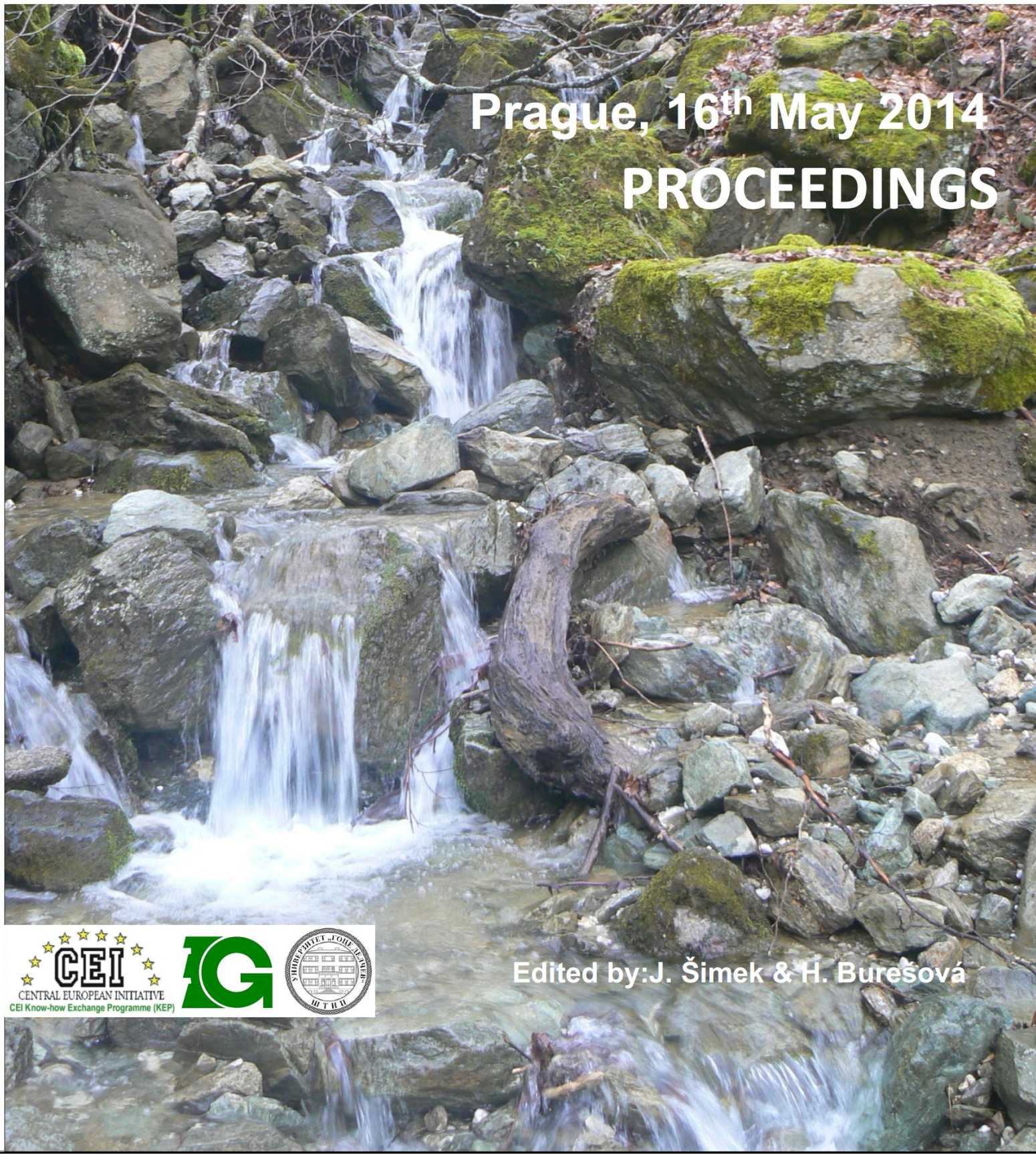
GIS-GEOINDUSTRY, s.r.o., Czech Republic CEI Know-how Exchange Programme

2nd INTERNATIONAL WORKSHOP

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



Prague, 16th May 2014

PROCEEDINGS

CEI
CENTRAL EUROPEAN INITIATIVE
CEI Know-how Exchange Programme (KEP)

Edited by:J. Šimek & H. Burešová

GIS-GEOINDUSTRY, s.r.o., Prague, Czech Republic with a grant from the CEI Know-how Exchange Programme (KEP) organizes

2nd INTERNATIONAL WORKSHOP
ON THE PROJECT

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

PROCEEDINGS

Edited by:
J. Šimek & H. Burešová

Prague, 16th May 2014

2nd International Workshop on the ENIGMA Project (Ref. No. 1206KEP.008-12)

16th May 2014, Prague – Czech Republic

Organizing Committee:

Ing. Pavel Míšek, *President*
GIS-GEOINDUSTRY, s.r.o., Czech Republic

Prof. D-r Todor Serafimovski
Faculty of Natural and Technical Sciences, University "Goce Delčev"– Štip, R. Macedonia

D-r Josef Šimek
GIS-GEOINDUSTRY, s.r.o., Czech Republic

Ing. et Mgr. Helena Burešová
GIS-GEOINDUSTRY, s.r.o., Czech Republic

Doc. D-r Goran Tasev
Faculty of Natural and Technical Sciences, University "Goce Delčev"– Štip, R. Macedonia

Ing. Daniel Kahuda
GIS-GEOINDUSTRY, s.r.o., Czech Republic

Scientific Committee:

Prof. D-r Todor Serafimovski, *President*
Faculty of Natural and Technical Sciences, University "Goce Delčev"– Štip, R. Macedonia

D-r Josef Šimek
GIS-GEOINDUSTRY, s.r.o., Czech Republic

Doc. D-r Goran Tasev
Faculty of Natural and Technical Sciences, University "Goce Delčev"– Štip, R. Macedonia

Prof. D-r Violeta Stefanova
Faculty of Natural and Technical Sciences, University "Goce Delčev"– Štip, R. Macedonia

Ing. Daniel Kahuda
GIS-GEOINDUSTRY, s.r.o., Czech Republic

Language: English for presentations and papers

REMARKS FOR HEAVY METALS TRANSPORT PATHWAYS IN GROUNDWATER AND SURFACE WATER OF ALSHAR AND DUDICA AREAS

Daniel Kahuda[1], Josef Šimek[1], Todor Serafimovski[2], Goran Tasev[2], Violeta Stefanova[2]

[1]GIS-GEOINDUSTRY, s.r.o., Czech Republic
[2]Faculty of Natural and Technical Sciences, University "Goce Delčev"– Štip, R. Macedonia

Abstract: Presented study summarizes results of field sampling campaign performed in 8–10th of April 2013 being part of the CEI funded project "Environmental Impact assessment of the Kozuf metallogenic district in southern Macedonia in relation to groundwater resources, surface waters, soils and socio-economic consequences (ENIGMA)." The campaign included identification of surface and ground water bodies and sources in the catchments of Alshar and Dudica areas. There were in situ measurements of physical parameters performed and consequently samples taken for identification of heavy metal distribution in flow pathways.

Key words: Kozuf area, water, heavy metals, environmental issues

Introduction

Coherently with previously and recently performed survey in the wider Kožuf metallogenetic area there was a short field campaign carried out during April 2013 to strengthen the knowledge of dissolved metallic compounds in surface and ground water of Roždenska, Mrežička and Stara river catchment areas (both being tributaries of Vardar river). This campaign was focusing on identification of surface and groundwater resources within the area of interest, determination of types based on field measurement of basic physical parameters. Consequently there were water samples taken and after their stabilization in situ they were analyzed for a wide range content of metals.

Material and methods

During the field campaign of the ENIGMA project the sampling of ground and surface water bodies was performed to collect data for further analyses and field recognition. Accordingly to previous surveys and studies in the area of interest the strongpoints of the field work was focusing especially on heavy metals pathways in the areas of interest.

Besides sampling of the sediments the works were scheduled and carried out to identify all the accessible groundwater sources as well as representing surface water bodies. Directly on side measurements of basic physical parameters were performed with use of field multiparametric measuring probe (pH, temperature, conductivity and RedOx potential). The measured values of electrolytic conductivity were recalculated with use of correction factors into standardized 25°C values to enable a comparison with surface and groundwater standards.

For the sampling campaign there were all accessible groundwater sources identified and for determination of background values the sampling included major surface water bodies in the area of interest. Field filtration of the samples could not be successfully applied.

The samples were kept in polyethylene containers previously cleaned with HNO_3, accordingly to ISO 5667-3(1) and stabilized with use of 10 ml 4% HNO3 and the solution thus obtained went under analysis by flame atomic absorption spectrometry (FAAS) and atomic emission spectrometry with inductively coupled plasma (ICP-AES) by the analytical laboratory of Stip University.

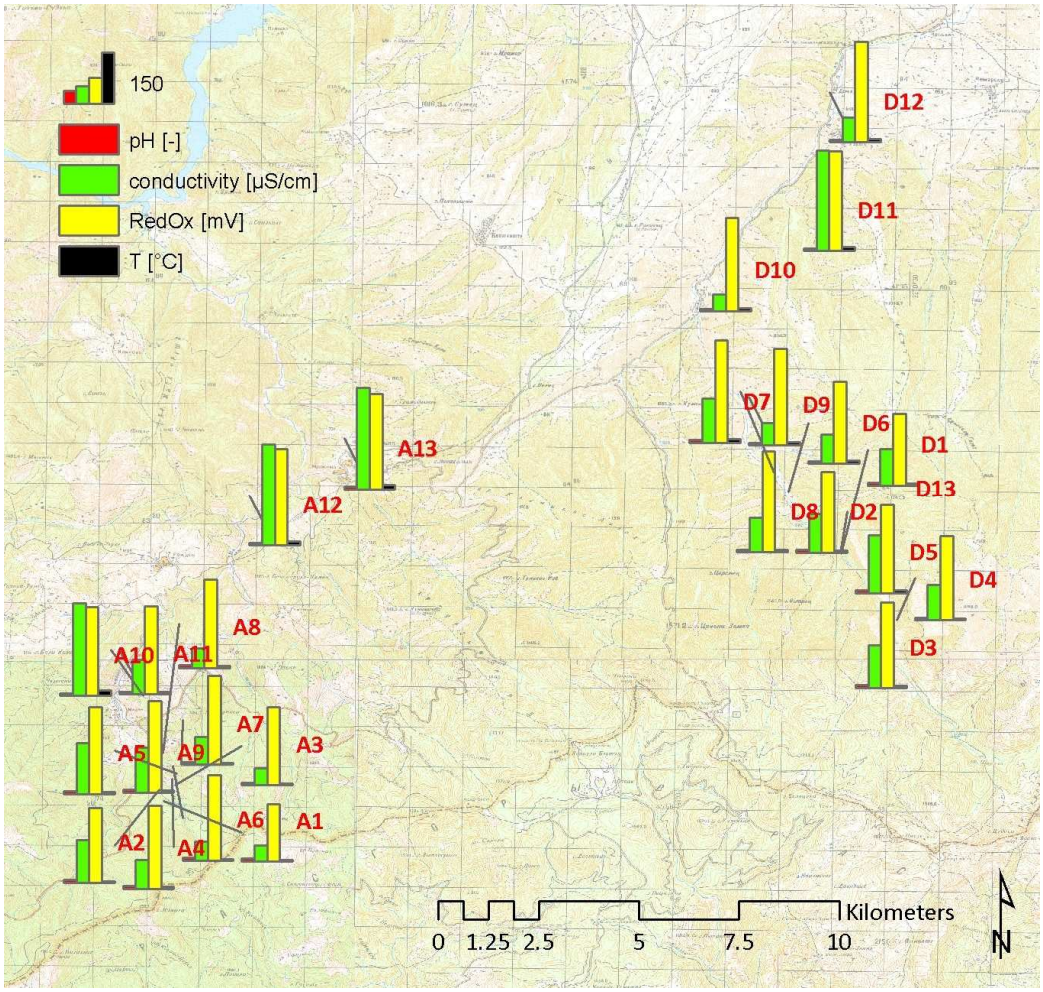


Figure 1: In situ measure physical parameters of surface and groundwater

Water characteristics in the area of interest

Despite of high carbonate presence specially in the Dudica area the measured values of electrolytic conductivity answer more to lowly mineralized rain/surface water or subsurficial water of shallow aquifers. Exceptionally there are values of 30 mS/m exceeded – namely for objects A10, A12, A13 a D11 – which indicate highest degree of mineralization within the water resources in the area of interest.

Values of RedOx potential keep entirely values of moderately oxidized zone. This confirms the type of shallow water discharged in short terms rather than deep circulation aquifers. The level of mineralization seems directly proportional to the temperature, which is another identifier of spring origin. Samples A10, A12, A13 and D11 showed significantly raised temperature than other sources, which can be most likely related to oxidation processes in the bedrock aquifers.

object	pH	conductivity [uS/cm]	conductivity for 25°C [mS/m]	RedOx [mV]	T[°C]
A1	8.25	47.5	8.04	170	4.1
A2	8.2	125.7	20.65	220.5	5.2
A3	8.18	51	8.63	231.4	4.3
A4	7.71	84.5	13.49	247.2	5.9
A5	8.26	150.6	24.04	255.9	6
A6	7.9	55.9	9.18	253.1	4.5
A7	8.06	83.3	13.29	263.3	5.9
A8	7.93	58.2	9.56	260.3	4.6
A9	8.16	133.5	21.31	272.2	5.8
A10	7.84	273.9	**33.55**	263.6	16.3
A11	7.98	101.2	15.70	260.3	6.9
A12	7.23	300	**41.70**	286.4	10.6
A13	7.32	300	**40.62**	283.1	12.1
D1	8.23	107.3	17.13	211.4	5.8
D2	8.26	114.8	17.81	240.8	6.8
D3	8.05	126.2	19.57	252.3	6.9
D4	8.03	105	17.25	250.6	5.4
D5	7.95	169.9	25.62	260.5	7.9
D6	6.47	86	12.62	241.5	9
D7	7.2	130.5	18.14	301.7	11
D8	7.51	100.8	15.63	301.1	6.7
D9	7.67	66.7	9.78	285.8	8.9
D10	7.06	49.5	7.26	275.2	9
D11	7.26	297.7	**39.30**	295.3	12.8
D12	7.47	73.1	10.72	295.9	8.7

Table 1: Physical parameters determined for surface and groundwater during field campaign in Alshar and Dudica

Flow pathways and groundwater vulnerability

The field sampling campaign was following expected water flow pathways down the surface streams were followed. All the available sources of groundwater have been searched out and sampled as well as surface water streams – closing profile of the catchment and its tributaries.

The natural background of the heavy metals is high in the area of interest. However, because of high elevated catchments, the prevailing part of groundwater flow springs from shallow aquifers having a quick response for rainwater infiltration. Because of presence of carbonates near to the surface the pH values rise typically over >7, so the migration of heavy metals is limited in all the range.

ID	Cr [µg/l]	Mn [µg/l]	Fe [µg/l]	Co [µg/l]	Ni [µg/l]	Cu [µg/l]	Zn [µg/l]	As [µg/l]	Mo [µg/l]	Ag [µg/l]	Cd [µg/l]	Sb [µg/l]	Tl [µg/l]	Pb [µg/l]	Bi [µg/l]	SO4 [µg/l]	Cl [µg/l]
A1	0.27	11.74	13.47	0.18	0.05	0.70	24.56	0.27	1.38	0.05	0.05	0.03	0.11	0.58	0.05	11.11	13.96
A2	2.55	12.60	39.35	0.44	2.17	0.89	37.97	0.72	4.30	0.05	0.05	0.42	0.17	0.40	0.05	15.36	18.99
A4	2.18	16.31	16.29	0.26	1.49	0.80	33.36	8.40	1.64	0.05	0.05	0.25	0.61	1.48	0.05	24.26	13.68
A5	0.49	14.20	39.53	0.42	1.12	0.87	40.28	1.00	1.23	0.05	0.05	0.03	0.18	0.46	0.05	10.35	17.04
A8	0.27	11.99	14.12	0.19	0.05	0.89	42.15	1.38	2.94	0.05	0.05	1.03	0.22	0.27	0.05	19.63	6.42
A9	0.53	3.30	26.04	0.22	0.05	0.78	25.13	3.95	2.42	0.05	0.05	0.75	0.65	0.39	0.05	9.02	10.05
A10	0.89	5.87	38.02	0.26	0.05	0.58	22.16	196.47	5.84	0.05	0.05	9.03	1.39	0.52	0.05	35.44	10.33
A11	0.03	1.26	18.07	0.15	0.05	0.66	20.66	6.67	1.64	0.05	0.05	0.35	0.18	0.26	0.05	13.55	12.01
A12	0.03	0.05	55.31	0.41	0.05	0.79	32.25	0.95	1.29	0.05	0.05	0.39	0.11	0.03	0.05	10.81	10.61
A13	0.25	0.05	60.96	0.39	0.05	1.10	26.23	27.31	9.75	0.05	0.05	0.37	0.10	0.03	0.05	16.04	14.52
D3	0.06	0.53	24.73	0.20	0.05	0.61	28.91	0.38	1.40	0.05	0.05	0.36	0.11	0.03	0.05	6.06	12.01
D4	0.17	3.59	22.01	0.19	0.05	0.78	24.13	0.22	1.40	0.05	0.05	0.03	0.12	0.74	0.05	11.70	11.73
D5	0.34	0.05	32.68	0.19	0.05	0.44	16.40	1.08	1.61	0.05	0.05	0.03	0.11	0.03	0.05	2.41	19.55
D6	0.03	4.87	18.08	0.10	1.81	0.77	20.90	0.60	1.93	0.05	0.05	0.03	0.11	3.13	0.05	12.98	12.85
D7	0.25	1.57	16.18	0.19	1.81	0.93	20.36	1.70	1.96	0.05	0.05	0.32	0.11	0.60	0.05	5.14	16.76
D8	0.03	32.57	19.42	0.21	4.29	1.16	86.88	0.36	1.38	0.05	0.79	0.03	0.11	6.47	0.05	10.96	15.64
D9	0.29	3.87	12.62	0.19	2.84	1.74	31.19	1.02	1.72	0.05	0.05	0.03	0.10	2.83	0.05	6.77	12.29
D10	0.03	3.25	9.05	0.18	0.05	1.12	34.50	0.53	1.14	0.05	0.05	0.03	0.10	1.41	0.05	13.20	13.96
D11	0.40	0.05	34.85	0.24	0.05	0.05	3.27	2.37	3.93	0.05	0.05	0.03	0.07	0.03	0.05	8.75	5.59
D12	0.03	4.42	12.25	0.19	1.36	1.49	110.79	0.48	1.46	0.05	0.05	0.23	0.10	1.68	0.05	9.93	15.92
D13	0.03	0.77	21.74	0.16	0.05	0.58	19.71	2.08	1.67	0.05	0.05	0.03	0.11	0.51	0.05	3.58	16.48

Table 1: Analyzed heavy metal concentrations

On the other hand groundwater of deeper structure is presented too (e.g. sample A10) referring to active volcanic layers in the depth and containing high loads of metal concentrations in the entire analyzed range. Despite heavy loads of metals in both the surveyed catchments their migration in surface and groundwater is limited by presence of carbonate buffer zone, that exist widely in the area of interest.

Water sources focused on deep groundwater flow are affected much of high concentration and are unsuitable for further use for both drinking and processing. Identified water sources are typically oriented to surface and shallow groundwater being highly mineralized by carbonates and having relatively low concentrations of heavy metals.

However, these sources are vulnerable to draughts so the water quality is varying accordingly to seasons.

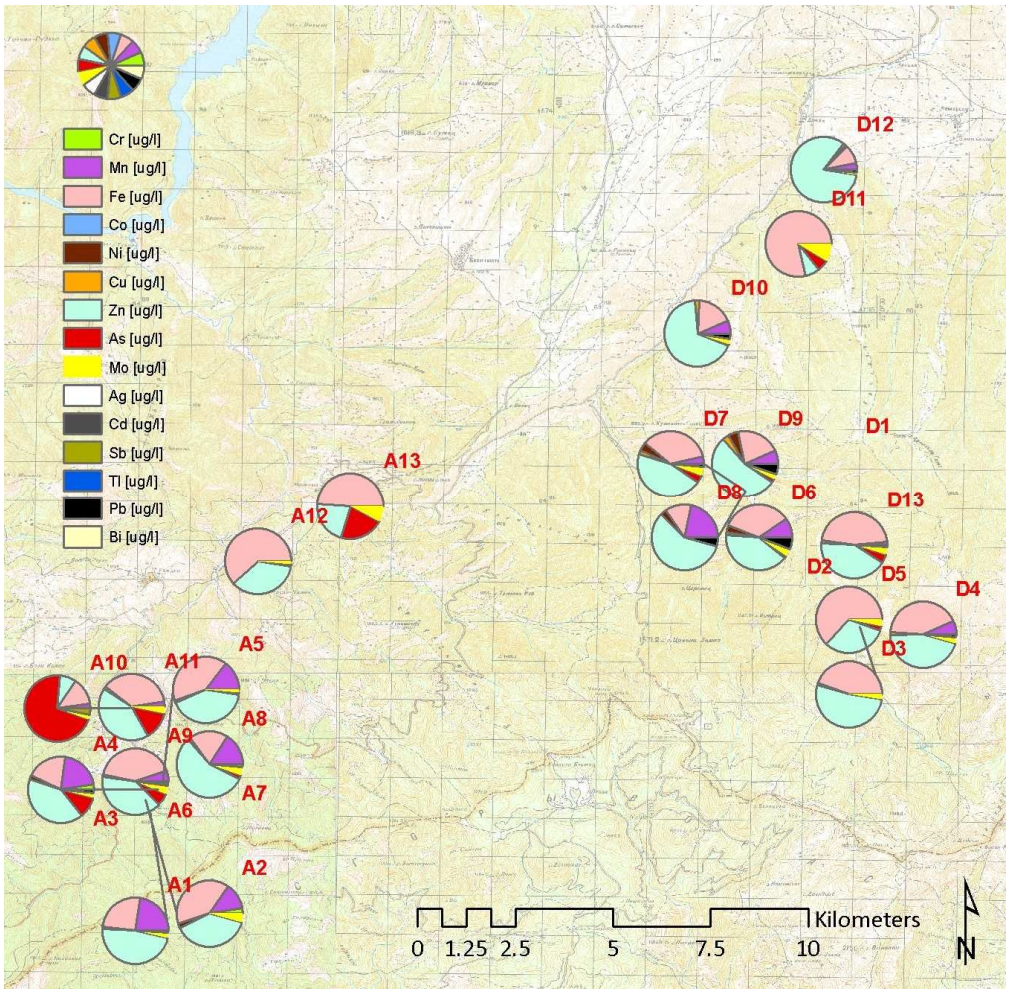


Figure 2: Overview of heavy metals concentration in the area of interest

References

Boev, B., Lepitkova, S.: The Alshar polymetallic deposit and its impacts on the water in lake Tikves, Faculty of mining and geology Stip, University st.Syril and Methodius Skopje, Macedonia, 2005
Boev, B., Mirčovski, V.: Hydrogeological characteristics of the area in the vicinity of the springs for water supply of the municipality of Kavadarci with regard to the determination of protection zones, Faculty of mining and geology Stip, University st.Syril and Methodius Skopje, Macedonia, 2005
Pitter, P.: Hydrochemie, Institute of chemical technology Prague, Prague 2009