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E-mail: sitzams@eunet.rs; www.sitzam.org.rs

ZA IZDAVAČA: *Prof. dr MIOMIR PAVLOVIĆ, predsednik UISKOZAM*

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CONTENTS | *SADRŽAJ*

Heavy metals in sediments along the river Zletovska in Eastern Macedonia

Orce Spasovski[1], Dejan Mirakovski[1], Emilija Ristova[2]

[1]Faculty of Natural and Technical Science Stip, Macedonia, University "Goce Delcev" Stip, [2]Faculty of Mechanical Engineering Vinica, Macedonia, University "Goce Delcev", Stip

Soils according to the chemical composition and physic-chemical processes occurring in them represent the most complex systems in heterogeneous lithosphere. Both, soils and along the river sediments are subject to different research objectives, which analysis can come to the important information about the pollution of waters and soils with heavy metals, and thereby identify the effects on human health. In this paper the results of pollution by heavy metals in the sediments from the river Zletovska and its surroundings are presented. An attempt to identify the actual condition in the test area is made and the presence of the heavy metals in the sediments of the mentioned river and its tributaries to be determined. Analysis of samples was conducted as part of a series of samples of the instrument Atomic Emission Spectroscopy with inductive coupled plasma (AES-ICP). Past experiences of contamination of areas such as the area of interest indicate that the next group of elements should be taken into consideration: Mn, Fe, Al, Pb, Zn, As, Cd, Cu, Ni, Co, Ag, Cr, Ti, as well as some elements that present higher concentrations of maximum permitted amounts. In our case, the great influence on the activities of the contamination have Zletovo mines and some tailing ponds, which are a by - product of several decades of activity of the eponymous mines.

INTRODUCTION

Environmental pollution in the past few decades was a topic to which was given minimal importance. Unlike the recent years, this topic has a high priority [1]. Of particular interest is the problem of the presence of heavy and toxic metals in sediments [2,9,10]. Moreover, if the water supply wells for drinking water of the local population belong to such of areas, then the situation is alarming [3]. This research focuses to areas found in contemporary alluvium of the river Zletovska, on the confluence of the river Koritnica. The fact that the water supply wells for drinking water can be found to those areas, poses a serious problem for all residents that are in the municipality Probistip.

Moreover, in the immediate vicinity of the mentioned area there are a number of agricultural lands used for production of various crops [11]. Past studies of geological, geochemical and environmental aspects indicate potential for natural contamination in researched area. Another important aspect is stricter legal standards for the quality of the environment in which people live and work in this region, as part of the mandatory EU environmental regulations implementation.

The area that was the subject of research comprises sediments from the immediate surroundings of the river Shtalkovska, Koritnica, river Kiselicka and River Zletovska to its estuary in the river Bregalnica (Figure 1). The field marked with a rectangle representing the area of the sediment samples.

In the past, the area that is the subject of research and its immediate surroundings has been studied by many researchers from different aspects [4,5,6,7,8].

METHODOLOGY

Within the planned studies were carried out preliminary field activities consisted of an initial monitoring of the ground in order to get initial impressions of the situation on the ground.

Starting with field activities, the points of research and also profile lines that describe the field of basic research are defined. Within the planned research, basic outreach activities that consist primarily of field monitoring by the topographic determinations of the points of research are carried out; also the profile lines from which the samples of sediments will be taken are determined. In this phase was processed ground covering the upstream of the river Zletovska and its tributaries, starting

from the river Shtalkovska by the valley Buchechki, to the estuary of the River Kiselica into river Zletovska, continuing to the part of Kocani (which includes the flow of the river Zletovska from the village Lepopelci to the village Zhiganci and until Ularci village), to the mouth of the river Zletovska into the river Bregalnica.

Figure 1. Map of Republic of Macedonia with the appointed position of the researching area

The initial phase is consisted of sampling of sediments from the already mentioned points of researching. Samples are taken by profiles set perpendicular to the flow of rivers and longitudinal intervals of 25 meters on both sides of the rivers. Samples taken from sediments are placed into plastic bags with appropriate labels for samples, place and date of taking the sample.
After the outreach activities, appropriate analysis is made. Preparation of sediment samples is consisted of four phases: drying of samples, crashing and sowing of samples, weighing the obtained sub-sample and dissolving of weighted samples.

RESULTS AND DISCUSSION

Within the planned research, 22 samples of sediments were taken at intervals twice in 25 m perpendicular to the river, on its left and right hand. Samples were collected in bags and further provided in the chemical laboratory of The Faculty of Mining Engineering and Geology in Stip for analysis. Each test is marked with a unique number and locations of samples taken in the field are shown on the topographic map (Figure 2).
Table 1 shows the results of chemical tests performed on samples taken from sediments with an ordinal number from 1 to 22. The results are compared with the values of standards established of heavy metals in sediments.
Based on the data in Table 1, certain conclusions about the presence of individual heavy metals in sediments in the vicinity of the river Zletovska and its tributary river Kiselicka as well as opinion about the reasons that contribute to the increased content of individual metals can be made.

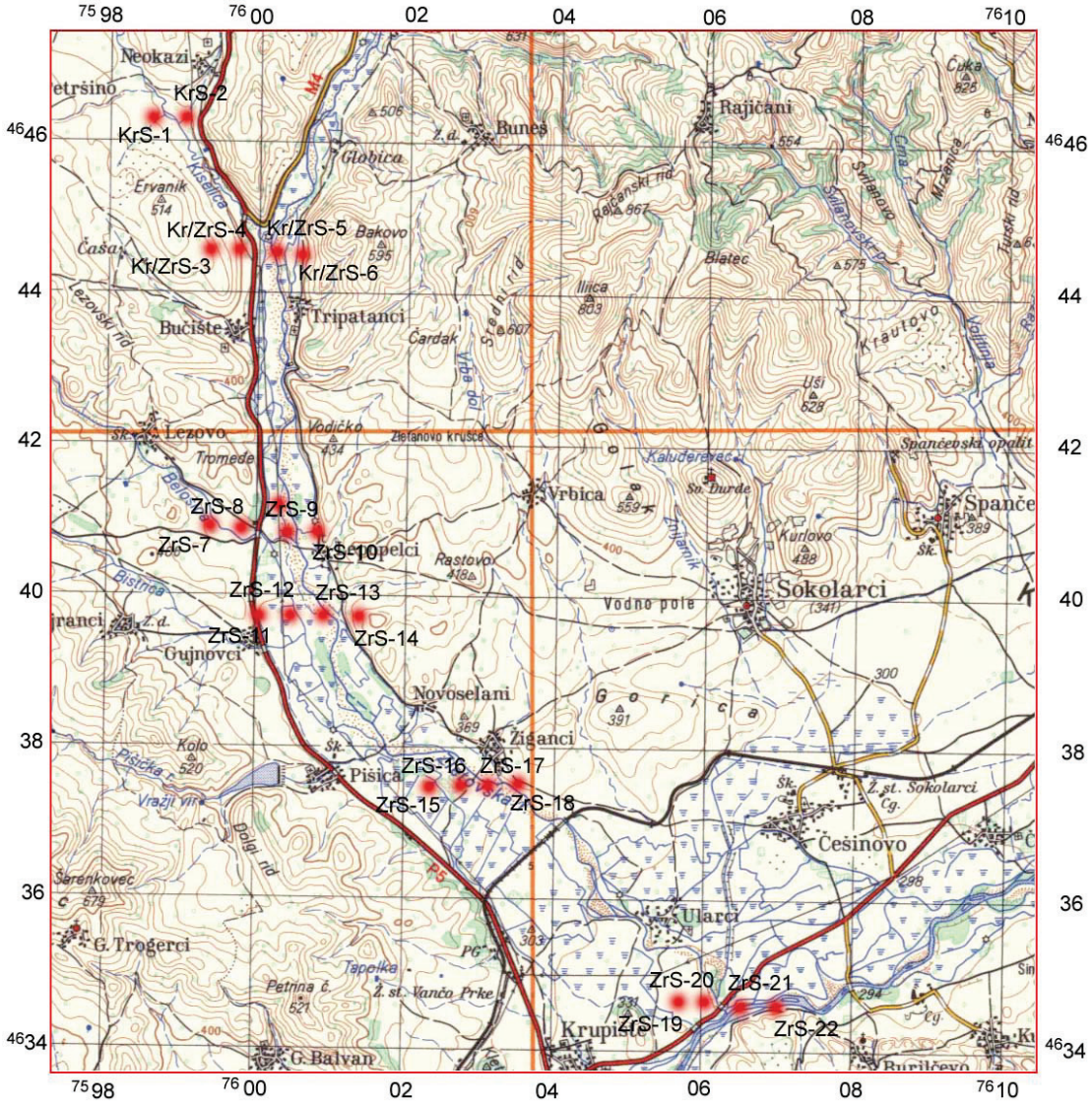

Figure 2. Topographic map with the specified position of samples of sediments

The data for the iron content (Table 1) indicate increased its presence in most of the analyzed samples. The highest content of iron is found in the sample ZrS-16 (7.73), sample from the right side along the river Zletovska between the villages Zhiganci and Ularci. The lowest content of iron is found in the sample KrS-2 (3.10), sample of sediments from the right side of the river Kiselicka. In general, it can be concluded that the researched area is contaminated with iron. Increased iron content due to the presence of iron oxides and sulphide (pyrite and limonite).

Particular attention is given to the high content of manganese in samples ZrS-15 (2.19 %) and ZrSr-16 (1 .. 84%), samples are taken from sediments in the right side of the river Zletovska between the villages Zhiganci and Ularci. The sample Kr/ZrS-5 taken at the estuary of the river Kiselicka into the river Zletovska and the sample ZrS-20 that is taken at the estuary of the river Zletovska into the river Bregalnica show a significant increase in manganese compared with standard content. The lowest content of manganese are found in sediments along the river Zletovska in the place called Lezovski Canton (sample ZrS-10). Contributions to the higher manganese contents in sediments of the rivers Kiselicka and Zletovska is the existing hydro slag that is located nearby mentioned rivers, and the presence of waste water from mines Zletovo where manganese is constant follower of lead - zinc mineralization.

Increased content of lead were observed in all samples analyzed, but the highest content of lead occur in samples KrS-1 (2630 mg/kg), ZrS -15 (1830 mg/kg) ZrS-16 (2740 mg/kg).

Zinc also occurs in content increased in all samples analyzed. Particular attention is given to the high content of zinc in the samples ZrS -15 (3050 mg/kg) ZrS-16 (2050 mg/kg) compared with that default values are larger by about 100 times.

Table 1. Concentrations of individual metals in sediments (mg/kg)

Elements	Pb	Zn	Mn (%)	Cu	Co	Cd	V	As	Ag	Fe (%)	Ni	Cr
Samples marked												
KrS-1	2630	1570	1.28	220	11	13	60	130	5	6.35	5.00	9.90
KrS-2	150	220	0.17	50	12	5	81	110	5	3.10	7.01	7.13
Kr/ZrS-3	920	990	0.38	100	13	10	69	120	3	4.69	15.76	20.0
Kr/ZrS-4	350	530	0.11	40	12	7	94	130	1	4.31	11.62	18.06
Kr/ZrS-5	1790	1680	1.01	200	8	13	110	170	5	6.10	5.22	12.53
ZrS-6	1350	1430	0.66	150	10	11	130	110	4	5.27	10.00	19.39
ZrS-7	570	900	0.36	69	15	9	170	28	2	4.81	15.44	19.09
ZrS-8	500	820	0.45	63	15	8	180	7	1	4.38	16.29	20.55
ZrS-9	140	280	.0.19	36	13	5	190	3	1	3.63	20.75	23.48
ZrS-10	56	130	0.10	48	13	5	200	5	1	3.74	20.00	24.83
ZrS-11	450	590	0.46	61	16	9	230	7	2	5.09	16.07	25.00
ZrS-12	400	670	0.29	59.87	11.78	8	150	1	1.48	4.22	19.14	20
ZrS-13	370	660	0.33	53.05	14.11	7	180	1	1.45	4.32	13.52	21
ZrS-14	440	760	0.37	62	15	8	190	1	2	4.54	16.00	23
ZrS-15	1830	3050	2.19	160	16.74	23	280	97.13	9.86	7.35	14.30	17
ZrS-16	2740	2050	1.84	190	18.45	23	240	53.88	9.26	7.73	10.74	17
ZrS-17	560	630	0.41	78.06	12.60	10	190	1	1.99	5.03	13.07	16
ZrS-18	250	260	0.15	44.45	14.43	6	200	1	1	4.09	13.57	20
ZrS-19	1000	1280	0.78	93.58	15.48	12	210	28.75	4.32	5.43	13.89	20
ZrS-20	1310	1080	1.11	120	15.63	14	150	36.59	4.75	5.83	12.54	22
ZrS-21	690	1050	0.65	80.65	14.79	10	200	7.33	2.14	4.64	16.15	24
ZrS-22	770	1190	0.62	84.66	14.45	10	100	5.33	2.77	4.30	15.75	21

Sampling: KrS – test sediments taken from the normal flow of the river Kiselicka; Kr/ZrS –samples from sediments taken in the estuary of the river Kiselicka into river Zletovska; ZrS – Samples from sediments taken downstream of the river Zletovska

Note: Analyses were made in the laboratory of the Faculty of Mining and Geology in Stip in 2010 by AES-ICP, Analyst: MSc V. Zajkova

Increased content of lead and zinc in sediments from the immediate environment of the rivers Kiselicka and Zletovska clearly confirm the high influence of hydro slag Zletovo and active operation of the lead and zinc mines Zletovo. Copper appears in content that are close to or greater compared with standard values. The highest content of copper is found in the test KrS - 1 (200 mg/kg) taken from the left side of the river Kiselicka and into the samples ZrS - 15 (160 mg/kg) and ZrS - 16 (190 mg/kg) taken from the right side of the river Zletovska between the villages Zhiganci and Ularci. Increased copper content is due to the presence of copper mineralization in the mines Zletovo and their immediate surroundings.

Chromium occurs in the contents that are higher but very close to default values, except in samples as KrS-1 (9.90 mg / kg) and KrS-2 (7.13 mg / kg) taken from sediments in the river Kiselicka with lower values compared with default values. This kind of distribution of chromium suggests that

mines Zletovo not contaminate explored space with chrome, but the presence of chromium in sediments of the river Zletovska is a consequence of the presence of the mentioned elements in the range near the river Zletovska.
Cadmium is a significant contaminant of the researched area because it occurs much more often than standard values. Contamination with cadmium is due to the presence of cadmium in the area in the immediate vicinity of the researched area, especially in mines Zletovo where it constantly monitor lead - zinc mineralization. Increased content of cadmium follows the parts that are contaminated with lead and zinc.
Arsenic occurs in some samples in which the contents are identical to standard values, but in a larger number of samples increased significantly in content. This element appears due to its presence within the copper mineralization in the vicinity of Tursko Rudare and partly in the lead and zinc ore in the mines Zletovo.
Cobalt is not a significant contaminant in the researched area because occurs in contents very close to standard values.
The data obtained for silver (Table 1) indicate that the silver is contaminant in the whole researching area. The accompanying data also show that silver occurs in higher concentrations in all samples analyzed and that it follows lead.
Vanadium occurs in contents significantly higher than standard values with the exception of samples taken at river Kiselicka and a test taken directly to the estuary of the river Kiselicka to the river Zletovska. The obtained values indicate significant contamination of the space with vanadium.
Nickel in the researching area in most of samples occurs in contents higher, but very close to the standard values. In the samples taken from sediments near the river Kiselicka and in a test taken near the mouth of a river Kiselicka in the river Zletovska, nickel occurs in contents much lower than the standard values. The obtained values for nickel indicate that this element is not a significant contaminant of the researched area.

CONCLUSION

The results of chemical tests performed on samples taken from the sediments show that in all analyzed samples the heavy metals content is higher compared to standard values. There are several reasons for this behavior of the heavy metals in sediments of the researched area, as it a significant impact of the anthropogenic factors and the geology of the explored area.
The highest values indicate the lead, the zinc, the copper, the iron and the cadmium; elements that are result of the contaminated region in a wider area. Also, a large share in the content of the analyzed elements has active operation of the mine Zletovo (it is about the lead zinc ore) and technological process of processing of lead and zinc ore that result in hydro slag Zletovo. Most of the examined elements occur in increased content as they tracking in lead zinc ore. Particular attention is given to samples ZrS-ZrS-15 and 16, taken from the sediments between the villages Zhiganci and Ularci where the most of the heavy metals show high contents, and the space is located at great distances from the mine Zletovo and hydro slag.
We state that the increased content of analyzed elements in this part of the explored area is due to the long term activity associated with the transport of lead-zinc concentrate from the railway station in Krupiste. The storage of the concentrate (for ex., loading the truck to rail transport) often is part of the winds that concentrate can translate to larger distances and thus come to the contamination of the environment (soil, water, sediments, etc.).

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