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GEOCHEMICAL PROPERTIES OF THE WATERS OF THE RIVER BREGALNICA

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SUMMARY

The paper presents the results of the geochemical properties of the waters of the River Bregalnica obtained after continuing monitoring of the water quality and the determination of the major parameters such as the concentration of heavy and toxic metals, organic pollutants and nutrient concentrations as well as the concentrations of cyanides, detergents etc.

The quality of the water of the River Bregalnica is unstable. The number of organic pollutants rises permanently and, like in other regions in Europe, the discharge of waste materials into the river is enormous.

The concentrations of heavy and toxic metals are within the levels allowed except for arsenic and manganese that yielded increased amounts.

Key words: geochemical, pollutants, have metals

Contamination of rivers by various substances in present day industrialised world has become very common. This is the result of waste water discharge, dust and waste gas emissions etc. that come from chemical companies, metallurgical, mining and other industrial plants which dispose of large volumes of heavy and toxic metals, organic effluents and nutrients.

The concentration of heavy and toxic metals in wastewaters is very high. Most of them are either man-made or discharged from industrial facilities.

Heavy metals are characterised by the inability to decompose biologically and they do not adhere to the sediment in the riverbed. Some heavy metals such as As, Se, Te and Au can be affected by biochemical change and transform into metallic organic compounds that are several times more toxic than their inorganic counterparts.

Increased concentrations of heavy and toxic metals in soils and water are a direct cause for their increased concentrations in various animal and plant species.

The most frequent pollutants of the environment are As, Cd, Cu, Pb, Hg, Ni, Zn, Mn and Cr. The most toxic are Hg, Pb, Cd, As, Se, Be.

Sn, Ni, Cu, Zn, Co may be poisonous when found in large quantities.

With heavy and toxic metals one must bear in mind the amount that defines the toxicity in certain secondary geochemical media. Some metals are necessary for the function of human organism and are important for many processes. They are regarded as harmful only when their concentrations have increased by several times.

Organic matter derived from diverse human activities is the major source of pollution that contaminates rivers. The decomposition and breakdown of this organic matter is performed by micro-organisms and takes place at the surface of the sediment and vegetation in small rivers and in the water column of large rivers.

As the process requires the consumption of oxygen, severe organic pollution may lead to rapid deoxygenating of rivers and aquatic invertebrates. The habitat then becomes uniform, with only a few robust species able to tolerate low oxygen concentration.

The most important sources of the organic waste feeding into rivers are domestic and industrial sewage. Downstream of sewage effluent, organic matter decomposition reduces the oxygen content of the water that results in the release of ammonium.

Further downstream the concentration of organic matter decreases as a result of dilution and continuing decomposition. As the distance from the effluent increases, bacteria oxidise the ammonium to nitrate, and oxygen enters the water via the water surface and thus increases the oxygen content.

Eventually the level of organic matter, oxygen and ammonium reach those present upstream the sewage.

This process of recovery is called self-purification. An example of this is the River Danube, which is polluted when it enters Hungary. When it flows in Hungary it is polluted by organic matter from tributaries and towns, particularly Budapest.

However, by the time the river leaves the country and enters Croatia some amount of organic matter equal to that discharged in Hungary has decomposed. Still, this does not imply that rivers can take up an unlimited amount of organic matter without suffering. Pollution can be so severe and widespread and last for a long time that self-purification is insufficient. Thus, the Danube is still polluted when it leaves Hungary and Rhine was polluted with excessive amounts of organic matter between World War II and the early 1070s. There was very serious oxygen depletion in its middle and lower courses that the river virtually died.

METHODS OF WORK

Samples were taken from sampling stations once a month for a time period of four months. Samples were divided into two parts. The first were preserved by HNO_3, and the second were analysed in laboratory in order to determine organic pollutants. Methods of analyses included ICP-AES, spectrophotometric (UVE-VIS), and volumetric and gravimetric methods.

RESULTS OBTAINED AND DISCUSSION

The results obtained about the quality of the water of the River Bregalnica are shown in Tables 1, 2, 3, and 4.

The results indicate that BOD values are in the range of 3.8 to 5.8 mgO_2/l (Table,1- 4), whereas COD values are in the range 17.2 to 21.2 mgO_2/l (Table 1- 4).

If we compare these values with the BOD and COD in the rivers of Europe, we can see that they match the values of 75% of the rivers in Europe that have BOD of 4.7 mgO_2/l and COD of 25 mgO_2/l.

In that regard, it can be said that the River Bregalnca is polluted by organic pollutants and its pollution is equal to the average pollution of 75% of the rivers in Europe.

Pollution is caused by urban settlements along the river course, the disposal of waste water and the discharge of industrial waste.

Nutrient constituents (nitrogen and phosphorus compounds) in the wasters of the River Bregalnica are shown in Tables 1, 2, 3, 4.

The results show that the river contains increased volumes of NO_3. compared with standard values. The increased contents vary depending on where the samples were collected. The lowest values of 0.9 mg/l were found with samples taken at site 8 (1.2 mg/l) and at the estuary of the Rivers Zletovica and Bregalnica, whereas at other measure points increased values of NO_3. were obtained.

If we compare these values with the average values in rivers in Europe that amount to 2.63 mg/l obtained after measurements carried out at 654 stations, we come to the same conclusion. Namely, only at measure points 8 and 4 the obtained values are lower than the average.

A comparison between the mean value of our measurements yields the value of 4 mg/l that matches 75% of the values in the rivers of Europe.

The increased values are due to the increased agricultural activities along the river course and the discharge of waste materials after communal activities.

The content of ammonium in the water of the River Bregalnica is within the limits.

The phosphorus contents are also within the limits except at one sampling station (sampling station no. 1, Istibanja) in which increased contents of phosphorus of 0.175 mg/l in the nutrient was found.

Cyanides and detergents were not found. With regard to pH value, we can say that no acidification was found in the medium and that the water has a standard value.

Analyses for the determination of the concentrations of heavy and toxic metals not only subject matter of the Agreement but even more were carried out.

The elements determined in the flowing water of the river are: Ca, Mg, Na, K, Al, Fe, Mn, Sr, Ni, Co, Cr, Zn, Cu, Pb, Cd, As, Mo, W, V and Ag.

Table 1. Concentration of heavy and toxic metals and nutrients (in mg/l) at sampling stations along the River Bregalnica in May 2003.

	1	2	3	4	5	6	7	8
Ca	60.06	57.83	58.74	58.05	70.82	48.23	46.11	30.34
Mg	17.24	15.36	15.36	14.02	13.68	11.78	13.61	8.09
Na	22.39	19.3	18.76	17.63	15.88	14.28	16.89	7.59
K	3.65	3.43	3.16	3	2.73	2.6	2.75	1.91
Al	0.372	0.375	0.369	0.368	0.414	0.305	0.313	0.203
Fe	0.347	0.378	0.256	0.294	0.133	0.547	0.207	0.06
Mn	0.215	0.087	0.235	0.35	0.115	0.406	0.033	0.03
P	0.184	0.063	0.053	0.057	0.032	0.044	0.046	0.056
Sr	0.365	0.352	0.358	0.333	0.491	0.237	0.241	0.13
Ni	0.004	0.007	0.022	0.007	0.003	0.005	0.003	0.001
Co	0.0046	0.0072	0.0037	0.001	0.002	0.0023	0.0026	0.0036
Cr	0.001	0.001	0.0016	0.0042	0.001	0.001	0.001	0.001
Zn	0.0061	0.0069	0.0058	0.0065	0.0063	0.0065	0.004	0.0971
Cu	0.0051	0.0092	0.0071	0.0102	0.0015	0.001	0.0077	0.013
Pb	0.005	0.005	0.0014	0.0025	0.005	0.0074	0.005	0.005
Cd	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
As	0.076	0.02	0.026	0.001	0.021	0.06	0.058	0.049
Mo	0.0149	0.001	0.001	0.0268	0.0092	0.0151	0.0004	0.0344
W	0.0494	0.0159	0.005	0.005	0.005	0.0219	0.0193	0.005
V	0.05	0.046	0.043	0.04	0.041	0.034	0.042	0.021
Ag	0.001	0.001	0.001	0.004	0.001	0.001	0.001	0.001
NO3-	5.8	4.6	8.2	0.7	3.5	2.3	3.8	1.1
NO2-	0	0.4	0.09	0.04	0.07	0.09	0.09	1
NH4+	0.04	0.1	0.05	0.05	0.04	0.06	0.05	0.05
SO42-	38.2	24.6	33.3	97	46.4	46	49.7	58.4
Cijanid	0	0	0	0	0	0	0	0
Detergent	0	0	0	0	0	0	0	0
pH	7.7	7.7	7.7	7.8	7.75	7.75	7.78	7.8

1. sampling station along the River Bregalnica at Istibanja.
2. the village of Orizari,
3. the town of Kocani,
4. the village of Cesinovo,
5. the village of Karbinci,
6. Makedonka settlement,
7. outskirts of Stip,
8. the area of the estuary of the Rivers Bregalnica and Vardar.

Table 2. Concentration of heavy and toxic metals and nutrients (in mg/l) at some sampling stations along the River Bregalnica in June 2003.

	1	2	3	4	5	6	7	8
Ca	63.2	58.2	55.26	57.2	68.2	50.21	48.52	35.62
Mg	16.5	15.24	14.52	13.25	13.21	12.5	12.56	7.85
Na	20.11	20.32	17.85	16.52	15.2	15.8	15.61	7.32
K	3.54	3.02	3.24	2.85	2.56	2.4	2.45	1.85
Al	0.341	0.364	0.32	0.421	0.425	0.321	0.254	0.21
Fe	0.32	0.354	0.241	0.221	0.125	0.52	0.231	0.05
Mn	0.2	0.074	0.212	0.31	0.124	0.368	0.025	0.02
P	0.175	0.052	0.045	0.047	0.028	0.054	0.052	0.045
Sr	0.352	0.364	0.387	0.258	0.389	0.254	0.231	0.1
Ni	0.004	0.005	0.012	0.007	0.003	0.005	0.002	0.001
Co	0.0041	0.0065	0.0025	0.001	0.002	0.0032	0.0024	0.0025
Cr	0.001	0.001	0.0014	0.0035	0.001	0.001	0.001	0.001
Zn	0.0057	0.0056	0.0045	0.0054	0.0058	0.0054	0.003	0.0852
Cu	0.0045	0.0084	0.0084	0.0121	0.0012	0.001	0.0058	0.01
Pb	0.005	0.005	0.0016	0.0027	0.005	0.0081	0.003	0.005
Cd	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
As	0.065	0.02	0.031	0.001	0.018	0.05	0.062	0.036
Mo	0.025	0.001	0.001	0.0231	0.0092	0.0142	0.0004	0.0254
W	0.0384	0.0123	0.005	0.005	0.005	0.0254	0.0241	0.005
V	0.05	0.041	0.032	0.04	0.058	0.041	0.032	0.024
Ag	0.001	0.001	0.001	0.004	0.001	0.001	0.001	0.001
NO3-	6.2	5.1	7.5	0.9	4.2	3.2	4.3	1.2
NO2-	0.2	0.6	0.08	0.06	0.08	0.08	0.06	1
NH4+	0.05	0.2	0.04	0.07	0.09	0.04	0.03	0.04
SO42-	39.5	25.7	35.2	92	50.1	42	48.6	55.2
Cijanid	0	0	0	0	0	0	0	0
Detergent	0	0	0	0	0	0	0	0
pH	7.7	7.7	7.8	7.8	7.8	7.8	7.75	7.8

1. sampling station along the River Bregalnica at Istibanja.
2. the village of Orizari,
3. the town of Kocani,
4. the village of Cesinovo,
5. the village of Karbinci,
6. Makedonka settlement,
7. outskirts of Stip,
8. the area of the estuary of the Rivers Bregalnica and Vardar.

Table 3. Concentration of heavy and toxic metals and nutrients (in mg/l) at some sampling stations along the River Bregalnica in July 2003.

	1	2	3	4	5	6	7	8
Ca	61.25	58.18	59.364	57.25	69.54	47.56	45.21	29.85
Mg	16.89	15.23	14.87	13.87	14	12.31	13.54	7.95
Na	22.65	18.54	18.21	16.98	14.58	13.25	17.84	6.87
K	3.54	2.98	3.54	2.87	2.98	2.45	2.65	1.54
Al	0.354	0.321	0.398	0.378	0.425	0.325	0.341	0.211
Fe	0.325	0.365	0.224	0.265	0.185	0.621	0.235	0.05
Mn	0.254	0.015	0.214	0.365	0.154	0.521	0.026	0.025
P	0.174	0.056	0.045	0.055	0.041	0.054	0.049	0.05
Sr	0.387	0.321	0.347	0.322	0.421	0.263	0.287	0.152
Ni	0.003	0.007	0.024	0.007	0.003	0.005	0.003	0.001
Co	0.0051	0.0053	0.0031	0.001	0.002	0.002	0.002	0.003
Cr	0.001	0.001	0.001	0.003	0.001	0.001	0.001	0.001
Zn	0.005	0.007	0.006	0.006	0.007	0.008	0.004	0.009
Cu	0.005	0.008	0.007	0.009	0.001	0.001	0.006	0.013
Pb	0.005	0.005	0.001	0.002	0.005	0.006	0.005	0.005
Cd	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
As	0.065	0.024	0.023	0.001	0.021	0.054	0.065	0.038
Mo	0.016	0.001	0.001	0.0251	0.009	0.0142	0.0004	0.0256
W	0.0587	0.0163	0.005	0.005	0.005	0.0312	0.0165	0.005
V	0.05	0.056	0.054	0.052	0.065	0.035	0.041	0.025
Ag	0.001	0.001	0.001	0.004	0.001	0.001	0.001	0.001
NO3-	6.5	5.2	7.6	0.9	2.8	2.4	3.6	1.2
NO2-	0.2	0.6	0.06	0.05	0.06	0.08	0.08	1.2
NH4+	0.05	0.15	0.06	0.04	0.05	0.07	0.04	0.06
SO42-	45.2	36.5	35.2	87	48.6	41.3	51.2	61.2
Cijanid	0	0	0	0	0	0	0	0
Detergent	0	0	0	0	0	0	0	0
pH	7.7	7.7	7.7	7.8	7.75	7.75	7.78	7.8

1. sampling station along the River Bregalnica at Istibanja.
2. the village of Orizari,
3. the town of Kocani,
4. the village of Cesinovo,
5. the village of Karbinci,
6. Makedonka settlement,
7. outskirts of Stip,
8. the area of the estuary of the Rivers Bregalnica and Vardar.

Table 4. Concentration of heavy and toxic metals and nutrients (in mg/l) at some sampling stations along the River Bregalnica and organic pollutants in August 2003.

	1	2	3	4	5	6	7	8
Ca	62.53	60.11	60.28	58.5	65.31	48.56	48.65	31.25
Mg	17.89	16.32	15.87	14.56	15.21	13.25	14.52	8.95
Na	23.65	19.54	17.65	17.85	15.32	14.52	18.65	6.54
K	3.21	2.85	3.65	2.65	2.85	1.65	2.54	1.45
Al	0.421	0.451	0.421	0.431	0.465	0.356	0.354	0.254
Fe	0.385	0.421	0.235	0.231	0.256	0.589	0.265	0.05
Mn	0.264	0.021	0.254	0.324	0.178	0.487	0.028	0.023
P	0.185	0.065	0.042	0.065	0.035	0.065	0.051	0.05
Sr	0.354	0.381	0.365	0.387	0.398	0.254	0.381	0.187
Ni	0.003	0.006	0.041	0.007	0.002	0.005	0.003	0.001
Co	0.0068	0.0054	0.003	0.001	0.002	0.002	0.002	0.003
Cr	0.001	0.001	0.001	0.003	0.001	0.001	0.001	0.001
Zn	0.005	0.006	0.005	0.005	0.006	0.009	0.006	0.005
Cu	0.005	0.007	0.007	0.008	0.001	0.001	0.006	0.03
Pb	0.005	0.005	0.001	0.002	0.004	0.005	0.005	0.005
Cd	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001
As	0.058	0.038	0.035	0.001	0.032	0.065	0.051	0.045
Mo	0.021	0.001	0.001	0.0354	0.008	0.0187	0.0004	0.0232
W	0.0421	0.0154	0.005	0.005	0.005	0.0256	0.0187	0.005
V	0.05	0.048	0.065	0.045	0.052	0.025	0.032	0.031
Ag	0.001	0.001	0.001	0.002	0.001	0.001	0.001	0.001
NO3-	6.2	4.8	6.8	1.5	2.5	3.2	4.5	1.1
NO2-	0.1	0.5	0.05	0.05	0.06	0.09	0.08	0.9
NH4+	0.05	0.21	0.04	0.04	0.05	0.08	0.04	0.06
SO42-	46.2	38.6	36.2	68	45.2	45.2	56.3	38.5
Cijanid	0	0	0	0	0	0	0	0
Detergent	0	0	0	0	0	0	0	0
pH	7.7	7.8	7.8	7.8	7.8	7.8	7.7	7.8
BOD	4.2	4.5	4.4	5.8	4.4	3.6	5.1	3.8
COD	19.8	19.3	17.5	17.5	18.3	21.2	20.3	17.2

1. sampling station along the River Bregalnica at Istibanja.
2. the village of Orizari,
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6. Makedonka settlement,
7. outskirts of Stip,
8. the area of the estuary of the Rivers Bregalnica and Vardar.

The contents of Ni at all measure points are below the concentration allowed.

The contents of Pb in all measure points are below the concentrations allowed.

The contents of As at measure points 1 and 7 (Istibanja and outflow of Bregalnica from Stip) yield higher values relative to the concentrations allowed.

At measure point 6 (Makedonka settlement) the arsenic content is within the limits allowed. At other measure points arsenic content is below the concentrations allowed.

The Cr content is below the limit at all measure points.

The Cu content is below the concentrations allowed at all measure points.

The Co content is below the concentrations allowed at all measure points.

The Cd content is below the concentrations allowed at all measure points.

The Zn content is below the concentrations allowed at all measure points.

The Mn content is below the concentrations allowed at all measure points except for measure points 7 and 8 (outlet of the Bregalnica from the town and inflow into the River Vardar).

The contents of Fe are below the limits at all measure points except for no. 6 (Makedonka settlement) where increased values were recorded.

CONCLUSION

Investigations carried out on the waters of the River Bregalnica in order to determine the presence of heavy and toxic metals made it possible to conclude that all parameters measured yielded concentrations that are below the limits, except for those of arsenic and manganese that indicated increased concentrations at some points.

The situation with organic pollutants and nutrients call for more detailed investigations by establishing permanent monitoring of flowing waters along the river course in urban areas.

It is worth mentioning that it would be useful to secure funds and establish automated stations for the control of water quality of the river and to make a registry of polluters of the river Bregalnica with detailed determination of waste materials that are discharged into the river by industrial plants and the population in the community.

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