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GEOCHEMICAL INVESTIGATIONS OF THE SOILS IN THE VICINITY OF THE RIVER ZLETOVSKA

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SUMMARY

The basic task of this paper is to obtain information according to which the degree of contamination to the soils with certain metals such as Fe, Mn, Pb, Zn, Cd, Cu, Cr, Ni, Co, As will be determined along the Zletovica River flow by means of geochemical exploration. These explorations should serve for making a study about the environment within the great project for the construction of the watereconomy site Zletovica.

The increased concentration of heavy metals in the samples of soil taken from the previously mentioned exploration wells at the both exploration profiles (I-II) is a potential danger for polluting the surface water flows of the rivers and the underground water that are in direct hydraulic relation to these water flows.

Looking downstream, the surface water from the mentioned rivers empty into the Bregalnica River. It, along its flow, has formed alluvial detritus where a confined type of aquifer with free level was formed. The city of Stip, as well as other inhabited places in the region, is being water supplied from such water aquifer.

For getting a final conclusion about the danger of pollution of great ground water quantities (aquifers) from local and regional aspect, it is necessary to carry out detailed hydrogeological and geochemical exploration works.

Key words : Contamination, Soils, Haeavy metals

INTRUDUCTION

Detailed geochemical explorations of several locations within the planned area, by means of field activities that include location of the exploration wells, drilling of these wells, taking samples from them.
Laboratory tests including procession of the collected material, measurements of the representativeness of the hard metals Fe, Mn, Pb, Zn, Cd, Cu, Cr, Ni, Co, As in the prepared soil samples and samples from the water extract in which the following metals should be determined: Fe, Mn, Pb, Zn, Cd, Cu, Cr, Ni, Co, As. The pH value as well as the temperature conductivity should also be defined.
There preliminary explorations concerning this type of explorations and they were publiched by (Boev & Lepitkova, 1997 ; Lepitkova &Boev et al. 1994; Lepitkova&Boev, 1995; Boev&Lepitkova, 1996, 2002; Lepitkova&Boev, 1998, 1999, 2002).

EXPLORATION METHODOLOGY

Sample preparation:

- Air drying;
- Cleaning from indecomposable organic residue, twigs, roots, coarse stones;
- Grinding in agate mortar;
- Screening through non-metal sieve with 1mm grid wholes;
- Separating of 100 g average sample for analysing the pH conductivity;
- Sample grinding in agate mortal to a size of 0.074 mm and proceeding with portions for chemical analyses of he required components;
- Preservation of duplicate sample.

Sample analyses for Cd, Cr, Co, Co, Cu, Pb, Mn, Ni, Zn, As

The analysis is performed according to the requirements of ISO 11047 by means of extraction with aqua regia and concentrations determined by AAS and ICP-AES.

The element As is determined according to ISO 11 466.

Water extract is made in the ratio 1:5 and 1:10. The elements in the extract are analysed according to ISO 11885 by means of ICP-AES

pH determination in water extracts in the ratio 1:2.5 by means of
potentiometer method according to ISO 10523

Conductivity determination according to the requirements of BDS EN 27888 by means of conduct metric method in water extracts in the ratio 1:25

Chemical analyses results

Table 1: Soils Samples ICP-AES (Profile I-Kiselica River)

Sample №	Pb, mg/kg	Zn, mg/kg	Cu, mg/kg	Co, mg/kg	Ni, mg/kg	Fe mg/kg	Cd mg/kg	As, mg/kg	Cr, mg/kg	Mn, mg/kg	pH
I-1-20	80	149	88	49	22	41520	<1	32	29	1100	6.3
I-1-40	82	184	84	47	24	40380	<1	33	32	1110	5.9
I-1-60	98	170	85	46	23	42900	<1	35	25	1100	5.8
I-1-80	80	144	93	46	24	42530	<1	34	33	970	5.9
I-2-20	2160	1140	230	31	7	67710	1	210	16	3140	2.3
I-2-40	2600	1420	230	40	12	63280	3	180	20	6740	2.4
I-2-60	5310	1940	345	42	9	72700	4	205	18	14120	2.4
I-2-80W	5940	1950	317	38	10	67200	6	190	18	14970	2.8
I-3-20	1860	1160	195	32	9	43490	3	104	15	7180	3
I-3-40	2170	800	170	23	<5	45600	<1	144	16	5300	3.3
I-3-60	2060	1140	206	33	<5	53150	2	164	13	5750	3.6
I-3-80	1950	1720	172	27	9	52440	3	172	13	10520	2.9
I-4-20	2240	1270	366	37	13	45570	<1	116	33	9940	3.2
I-4-40	2310	953	335	35	8	47370	<1	147	20	6080	3.4
I-4-60	3390	1240	235	30	<5	49840	1	160	13	4670	3.8
I-4-80W	1670	1420	220	31	6	37040	4	83	13	2020	6.9
I-5-20	1010	1370	170	56	21	53320	2	79	24	7250	4
I-5-40	197	850	123	50	20	48460	3	40	17	3640	4.1
I-5-60	128	690	96	50	22	56220	<1	46	20	2400	6
I-5-80	336	476	114	63	24	67020	<1	68	20	2280	6.4
I-6-20	436	205	75	42	9	30030	<1	21	19	1360	5.4
I-6-40	894	500	108	21	10	33300	<1	45	24	3170	4
I-6-60	1040	510	110	20	10	37610	2	50	17	3700	3.9
I-6-80	237	300	86	18	7	33380	<1	20	21	2470	3.9
I-7-20	230	110	75	34	5	22960	<1	15	18	1080	5.7
I-7-40	70	65	51	29	15	29980	<1	18	18	850	6.1
I-7-60	62	80	54	36	12	30740	<1	13	16	920	6.1
I-7-80	92	81	85	32	13	30470	<1	19	17	920	6.1

Finding and implications of the results

From the geochemical explorations carried out, we could conclude the following:

Profile I – I

At this profile, which is situated at the Kiselica River, 7 wells were drilled according to the Program and 28 samples were collected. The results obtained are the following:(Table 1):

The well 1

It might be concluded that in the well I, the Pb content (80-98mg/kg as well as the pH value from 5.8-6.3). If we compare it with the standards used, we may conclude that the results obtained in this well for the Pb content range within the following standard values.

The Zn content is (144-184mg/kg and the pH value from 5.9-6.3). Concerning the standards, it might be concluded that the Zn content is a little lower than the standard values.

The Cu content is(84-93 mg/kg at pH value from 5.9-6.3). Concerning the standard values it might be concluded that the Cu content is lower in relation to the standards.

The Co content is (46-49 mg/kg at pH from 5.9-6.3). According to the standard values (10-15 mg/kg) it could be concluded that the Co content is greater.

The Ni content is (22-24 mg/kg at pH from 5.9-6.3).Concerning the standards, it might be concluded that the Ni content is lower than the allowed concentrations.

The Cd content is far below the allowed concentrations.

The As content is (32-35 mg/kg at pH from 5.9-6.3). Concerning the standards, it might be concluded that the As content is a little greater than the allowed concentrations.

The Cr content is (25-33 mg/kg at pH from 5.9-6.3). Concerning the standards, it might be concluded that the Cr content is lower than the allowed concentrations.

The Mn content is (970-1100 mg/kg at pH from 5.9-6.3). Concerning the standards it might be concluded (500-1000 mg/kg), that the Mn content is about the allowed concentrations.

The Fe content is (40380-42900, at pH from 5.9-6.3). Concerning the standards (to 30000 mg/kg) it might be concluded that the values are greater than the allowed concentrations.

The well 2

It could be concluded that in the well II, the Pb content is (2160-5940 mg/kg and pH values range from 2.3-2.8). If we compare with the standards used, we might conclude that the results for the Pb content in this well are far greater in relation to the standard values.

The Zn content (1140-1950 mg/kg and pH value from 2.3-2.8). Concerning the standards, it might be concluded that the Cu content is far greater in relation to them.

The Co content is (31-42 mg/kg at pH from 2.3-2.8). Concerning the standard values (10-15 mg/kg) it might be considered that the Co content is greater.

The Ni content (7-10 mg/kg at pH from 2.3-2.8). Concerning the standards, it might be concluded that the Ni content is less than the allowed concentrations.

The Cd content (1-6 mg/kg at pH from 2.3-2.8) is far greater than the allowed concentrations.

The As content (180-210 mg/kg at pH from 2.3-2.8). Concerning the standards, it might be concluded that the As content is far greater than the allowed concentrations.

The Cr content (16-20 mg/kg at pH from 2.3-2.8). Concerning the standards it might be concluded that the Cr content is lower than the allowed concentrations.

The Mn content (3140-14970 mg/kg at pH from 2.3-2.8). Concerning the standards, it might be concluded (500-1000 mg/kg), that the Mn content is far greater than the allowed concentrations.

The Fe content (63280-72700 mg/kg, at pH from 2.3-2.8). Concerning the standards (to 30000 mg/kg) it can be concluded that the values are greater than the allowed concentrations.

The well 3

It can be concluded that in the well III, the Pb content is (1860-2170 mg/kg and the pH value from 2.9-3.6). If we compare it with the standards used, it could be concluded that the results obtained for the Pb content in this well are far greater in relation to the standard values.

The Zn content (800-1720 mg/kg and the pH value is from 2.9-3.6). As regards to the standards values, we could conclude that the Zn content is far greater than the standard values.

The Cu content (170-206 mg/kg at pH value from 2.9-3.6). Concerning the standard values (10-15 mg/kg) it might be concluded that the Co content is far greater in relation to the standards.

The Co content is (23-33 mg/kg at pH from 2.9-3.6) concerning the standard values (10-15 mg/kg) it can be concluded that the Co content is greater than the allowed.

The Ni content (to 9 mg/kg at pH from 2.9-3.6). As regards to the standards, we may conclude that the Ni content is less than the allowed concentrations.

The Cd content (to 3 mg/kg at pH from 2.9-3.6) is far greater than the allowed concentrations.

The As content is (104-172 mg/kg at pH from 2.9-3.6). As regards to the standards it can be concluded that the As content is far greater than the allowed concentrations.

The Cr content (13-16 mg/kg at pH from 2.9-3.6). Concerning the standards, it may be concluded that the Cr content is lower than the allowed concentrations.

The Mn content (5300-10520 mg/kg at pH from 2.9-3.6). Concerning the standards we may conclude (500-1000 mg/kg), that the Mn content is far greater than the allowed concentrations.

The Fe content (43490-53150 mg/kg, at pH from 2.9-3.6). As regards to the standards (to 30000 mg/kg) we might conclude that the values are greater than the allowed concentrations.

The well 4

In the well IV, the Pb content is (1670-3390 mg/kg and the pH value is from 3.2-6.9). If we compare it with the used standards, we might conclude that the results obtained for the Pb content are far greater in relation to the standard values in this well.

The Zn content (953-1420 mg/kg and the pH value is from 3.2-6.9). Concerning the standards, it might be concluded that the Zn content is far greater than the standard values.

The Cu content is (220-366 mg/kg at pH value from 3.2-6.9). Concerning the standard values it might be concluded that the Cu content is far greater in relation to the standards.

The Co content (31-37 mg/kg at pH from 3.2-6.9). Concerning the standard values (10-15 mg/kg) we may conclude that the Co content is greater than the allowed one.

The Ni content (to 13 mg/kg at pH from 3.2-6.9). Concerning the standards we may conclude that the Ni content is less than the allowed concentrations.

The Cd content (to 4 mg/kg at pH from 3.2-6.9) is far greater than the allowed concentrations.

The As content (83-160 mg/kg at pH from 3.2-6.9). Concerning the standards it might be concluded that the As content is far greater than the allowed concentrations.

The Co content is (18-42 mg/kg at pH from 3.9-5.4). Concerning the standard values (10-15 mg/kg) it might be concluded that the Co content is greater than the allowed one.

The Ni content is (7-10 mg/kg at pH from 3.9-5.4). Concerning the standards, it might be concluded that the Ni content is less than the allowed concentrations.

The Cd content is (to 2 mg/kg at pH from 3.9-5.4) is far greater than the allowed concentrations.

The As content is (20-50 mg/kg at pH from 3.9-5.4). Concerning the standards, it might be concluded that the As content is greater than the allowed concentrations.

The Cr content is (17-24 mg/kg at pH from 3.9-5.4). Concerning the standards, it might be concluded that the Cr content is lower than the allowed concentrations.

The Mn content is (1360-3700 mg/kg at pH from 3.9-5.4). Concerning the standards, it can be understood that (500-1000 mg/kg), that the Mn content is far greater than the allowed concentrations.

The Fe content is (30030-37610 mg/kg, at pH from 3.9-5.4). Concerning the standards (to 30000 mg./kg) it can be concluded that the values are greater than the allowed concentrations.

The well 7

It can be concluded that in the well VII the Pb content is (62-230 mg/kg and pH value is from 5.7-6.1). If it is compared to the standard used, it may be said that the results obtained for the Pb content in this value in the interval of 20 cm are far greater in relation to the standard values, while in the other intervals they are very close to the standard ones.

The Zn content is (81-110 mg/kg and the pH value is from 5.7-6.1). In relation to the standards, it might be concluded that the Zn content is within the standard values.

The Cu content is (51-85 mg/kg at pH value from 5.7-6.1). Concerning the standard values, it might be concluded that the Cu content is within the standard ones.

The Co content is (29-36 mg/kg at pH from 5.7-6.1). Concerning the standard values (10-15 mg/kg) it might be concluded that the Co content is greater than the allowed one.

The Ni content is (5-13 mg/kg at pH from 5.7-6.1). Concerning the standards, it could be concluded that the Ni content is less than the allowed concentrations.

The Cd content is (< 1 mg/kg at pH from 5.7-6.1) is within the allowed concentrations.

The As content is (13-19 mg/kg at pH from 5.7-6.1). Concerning the standards, it could be concluded that the As content is within the allowed concentrations.

The Cr content is (16-18 mg/kg at pH from 5.7-6.1). Concerning the standards it may be concluded that the Cr content is lower than the allowed concentrations.

The Mn content is (920-1080 mg/kg at pH from 5.7-6.1). Concerning the standards it might be concluded that (500-1000 mg/kg) the Mn content is within the allowed concentrations.

The Fe content (22960-30740 mg/kg, at ph from 5.7-6.1). Concerning the standards (to 30000 mg/kg) it might be concluded that the values are within the allowed concentrations.

CONCLUSION

The increased concentration of heavy metals in the samples of soil taken from the previously mentioned exploration wells at the both exploration profiles (I-II) is a potential danger for polluting the surface water flows of the rivers and the underground water that are in direct hydraulic relation to these water flows.

Looking downstream, the surface water from the mentioned rivers empty into the Bregalnica River. It, along its flow, has formed alluvial detritus where a confined type of aquifer with free level was formed. The city of Stip, as well as other inhabited places in the region, is being water supplied from such water aquifer.

For getting a final conclusion about the danger of pollution of great ground water quantities (aquifers) from local and regional aspect, it is necessary to carry out detailed hydrogeological and geochemical exploration works.

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