih nevarnih snovi v tleh. *Uradni list*, 68, 5773-5774.

YANG, Q.W., SHU, W.S., QIU, J.W., WANG, H.B., LAN, C.Y. (2004): Lead in paddy soils and rice plants and its potential health risk around Lechang Lead/Zinc Mine, Guangdong, China. *Environment International*, 30, 883-889.

WEDEPOHL, K.H. (1974): *Handbook of Geochemistry (1st ed.)*. Berlin : Springer–Verlag.

WHITBY, L.M., GAYNOR, J., MACLEAN, A.J. (1978): Metals in soils of some agricultural watersheds in Ontario. *Canadian Journal of Soil Science*, 58, 325-330.

WITTE, K.M., WANTY, R.B., RIDLEY, W.I. (2004): Engelman Spruce (Picea engelmannii) as abiological monitor of changes in soil metal loading related to past mining activity. *Applied Geochemistry*, 19, 1367-1376.

WONG, S.C., LI, X.D., ZHANG, G., QI, S.H., MIN, Y.S. (2002): Heavy metals in agricultural soils of the Pearl River Delta, South China. *Environmental Pollution*, 119, 33-44.

IDENTIFICATION OF HARMFUL IMPACT ON THE WORKING ENVIRONMENT OF OPERATIONS IN " BUCHIM " MINE

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Abstract

The tailing is one of the riskiest facilities within the mining complex. The data show that the tailingthere is a largest share of adverse impacts on the environment and possible-disruption of thestability of the tailing dam and the consequence is the outpouring of waste rock out of mine. In this paper will be present the harmful environmental impacts caused by the performance of workoperations within the mine and that: adverse impacts on water, air and land and will be proposed measures for their reduction.

Introduction

The environment is a complex system whose components are interrelated and dependent on each other so that changes in one part can cause changes in other parts. That is why the issue of protecting the environment from harmful influences, can only be dealt with systematically integrated approach. Tailing dumpas object is certainly one of the riskiest facilities throughout ore complex. FlotationTailing dump which accumulate large amounts of very fine, mixed with chemically contaminated water, a technological need, but also a real danger to the environment.

In order to provide protection measures, it is good to know the negative impacts of flotation tailingflotaciskitejalovishta. Within this paper will be referred to the harmful environmental impacts caused by the performance of work operations within the "Buchim" mine and will be proposed measures for their reduction.

The impact of talling on environment

Influence of flotation tailing on the environment, in terms of design and controlled exploitation can be viewed through the following elements:

- Takingof land for their establishment;
- Pollution of surface water flows in the discharge of excess water or overall deposition lake and discharge of drainage waters;
- Pollution of underground water flows and filtration waters;
- Air pollution in fine particles from the parched slag, which are distributed under the effect of air currents;
- Pollution of land in the deposition of particles blown by the wind or a contamination by polluted waters;
- The potential risk of accidents during the destruction of levees that can result in major damage and possible casualties.

Adverse impacts on the environment and the immediate working environment of the working operations to be carried out within the process of surface mining of copper ore mine in the mine can be grouped into two main groups:

- degradation of the earth's surface and
- Pollution of the environment.

The pollution of the environment is manifested through pollution: soil, water and air.

Soil pollution

The pollution of soil in the vicinity of the mine "mine" is limited to the immediate area around the mine through aerosedimentation or accumulation of dust emitted during mining operations, as well as the soil near the beds of rivers that flow through the mine waste water. Actual analysis of samples of soil near the river Topolnica confirm that the level of contamination with salts of heavy metals in soil is above the allowed (Table 1). These assays are made within the study for assessing the environmental impact of the operation of the Buchim mine.

Test samples were taken at a distance of 25 m left and right along the River. Samples of soil taken from the layer which is located under the humus layer near the flotation tailing above village Topolnica.

Through chemical analysis performed on samples of soil along the river Topolnica identified increased concentrations of heavy metals in soil Fe, Cu, then Al, Ba, Ni, Zn, Cd, As and these concentrations are above the maximum allowable.

Special measures to protect soils from pollution by harmful substances are not provided because their pollution will be prevented through indirect measures to be taken for purification of waste water and measures to protect against air pollution.

Table 1. Results of the chemical analysis of soil samples

MDK	**Metal**	**Buchim**
		measured values (µgr/l)
		Tailing dump
(%)		(%)
0,26	Al	2,20
1,40	Fe	4,84
	Ca	1,65
	Mg	2,00
	Ma	0,131
	K	1,41
0,040	Mn	0,072
	Ti	0,182
	P	0,162
[mg/kg]		[mg/kg]
17,50	Cu	35,00
49,00	Sr	20,81
0,70	Ba	244,05
9,90	Ni	25,84
10,00	Cr	55,22
22,50	Zn	87,97
10,50	Pb	8,71
10,00	Co	19,68
0,20	Cd	6,64
50,00	V	79,00
1,10	As	3,08
< 0,5	Ag	0,53

Note: analysis was made in chemical laboratories of FNTSStip

Water pollution

Although almost 95% of the wastewater system through technological processes of recirculation of the dam Topolnica again returned to production processes still a fraction of the contaminated water is discharged into nearby waterways performing their contamination with harmful substances.

According to the performed chemical analysis of samples of wastewater was determined that under the water klasification these waters belong to water class III, or contaminated water, which is especially pronounced concentrations of copper. Because it is polluted waters is proposed the following measures to protect water:

- measures to reduce the amount of water coming out of the zone of mine
- measures for purification and quality control efluentnite waters.

Also, as a result of long term discharge of contaminated water comes to the accumulation of harmful substances on the sides of the bed and around him, which leads to contamination and the surrounding land. So, water is a transporter of hazardous substances.

The waters of the drainage system from tailing dump of Buchim mine directly goes in the Topolnica river on which bed is built landfill for flotation slag, essentially is neutral to basic (pH 6-7) because flotation slag which is discharged into the landfill is extremely basic.

Table 2. Results of chemical analysis of water from r.Topolnic apropos draining water from tailing dump

Classification according regulation of division of water			metals	Water from r. Topolnicainflow JasenovDol	
I-II class	III-IV class	V class		measured values (μgr/l)	
MDK (μgr/l)				TP1	class
30	50	>50	As	169,27	V
2	20	>20	Ag	0,1047	I
100	100	>100	Ti	25,452	I
1500	1500	>1500	Al	150,14	I
1000	4000	>4000	Ba	56,405	I
50	100	>100	Ni	1,7152	I
50	1000	>1000	Mn	57,104	III-IV
300	1000	>1000	Fe	43,837	I
50	100	>100	Cr	-0,673	I
100	200	>200	V	1,6428	I
			P	47,352	I
100	200	>200	Zn	3,3533	I
10	50	>50	Cu	57,745	V
10	30	>30	Pb	11,497	III-IV
0.1	10	>10	Cd	0,106	III-IV
100	2000	>2000	Co	3,9109	I

Note: analysis was made in chemical laboratories of FNTSStip)

All the above mentioned findings on the impact of tailing dumps on surface water flows related to the controlled conditions of their exploitation.In practice very often, due to various objective and subjective factors, uncontrollable situations arise, that lead to it in a short period of time the emission of the water hazards increase many times.The reason for their occurrence mostly minor or major cancellations in the transport systemflotation slag, and defects of other ancillary systems tailing landfill. It is especially dangerous if it came directly to the outpouring of slag flotation in the rivers.

Air pollution

Air pollution is generally expressed by:

- Air pollution with floating fractions of mineral dust (particulate matter) various gases (SOx, NOx, CO), volatile organic substances (VOC `s), methane and other harmful substances including radionucleides

-Change the microclimate and the creation of zones with a specific microclimate, the climate different from the surrounding area, etc.

- Noise as a separate factor of pollution of the atmosphere, both psychological (comfortable) and the physiological aspect.

Characteristic of surface exploitation of mineral resources is that in almost all stages of development of the technological process:escavation earth masses, their transport and again deposition, results with separating the floating mineral particles.

By separating the dust comes in other operations that are part of the evaluation of the mineral resource. These include operationscomminution, purification, enrichment and primary processing of mineral raw materials.

Some minor amounts of dust emitted in the phase of geological research and the development of pit and stage in the development of trench in which to build access roads, the useciteotvoranje and various ancillary facilities,creates dust, but with less intensity, which usually differs from the intensity of the separation of dust in the same activities that are not part of the mining industry.

Machinery, vehicles and other mining equipment used in the process of getting the copper emissions NOx, SOx, CO and volatile organic compounds, which increase the amount of harmful substances present in the air.

Given the fact that the mine mine were not done measurements of emissions of harmful components, is made the same assessment. To this aim ,is used methodology which was recommendation by the USEPA and Australian NPI for Mining Industry.

The estimate is based on real (material) parameters for the intensity of individual activities (mentioned above) in the mine that are considered sources of emissions of harmful components in the air.These estimates of emissions aircontamination which assumes that goes out from the immediate area of mining activity and has national significance (such as greenhouse gases).

Depending on the degree of sigurnost factor of any given set of factors is an evaluation (rating) according to the following system:

A - Excellent reliability
B –above average security
C - average security
D – below average security
E - small security
U –unranging

Table 3. Assessment of fugitive emission from primary processing (preparation) of metallic mineral resources of the Buchim mine

Data on working hours					
Total working days					240 anual
Total hours					16daily
Working hours per year					3840 h/year
Capacity					4000000 t/year
	DEF (kg/t)		Фактор	Estimated emission (kg/god)	
	TSP	PM_{10}		TSP	PM_{10}
Activity					
Primary crushing	0,2	0,02	C	800000	80000
Secondary crushing	0,6	0,06	D	2400000	240000
Tertiary crushing	1,4	0,08	E	5600000	320000
Sowing, classification	0,08	0,06	C	320000	240000
Loading, unloading, transport and storage	0,06	0,03	C	240000	120000
Total plant for the preparation of mineral raw materials				**9360000**	**1000000**

Table 4. Total fugitive emissions and solid particles in the air from mining operations and facility for primary processing of mineral raw materials

Source of show	kg/anual					
	TSP	PM_{10}	CO	NO_x	SO_x	VOC_s
Blasting	5451,94					
Transportation	421950	104400				
Reciprocating internal combustion		14602	15505	40275	1918	3140
Primary plant preparation (comminution and classification)	9360000	1000000				
Flotation slag dump	97500	48750				
TOTAL	**9884902**	**1167752**	**15505**	**40275**	**1918**	**3140**

Because visibility light emission of gases and dust resulting in a series of negative changes, which significantly impair the overall environmental acceptability and image of mine, condition and possible problems before the inspection authorities are responsible for control of hygienic and technical conditions at work, because it is urgently necessary to overcome it.

To prevent the broadcasting of harmful particulate matter in air are proposed following categories of safeguards:

-control measures fugitivnata dust in production processes, and
-Measures to control dust that occurs as a result of erosion eol flotation tailing.

In the first category of measures include:

- measures to reduce the dust in the process of the ore usitnuvanje (mills, screens, open disposal sites, etc..)
- measures to suppress dust transport pathways in the mine.

In the category of measures to control dust that occurs as a result of eol erosion tailing flotation include:

- planting vegetation on the final part of the dam,
- technologies for surface stabilization of dust (spray with water and use binderi to create a surface layer).

Conclusion

Starting from the fact of interconnection and interaction of individual parts of the ecosystem, as well as technological processes taking place in the mine as the only way that can provide efficient and cost effective solution to the identified problems is integrated - systemic approach in their resolution.Namely, in order to ensure maximum efficiency of the proposed measures, and to ensure their successful implementation, it is their integration into a comprehensive *Plan for control and environmental management (EMP) in the zone of influence of mine.*This plan will be the basis for the possible establishment of a *System for Environmental Management (Environmental Menagement System-EMS)* in accordance with the recommendations of the ISO 14000 series standards.

Flotation postponement could be rehabilitated in the direction of creating new values in the first new plant and animal habitats, forest communities, aquatic habitats and the like.

References

Крстев, Б., 2004, „Флотацискихидројаловишта”.

Рударско-геолошкифакултетШтип, 2006, тудија за процена на влијанието врз животната средина од работењетонарудникот„Бучим”

Хаџи-Николова, М., 2008 „Загрозување на животната средина предизвикано од нарушување на стабилноста на земјени брани под дејство на сеизмички побуди“- Магистерски труд.

Case studies on tailings management, International Council on Metals and the Environment United Nations Environment Programme

Management of Tailings Facilities prepared by the Mining Association of Canada, 1998

HEAVY METALS IN GROUND WATERS IN THE ALLUVIUM OF THE MAVROVICA RIVER-SVETI NIKOLE (EASTERN MACEDONIA)

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Abstract

Within this paper are given the results and conclusions from study of heavy metals pollution of Mavrovica river alluvium. Our study managed efforts to get insight into the condition with presence of heavy metals in ground waters of the aforementioned river. The water samples were taken at few points (wells), from 10-15 m depth and they have been analyzed within one series of analyses at the instrumentation atomic emission spectrometry-inductive coupled plasma (AES-ICP). From up to date experiences with contamination of similar areas it should be concluded that we have to pay attention to the following group of elements: Mn, Fe, Al, Pb, Zn, As, Cd, Cu, Ni, Co, Ag, Cr and Ti with possibility to study some other elements that will show increased concentrations compared to MDK (maximally allowed concentrations).

After the analysis and interpretation of data were not determined increased values for the most of the analyzed elements.

Key words: heavy metals, pollution, AES-ICP, Mavrovica river, increased concentrations, water, maximal allowed concentrations.

Introduction

Pollution of the environment in past few decades, used to be a topic to which was given minimal importance, but however in last few years this topic gained top priority. Of special interest is the presence of heavy and toxic metals in waters. It is important to point out the presence of metals-contaminants in drinking water.

In the adjacent vicinity of the aforementioned area there are numerous farmlands used in production different crops. Up to date studies from the geological-geochemical and environmental aspect are pointing to a potential for natural pollution of the studied area. Even the more important reasons for performing this study were the more strict law norms for the quality of the living environment, where have been located settlements of the local population.

In the study of chemical and geochemical features of water from the hydro-accumulation Mavrovica and its adjacent areas have participated numerous researchers. Data related to this issue can be found in Spasovski et al., (2007, 2009, 2010), Ракичевиќ и др. (1968), Ѓузелковски (1997), Карајовановиќ и др. (1975, 1983), Думурџанов и др. (1976).

The area, which have been subject of study encloses aluvion of the Mavrovica River at distance of around 4 km northeast from Sveti Nikole (Fig. 1).

Fig. 1.Map of the Republic of Macedonia with pointed position of the studied area

Results and discussion

Within the planned studies have been sampled wells located in the close vicinity of the Mavrovica river flow (Figure 2).

Obtained results for concentration of heavy metals in ground waters from the Mavrovica river alluvium are shown in Table1.

To get a more complete impression about the concentrations of the analyzed elements in water samples taken from the Mavrovica river alluvium in the review below we are going to present and discuss data from performed study.

Within the same table are given standard values for concentrations of analyzed elements in spring waters, to be able to compare obtained values with standard ones.

According to Table 1 certain conclusions regarding the presence of particular heavy metals in river water and its tributaries arise, as well as the conclusions about the reasond that have contributed to increased concentrations of particular metals.

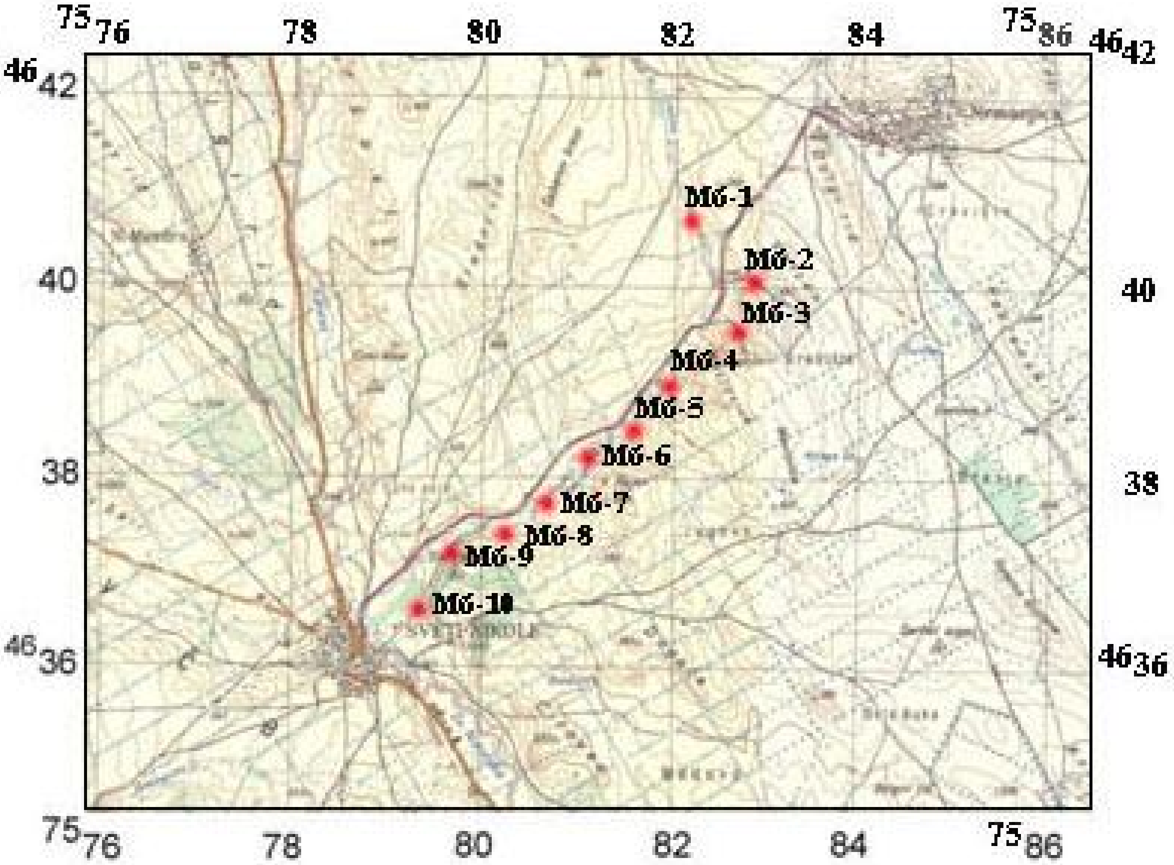

Fig. 2. Topographic map with desiganted sampling positions

Table 1. Concetrations of heavy metals in spring water samples (mg/l)

	Mb-3	**Mb-2**	**Mb-1**	**Mb-4**	**Mb-5**	**Mb-6**	**Mb-7**	**Mb-8**	**Mb-9**	**Mb-10**	**Sr**
As	<0.005	0.03	0.026	0.033	<0.005	<0.005	<0.005	<0.005	<0.005	0.103	0.1293
stand.	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Al	0.009	0.009	0.004	0.001	0.012	0.010	0.007	0.032	0.009	0.007	0.010
stand.	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Ca	115.8	115.6	64.8	37.2	162.4	133.9	114.2	112.9	170.3	92.1	111.92
stand.	200	200	200	200	200	200	200	200	200	200	200
Ni	<0.005	<0.005	0.020	0.0066	<0.005	0.0023	<0.005	0.0078	0.0204	0.005	0.0082
stand.	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Mn	<0.001	<0.001	<0.001	0.0025	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.0011
stand.	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Fe	0.006	0.001	0.001	0.022	0.002	0.004	0.003	0.005	0.0009	0.006	0.0455
stand.	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Cr	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
stand.	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Mg	96.45	56.27	15.33	7.23	74.19	57.95	80.22	61.59	159.99	98.77	70.799
stand.	150	150	150	150	150	150	150	150	150	150	150
Zn	0.0096	0.011	0.007	0.017	0.013	0.007	0.006	0.280	0.003	0.707	0.1060
stand.	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Cu	0.015	0.0001	0.007	0.014	0.008	0.007	0.005	0.009	0.009	0.007	0.0081
stand.	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Pb	<0.005	<0.005	0.009	<0.005	0.008	0.006	<0.005	<0.005	<0.005	<0.005	0.0058
stand.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Cd	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
stand.	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01

Manganese concentrations in spring waters compared to maximal allowed concentrations is shown at Figure 3.

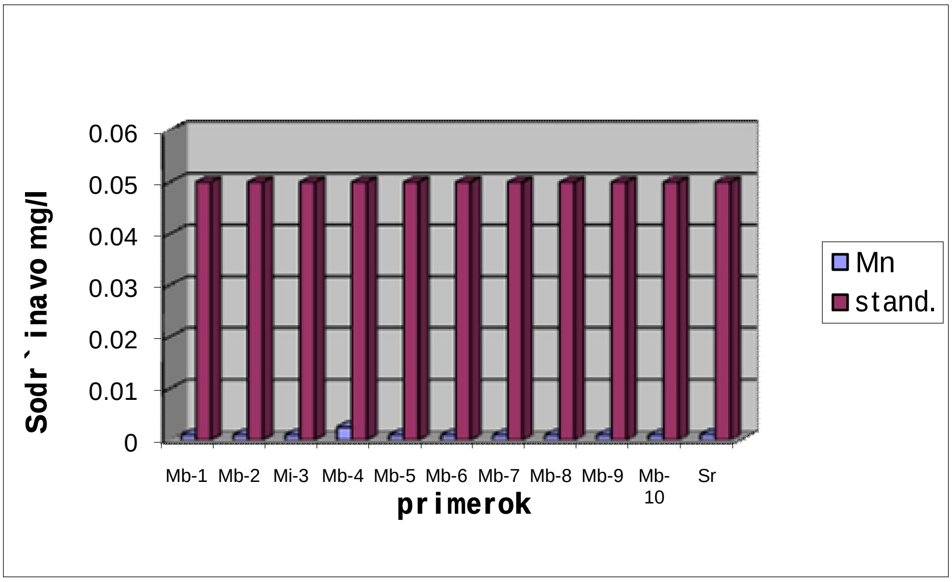

Fig. 3. Plot of manganese concentrations in samples from spring waters of the Mavrovica river alluvium

Very low concentrations of iron were detected in all collected samples, in comparison to the maximally allowed concentrations in drinking water (Table 1). The highest concentration has been determined in sample Mb-4 reaching 0,022 mg/l, while the lowest concentration has bee-n detected in sample Mb-9 with 0,0009 mg/l. From the Table 1 it can be seen that the magnesia concentrations were lower compared to the MDK and only in one sample (Mb-9) concentration is higher than the MDK. As it was mentioned earlier, the maximal allowed concentration was detected in sample Mb-9 and it reaches 159,99 mg/l, while the lowest concentration was detected in sample Mb-4 reaching 7,23 mg/l. Average magnesia concentrations were around 70,799 mg/l. Comparison of determined Mg concentrations in analyzed samples versus maximally allowed concentrations is given in Figure 5.

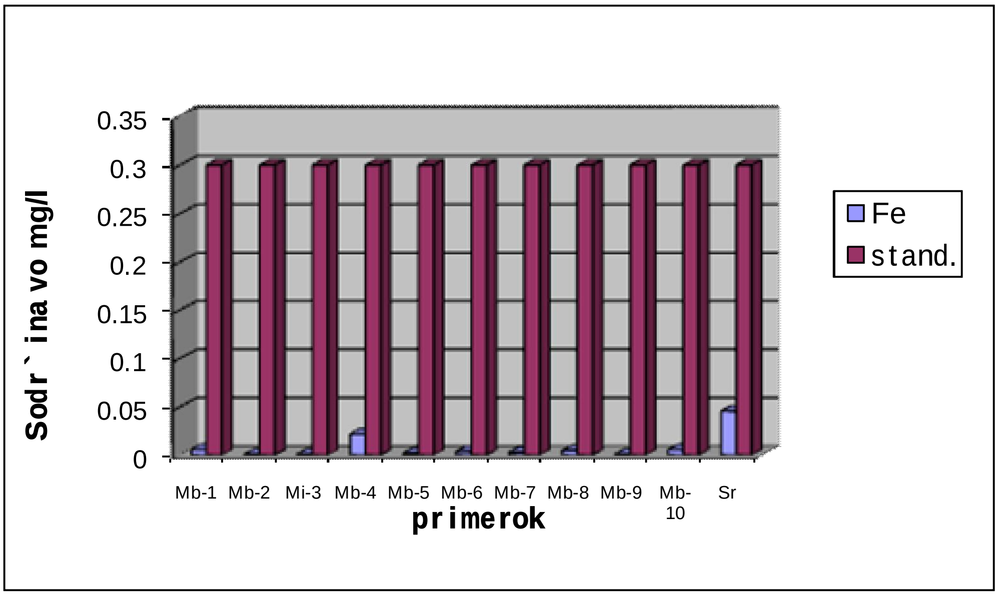

Fig. 4. *Plot of iron concentrations in spring water samples from the Mavrovica river alluvium.*

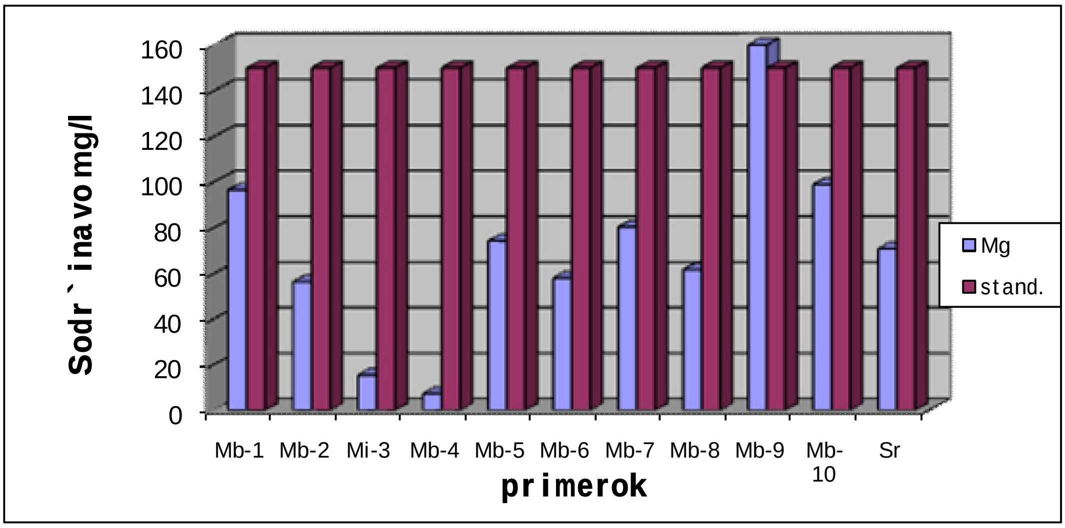

Fig. 5. Plot of magnesia concentrations in spring water samples from the Mavrovica river alluvium.

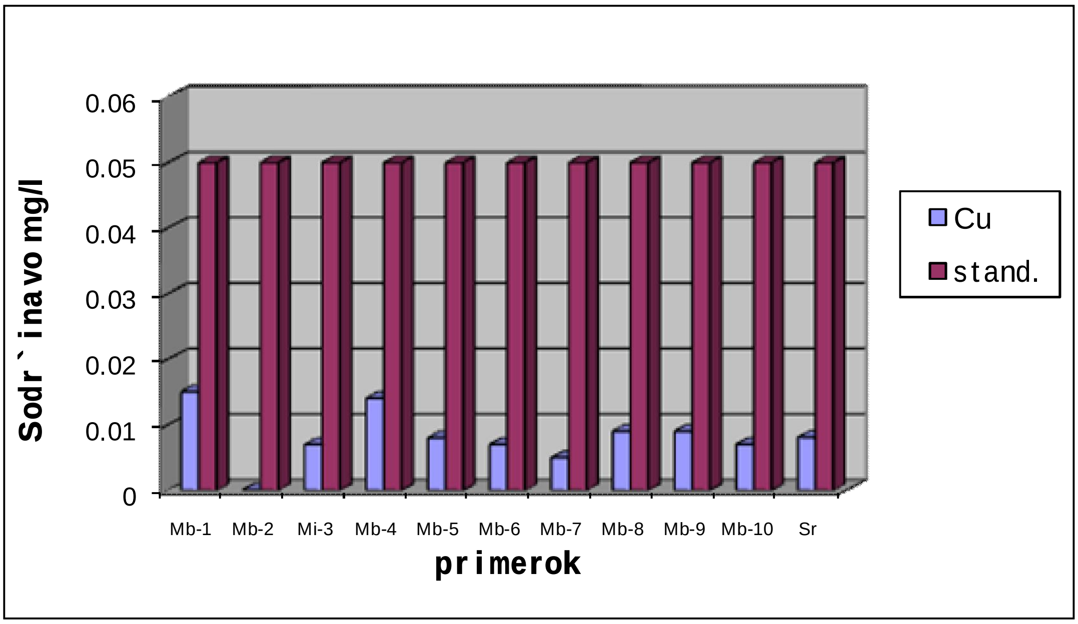

Fig. 6. *Plot of copper concentrations in spring water samples from the Mavrovica river alluvium.*

According to the results shown in Table 1, it may be concluded that similar as it was case with other heavy metals, lead concentrations in all ten samples are significantly lower than maximally allowed concentrations. Maximally allowed concentrations for lead in drinking water is set to 0,1 mg/l, while the maximall concentration of lead in analyzed samples was 0,009 mg/l in Mb-1 and minimal concentration was 0,005 mg/l.

An average concentration of lead was around 0,0058 mg/l.

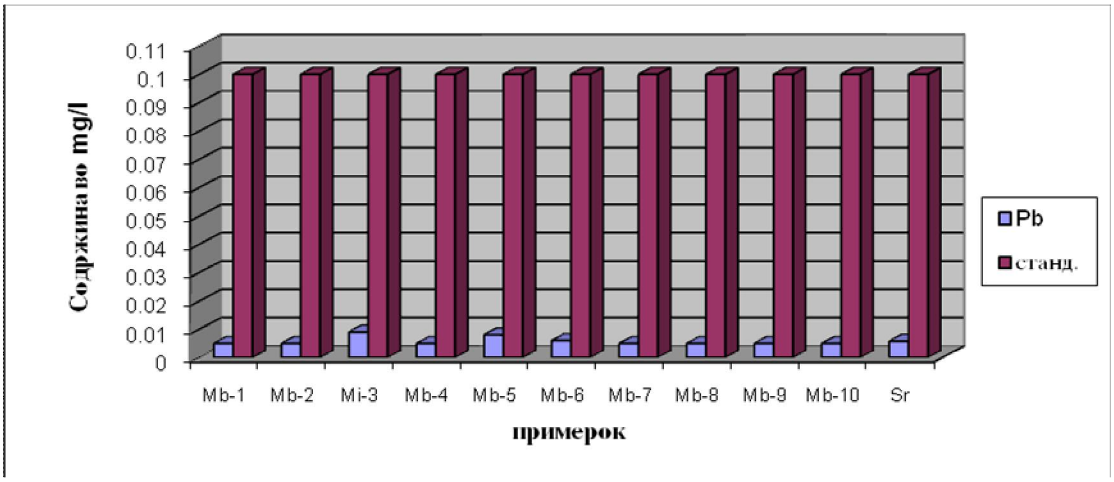

Fig. 7. *Plot of lead concentrations in spring water samples from the Mavrovica river alluvium.*

Conclusion

As we have shown above, none of the analyzed heavy metals (Mn, Mg, Fe, Cu, Ni, Cr, Cd and Pb), are not in concentrations, which could pose environmental and human health treat. Data have shown that the concentrations a far below the maximally allowed concentrations, which makes the analyzed water safe to consume.

References

Alloway, B. J., and Ayres, D. S., 1963: Chemical Principles of Environmental Pollution, Blackwell Scientitic, Piblications, London.

Appelo C.A. J., Postma, D., 2005:*Geochemistry, Grounwater and pollution. 2nd Edition*.A.A. Balkema, Rotterdam/Brookfield. pp 649.

Ѓузелковски, Д., 1997: Подземните води (издан) за решавање на водоснабдувањето на Република Македонија и нивна заштита, Институт-Геохидропроект, Скопје.

Думурџанов, Н., Христов, С., Павловски, Б., Иванова, В., 1976: *Толкувач за основната геолошка карта на Република Македонија за листот Штип, ОГК СФРЈ 1 : 100 000*, Геолошки завод Скопје;

Карајовановиќ, М., Хаџи-Митрова, С., Аранѓеловиќ, Р., 1975: *Основна геолошка карта на Република Македонија за листот Титов Велес. , ОГК СФРЈ 1 : 100 000*, Геолошки завод Скопје;

Карајовановиќ, М., Хаџи-Митрова, **С.,** 1975: Толкувач за листот Титов Велес, ОГК СФРЈ 1 : 100 000, Геолошки завод Скопје;

Ракичевиќ, Т., Думурџанов, Н., Петковски, П., 1968: *Основна геолошка карта на Република Македонија за листот Штип , ОГК СФРЈ 1 : 100 000*, Геолошки завод Скопје;

Spasovski, O., Doneva, B., 2007: *Heavy metals in the water of the River Zletovska and the Vicinty*. 2nd Balkan mining congress, Belgrade.

Spasovski, O., Dambov, R., 2009: *Heavy Metals in the Water of the River Kalnistanska and the Vicinty*. 3rd Balkan Mining Congress, Izmir-Turkey, pp. 667-671

Spasovski. O., Ristova, J., Mitev, T., 2010: *Heavy metals in sediments of Artifical Hydro Accumulation Mavrovica and Orelska Reka, Eastern Macedonia*. 15 th Congress of Geologists Serbia, With International participation, Belgrade, pp. 657-661.

CADMIUM CONCENTRATION IN THE SOILS OF THE VILLAGE GUJNOVCI

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Abstract

This paper is an overview of the soil contamination of heavy metals in the village Gujnovci particularly of Cd. The region is known for use intense agricultural and other anthropological activates, mining activates that also have an impact on the distribution of some microelements in the soils. The highest value for cadmium in soil is 8.38mg.kg^{-1}, and the minimum value is 6.01mg.kg^{-1} , the mean value is 7.20mg.kg^{-} . The content of Cd in wheat crops in the soils of the village Gujnovci is >.0.01 mg/kg. The examinations were carried out in the laboratory of the Faculty of Mining and Geology in Stip.

Key words: cadmium, soil, heavy metal,wheat

Introduction:

Cadmium is regarded as one of the most toxic trace elements in the environment.

Two trace elements of great risk for the environmental health are lead and the cadmium, *Kabata 1992*. Cadmium in soils is derived from both natural and antropogenic sources. Natural sources include underlying bedrock or transported parent material such as glacial till and alluvium. Antroopogenic input of cadmium to soils occurs by aerial deposition and sewage sludge, manure and phosphate fertiliser application. Cadmium is much less mobile in soils than in air and water. The major factors, governing cadmium speciation , adsorption and distribution in soils are pH, soluble organic matter content, hydrous metal oxide content, the composition of the soil, particularly clay content and type, presence of organic and inorganic ligands and competition from other metal ions (OECD 1994, 1996)

The use of cadmium-containing fertilisers and sewage sludge is most often quoted as the primary reason for the increase in the cadmium content of soils over the last 20-30 years in Europe (Jensen and bro-Rasmussen 1992).

Cadmium in soils must be distinctly classified in three separate areas with regard to their relative effects on human health and the environment. These three areas are agricultural soils, non-agricultural soils and controlled landfill.

Cadmium in agricultural soils is like wise relatively immobile under normal conditions, but could become more mobile under certain conditions such as increased soil acidity and its cadmium level may be enhanced by the usage of phosphate fertilisers, manure or sewage sludge. The average natural abundance of cadmium in the earth's crust has most often been reported from 0.1 to 0.5 ppm, but much higher and much lower values have also been cited depending on a large number of factors.

The content of Cd depends on the mineral and texture of the soil (Pospilova and Lastinkova 1988) as well as on the primary material that formed the soil (Mengel and Kirkby 1979)

Changes of heavy metal presence in the soil are the result of various interaction processes that can be grouped as follows:

-anthropogenic; changes resulting from agricultural amangement (e.g. fertilizers) and atmospheric deposition
-soil dynamic: change resulting from soil cultivation (e.g. tillage) biological activity (e.g. earth worms), dissolved or as particles that are transported by water flow, erosion or other processes.
-Procedure errors: changes resulting from all kinds of possible errors associated with soil sampling, physical soil preparation and analytical procedure.

As heavy metal Cd is dangerous to the environment The danger ensuing from this metal derives from its tendency to accumulate in the vital organs of humans, animals and plants.

Among all the heavy metals, cadmium plays an important part in soil pollution. Owing to serious cadmium pollution, much attention has been paid to its effect. Cadmium can damage kidney, liver, skeleton and other organs; what is more, cadmium is a definite carcinogen, it can cause cancer in many organs.

Results and discussion

Determination of macro elements, trace elements was done on 15 soil samples taken from wheat fields. Samples were taken 20 cm in depth.

Samples were dried for 48 hours at 40°C. Dry samples were prepared according to ISO 11464. They were crushed and sieved through 45 μm sieve.

One gram of sample was wetted in 2.0 mL redistilled water and with slow and constant stirring 12 ml HCL and 6 mL HNO_3 were added. The glass was covered with a glass watch and kept at room temperature for 16 hours and heated until wet salts were obtained. Wet salts were closed in 5 mL concentrated HNO_3 and the content was filtered through paper with white track. The material was put in a 100 mL measure flask. Determination of macro elements and trace elements was done by AES-ICP. Values of macroelements (in %) and micro elements (in mg/kg) in the soils of Gujnovci are shown in table 1 and 2

Table 1. Values of macroelements (in %) and micro elements (in mg/kg) in the soils of Gujnovci.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Al	4,39	4,13	4,20	3,21	4,79	5,16	4,50	5,68
Fe	3,92	3,94	3,78	3,52	3,68	3,88	3,72	4,19
Ca	0,88	0,93	0,91	1,79	3,59	1,35	2,67	1,21
Mg	0,96	0,93	0,97	1,08	1,49	1,33	1,46	1,38
Na	2,31	2,60	1,61	0,51	1,29	0,76	0,99	1,05
K	0,91	0,92	1,01	0,60	0,87	0,62	0,82	0,62
Mn	0,10	0,10	0,10	0,26	0,11	0,08	0,13	0,08
Ti	0,05	0,05	0,06	0,04	0,06	0,09	0,08	0,11
P	0,04	0,05	0,05	0,07	0,07	0,03	0,08	0,03
Sr	143,49	161,44	142,87	143,93	216,60	135,64	189,18	137,96
Ba	565,34	708,93	627,80	519,66	370,10	508,16	386,31	582,01
Ni	17,90	17,23	20,52	41,71	58,26	29,75	51,59	24,43
Cr	23,22	22,19	27,81	33,71	56,62	39,30	50,34	35,34
Zn	87,39	89,46	88,60	414,05	99,85	80,43	136,35	91,05
Cu	21,54	22,52	23,29	58,28	33,33	20,43	38,35	22,82
Pb	46,74	51,26	43,73	466,95	47,18	31,85	71,75	40,82
Co	15,55	15,33	15,51	18,23	19,37	16,78	19,71	17,17
Cd	6,54	6,60	6,39	7,43	6,58	6,60	6,20	7,21
V	289,94	255,75	333,99	507,47	420,51	670,59	507,77	729,18
Mo	3,12	3,06	2,70	2,41	1,79	2,92	1,98	2,99

Table 2. Values of macro elements (in %) and micro elements (in mg/kg) in the soils of Gujnovci

	9	**10**	**11**	**12**	**13**	**14**	**15**
Al	5,44	3,70	3,27	3,15	4,27	3,47	2,89
Fe	4,11	3,43	4,19	4,00	3,98	3,67	3,52
Ca	1,04	2,03	1,66	1,40	1,79	1,93	1,62
Mg	1,37	1,24	1,12	1,09	1,39	1,29	1,12
Na	2,42	1,60	1,45	1,21	2,08	1,22	1,13
K	0,70	0,65	0,58	0,55	0,82	0,64	0,50
Mn	0,08	0,09	0,16	0,19	0,12	0,09	0,11
Ti	0,08	0,07	0,08	0,10	0,05	0,11	0,10
P	0,03	0,09	0,09	0,10	0,09	0,09	0,11
Sr	160,18	200,47	198,02	179,01	211,65	188,92	177,20
Ba	524,68	402,69	470,83	483,67	531,83	481,86	444,59
Ni	25,28	32,56	33,30	35,37	36,88	32,54	30,01
Cr	36,71	31,08	32,03	31,44	39,53	32,56	27,78
Zn	93,88	124,68	403,03	337,34	101,15	138,94	107,02
Cu	21,13	29,93	40,37	51,69	32,17	37,01	33,48
Pb	42,21	64,38	268,83	245,14	53,36	54,40	51,59
Co	16,29	16,03	20,85	20,41	18,12	17,63	16,10
Cd	6,76	6,10	8,38	7,58	6,54	6,21	6,01
V	553,29	488,67	583,31	816,15	359,56	17,72	784,81
Mo	2,28	2,52	3,13	2,85	2,78	2,78	2,63

Table 3. Normal intervals of contents and maximum allowable limits of heavy metals in soils (Kloke, 1980).

Element	**Intervals of normal contents mg/kg**	**Maximum allowable limits**
Cd	0.1-1.0	3
Co	1-10	50
Cr	2-50	100
Cu	1-20	100
Ni	2-5	50
Pb	0.1-20	100
Zn	3-50	300

Fig1 shows that the concentration of Cd is high in all samples

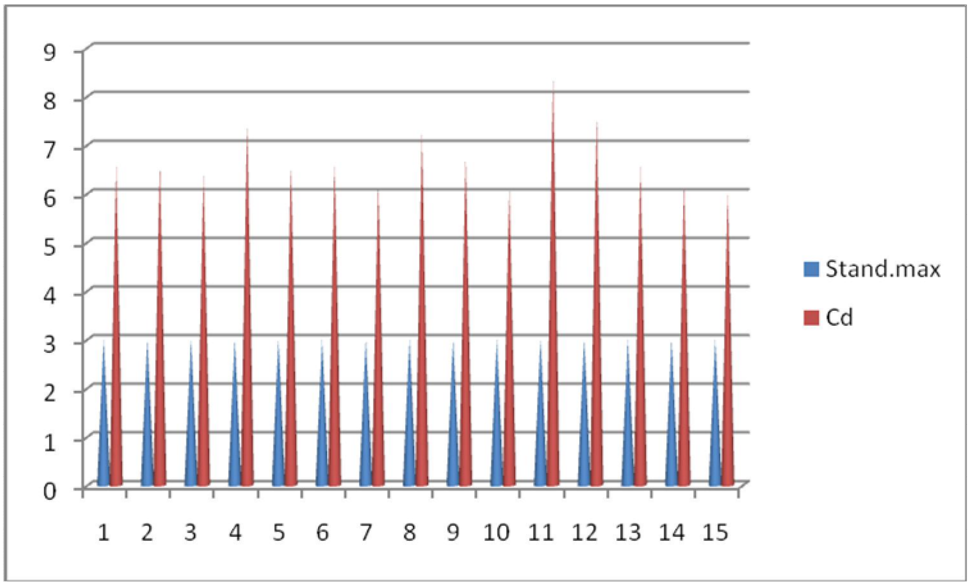

Fig. 1. Concentration of Cd in soils of village of Gujnovci

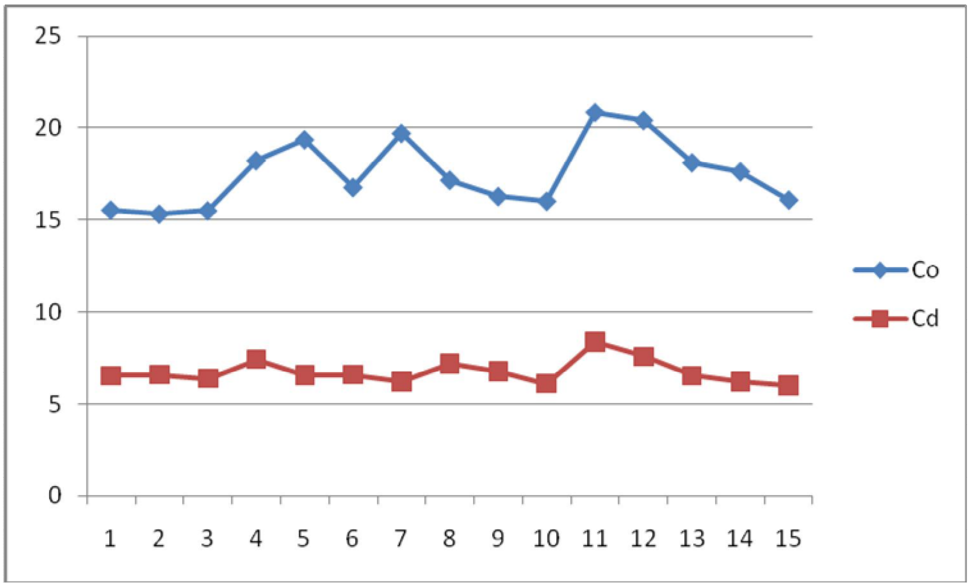

Fig. 2. Proporcional dependence between Co and Cd

Fig 2 shows the proporcional dependence between Co and Cd

In table 4 is shown comparison between cooncentracion of heavy metals in soils of Gujnovci, some soil in Japan and some soils in World.

Table 4 Average concentracion of heavy metals in Gujnovci-Macedonia,Japan by Yamasaki (2001),and World by Kabata-Pendias (2001).

	Gujnovci	Japan	World
Cd	6.01-8.38	0.02-3	0.01-4
Cr	22.19-56.62	1.4-233	1-1500
Co	15.33-20.86	0.2-61.3	0.1-275
Ni	17.19-58.26	0.2-107.4	0.2-3240
Cu	21.13-38.28	0.9-234.9	1-323
Zn	80.43-403.03	2.5-331	3-770
Pb	43.73-466.95	1-1098	1.5-286
Mo	1.98-3.13	0.1-8	0.2-17.8

International standard value of Cd concentration in crops adopted by Codex 0.2(mg/kg)

International standard value (Codex) of Cd in wheat crops is 0.2 mg/kg)

Value of Cd concentration in wheat crops of the village Gujnovci is >.0.01 mg/kg. The concentration of other elements is as follows:*Ca-350, Mg-1530; Na-100; P-2250; k-4320; Fe-34; Mn-25; Al-5; Zn-22; Cu-6.3; Ba-3.7; Sr-3.5; Ni>0.12; Ti- 0.9; Cr->0.05; As->1.0; Mo-0.7; Pb->3.8; Co->0.01; V-0.2; Ag->0.55*

Data in tables 1 and 2 show that concentration of cadmium is up 6.01 mg/kg to 8.38 mg/kg .

The results have proved that Cd content in all samples is significantly higher than the standard values.

Conclusion:

The investigations carried out on the presence of trace elements in soils in the vicinity of Gujnovci are characterized by increased anthropogenic impacts. Investigations revealed increased concentrations of Cd. The high Cd concentrations is due to the intense anthropogenic influence, notably the disasters that occurred in the lead and zinc flotation dams. The region is built up of volcanic tuffs of Tertiary age so that pedogenesis of the soils consists mainly tuffs.

The increased cadmium concentrations come from the flotation plants of the Zletovo Mines. The mines is situated 20 Km far away from Gujnovci.

The highest value found for cadmium in soil is 8.38mg.kg^{-1}, and the minimum value is 6.01mg.kg^{-1} , the mean value is 7.20mg.kg^{-} , The concentrations of other rare elements are within the allowed limits and the values reported for such types of soils.

Wheat crops from investigation soils not contained increase concentration of cadmium.

These cadmium contaminated soils can be cleaned by using plants for phytoremeditation. Phytoremeditation is a method of remedying environmental contaminates with hazardous substances utilizinig the innate capabilities of plants.

References:

CODEX ALIMENTARIUS COMMISSION ("Codex"), 2005. Report of the 37th session of the Codex Committee on Food Addirives ande Contaminants. Alinorm 05/28/12, 1-189.

OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION (1992), occupational Exposure to Cadmium, Final rules, U.S. Department of Labor 29 CFR part 1920.1027, September 14, 1992.

ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT (OECD), (1994), Risk Reduction Monograph No, 5: Cadmium OECD Environment Directorate , Paris, France

ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT (OECD), (1996), Report From Session F, " Sources of Cadmium in Waste" Chairman's Report of the Cadmium Workshop ENVIMCICHEMIRD (96) 1, Stockholm, Sweden, October 1995.

Klok,A. (1980): Richwerte'80. Orientierungsdaten fur tolerierbare Gesamtgehalte einiger Elemente in Kulturboden,Mitt. VDLUFA, H.2,9-11

Kabata, A.P., 1992, Trace Elements in soil and plants. 2 nd edition, Sc CRC Press, Printed USA.

Kabata-Pendias, A., 2000. *Trace Elements in Soils and Plants Third Edition*, CRC Press Inc., Florida.

Mengel and Kirkby 1979. Principles of plant nutrition 2 ed. Int. Potash Inst. Bern.

Pospilova L., Lastincova I. 1998 Determinacion of some trace elements in soil using ICP-AES method Rostl, V'yr., 47, 7-13

World health Organistaion (WHO) (1992). Environmetal health Criteria 134-Cadmium International Programme on Chemical Safety (IPCS) Monograph

Jensen, A., AND BRO-Rasmussen, F., (1992). "Environmental Contamination in Europe," Reviews of Environmental Contamination and Toxicology, Volume 125, pages 101-181.

Yamasaki, S. Takeda, A. Nanzyo, M. Tanjyama, I. and Nakai, M., 2001. Background Levels of Trace and Ultra-Trace Elements in Soils of Japan, Soil Science and Plant Nutrition, 47:755-765.

LICHEN INFLUENCE ON VARIOUS MINERAL SUBSTRATA

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Lichens are composite organisms comprising a fungal component, the mycobiont, and and an alga or cyanobacteria, the photobiont. This symbiotic organisms colonize all types of rocks and can survive in any climatic conditions. They also colonize stone monuments and historical buildings. This fact makes their interaction with various types of rocks interesting not only to biologist and geologist, but also to archeologist and restorers.

Four rock samples were analyzed, all of which are different mineral structure, and also of different environmental origin. Their common characteristic is the presence of lichens on their surface. Investigated samples were: calcarenite rich in fossil fragments from island Brusnik, phosphorite from Ervenik, mica schist from Namibia and quartz from Trepča. The lichens were analyzed using macroscopic and microscopic methods. The cross – sections for all samples were prepared, so contact of the lichen and the rock could be visible on polished surface. The lichens were brought in contact with water to determine whether they could still be considered living organisms or not and to recognize the taxa of the lichen. By way of an x-ray diffraction analysis, powdered samples of thallus surfaces from all four rock samples were recorded.

By macroscopic and microscopic methods the samples were observed and the certain taxa of the lichen were determined. On sample from Brusnik at least two different lichens were reported, *Caaloplaca sp*. and *Protoneliopsis muralis*. One form left undetermined. On sample from Ervenik was also reported taxon *Protoneliopsis muralis*. *Caloplaca sp.* was determined on sample from Namibia, as well as on sample from Brusnik, in spite the tremendously different environment where these two samples were found. On sample from Trepča species *Rhizocarpon geographicum* was determined.

Experiment of bringing lichens in contact with water showed that all lichens when became moist, enlarged their volume and changed colour into green. This is because water makes the fungal pigments translucent, allowing sunlight to reach their algal partner and allowing the green color of the alga (chlorophyll) to emit outward. The lichen becomes photosynthetically active when moisture is abundant (Nash III, 2008). The changes of colour are showed on example of *Protoneliopsis muralis* (Fig. 1 and Fig. 2).

Fig. 1 – Lichen *Protoneliopsis muralis* dry (sample from Brusnik)

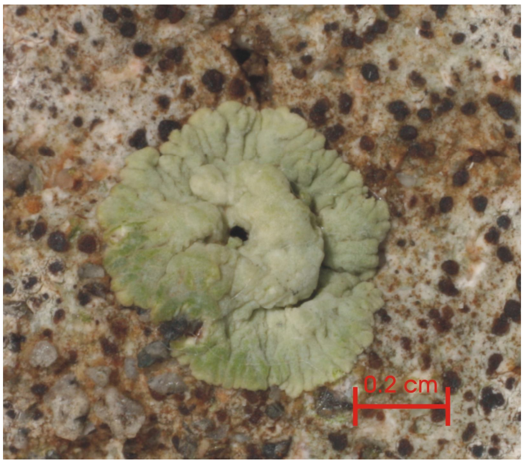

Fig. 2 – Lichen *Protoneliopsis muralis* wet (sample from Brusnik)

The lichen-rock interfaces were reported on polished surfaces. On the contact of lichen *Protoneliopsis muralis* and calcarenite (sample from Brusnik), the zone of disaggregation and fragmentation of the rock could be seen immediately below the lichen thallus. This is the result of hyphal penetration into rock (Fig. 3). In this case hyphae penetrated few hundreds micrometers into rock.

The other sample, where the hyphal penetration was reported, was mica schist from Namibia. On this sample hyphae of *Caloplaca sp.* penetrated over a milimeter into rock, through foliation fissures (Fig. 4). Previously reported examples of the depth of hyphal penetration are 1.5 – 10 mm for foliated rocks and 0.3 – 16 mm for calcareous rocks (Lee, 2000).

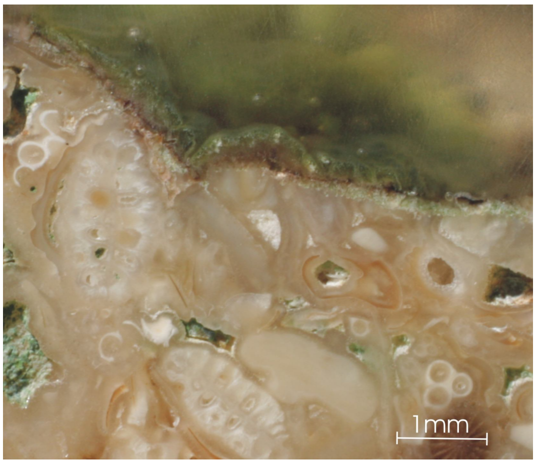

Fig. 3 – Lichen *Protoneliopsis muralis* – calcarenite contact (sample from Brusnik)

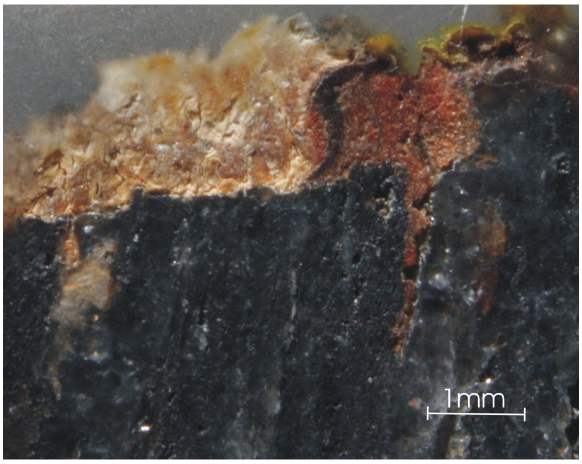

Fig. 4 – Lichen *Caloplaca sp.* – mica schist contact (sample from Namibia)

The x-ray diffraction analyses showed the presence of calcium oxalate monohydrate whewellite in thallus of lichens for all samples, except the one from Trepča. Calcium oxalate dihydrate weddellite was present only in the thallus of *Protoneliopsis muralis* from calcarenite (sample from Brusnik). Calcium oxalate mineralization was recorded before in thalli of lichens, which lived on rocks containig calcium, even in very small concentrations (Ariño *et al.*, 1995; Prieto *et al.*, 1997).

The absence of calcium oxalate in thallus of Rhizocarpon geographicum is the result of mineral structure of the rock, which is only quartz what is in accordance with earlier investigation.

The lichens deteriorate rocks physically and change mineral structure of the rock by their own metabolitic products. On the other hand, it also has a protective role for the rock. The calcium oxalate forms a crust over the thallus (Giordani *et al.*, 2003). Calcium oxalate monohydrate has very low solubility ($K_{sp} = 2.32\times10^{-9}$), so lichen thallus with calcium oxalate crust retains water and decreases dissolution of the rock minerals (Ariño *et al.*, 1995).

Nowadays, most of the research in this field is related to interaction between lichens and historical buildings or monuments. It is still to be found out weather lichens deteriorate or protect the rock.

References:

Ariño, X., Ortegacalvo, J.J., Gomez-Bolea, A. i Saiz-Jimenez, C. (1995): Lichen colonization of the Roman pavement at Baelo-Claudia (Cadiz, Spain) – biodeterioration vs bioprotection. *Science of The Total Environment* **167**, 353-363

Giordani, P., Modenesi, P. i Tretiach, M. (2003): Determinant factors for the formation of the calcium oxalate minerals, weddellite and whewellite, on the surface of foliose lichens. *Lichenologist* **35**, 255-270.

Lee, M.R. (2000.): Weathering of rocks by lichens. In: *Environmental Mineralogy: Microbial Interactions, Anthropogenic Influences, Contaminated Land an Waste Management,* (Eds. Cotter-Howells, J.D., Campbell, L.S., Valsami-Jones, E., Batchelder, M.), Mineralogical Society of Great Britain & Ireland, London, pp.77-107.

Nash III, T.H. (2008) Introduction. In: *Lichen Biology*, 2nd edition, (Ed. Nash III, T.H.), Cambridge University Press, New York, pp. 1-8.

Prieto; B., Silva, B., Rivas, T., Wierzchos, J. i Ascaso, C. (1997): Mineralogical transformation and neoformation in granite caused by lichen *Tephromela atra* and *Ochrolechia parella. International Biodeterioration and Biodegradation* **40**,191-199.

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