ENVIRONMENTAL MONITORING OF LEAD-ZINC MINING FIELDS IN THE BULGARIAN AND MACEDONIAN PART OF OSOGOVO MOUNTAIN

Kamen Dimitrov[1], Alexander Peychev [2], Konstantin Radenkov[3], Anton Sotirov[4], Vladimir Gaberov[5], Kire Deyanovski[5], Zoran Bozinovski[5], Desa Yakomivska[5]

[1] Southwest University, 2700 Blagoevgrad, Bulgaria
[2] Sofia University "St. Kliment Ohridski", 15 "Tzar Osvoboditel" Str., 1504 Sofia, Bulgaria
[3] Vitren Co., 1 "Skrinski pat" Str., 2500 Kyustendil, Bulgaria
[4] Agency for Regional Development, 44 "Demokratsiya" Str., 2500 Kyustendil, Bulgaria
[5] Ecological Society "Flora", Skopie, Macedonia

Introduction

This study presents the results from project №98-BG/MK-03S02 with manager Kamen Dimitrov, financed by the Program PHARE Credo of the European Union and executed by the Agency for Regional Development-Kyustendil, Society for Protection of the Nature in Bulgaria, Ecological Society "Flora"-Macedonia, and Municipality Kriva Palanka-Macedonia. The study summarizes data from 90 samples of air, soil and water at 55 points on both sides of the state border between Bulgaria and Macedonia. The objective of this study is to determine the degree of contamination of the environment of Kamenichka basin, the northern slopes of Osogovo Mountain and the valley of the river Kriva reka, located in the border areas of Kyustendil Municipality-Bulgaria and Kriva Palanka Municipality-Macedonia.

Material and methods

The water samples were taken three times during the autumn-winter period of second low-water level, during the period of spring high-water level and during the summer low-water level. The samples were summarized as they were taken during five-hour period at one-hour intervals. The quantity of each sample was 1 liter.

Measurement of the temperature of the air and water was done, parallel with the sampling. Samples from the air were taken during different seasons and places – closely to the mining fields, ore-processing plants, landfills, and the closest settlements. The aspiration method for air sampling was used for determination of dust concentration with exposition 120 min. (Bulgarian State Standard - BDS-17.2.4.20-83). The relative error margin in the analysis method used is within the limits 3-5%.

Eighteen soil samples were taken from the Bulgarian part and 18 from the Macedonian part of Osogovo Mountain from A soil horizon. The samples from non-agricultural lands were taken from 0-10 cm depth, but the samples from agricultural lands were taken from a depth of 0-20/25 cm. The laboratory analyses for heavy metals are done according to the Bulgarian State Standard - BDS 17.4.4.02-80. The samples are treated with HF and $HClO_4$ and the measurements of the element concentrations were done with an atomic-absorbtion spectrometer Perkin-Elmer 4100.

Results and discussion

Water conditions during the study period. The water conditions of the rivers Lebnitsa, Bistritsa and Kriva reka satisfy the conditions for waterways II category. The concentrations of lead, cadmium, nitrogenous nitrite, manganese, cyanides, and copper in the water are higher than the background of the environment. The concentrations of lead, cadmium, manganese, and insoluble chemicals in many samples exceed the permissible breaking concentrations (PBC) (Table 1).

Condition of the air. The present study established that the dust contamination in the areas around the ore-processing plant and landfill near Gyueshevo village in Bulgaria is high. The sampling was done in windy weather. Dusty winds are a frequently met phenomenon in the studied area. The composition of the dust is the same as the ore and the ore waste. The amount of the dust in the atmosphere during non-windy weather is below the permissible breaking concentrations (PBC) in the above-mentioned areas as well as in the area of the ore-processing plant "Toranitsa"-Macedonia. The measured dust concentration in the Bulgarian part of Osogovo was between 0.1875 mg/m^3 and 0.8975 mg/m^3 as the PBS is 0.5000 mg/m^3, but the dust concentration in the Macedonian part varied between 0.1510 mg/m^3 and 0.2500 mg/m^3.

Condition of the soil. The soils of the studied areas show concentrations of lead and zinc, which exceed the permissible breaking concentrations for heavy metals (PBC) (Fig. 1). The soils around the ore-processing plan and purifying plant for landfill cyclic water supply, situated in the valley of Lebnitsa river, contain concentrations of heavy metals, which exceed the PBC. The two-kilometer alluvial zone near the landfill, situated in the valley of river Kriva reka is highly contaminated. The concentration of cooper is below the PBC in soils with every kind of acidity. Some areas are contaminated with cadmium.

Conclusion

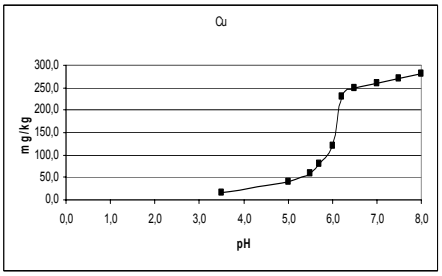
Ore-mining and ore-processing industry in the Osogovo Mountain, as well as the deposition of waste, resulting from this industry, have a negative influence on the components of the environment. The air, water and soil in the area are seriously contaminated. The concentrations of hazardous elements in many samples exceed many times the permissible breaking concentrations (PBC), which is a risk for the human health. The areas around the ore-processing plants and landfills are seriously contaminated. The

Table 1. Results from physico-chemical analyses of water from the mining areas in Osogovo Mopuntain (mg/l); n.d. – no data

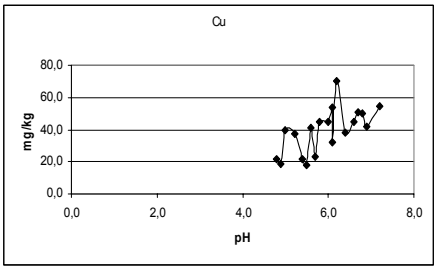
INDICATORS	Permissible concentrations		December 1999 Bulgaria						August 2000 Bulgaria					
	II categ.	III categ.	River Bistritsa beneath Ruen Mine	River Bistritsa after River Lebnitsa flow	River Bistritsa at Garlyano village	River Lebnitsa beneath Ruen Plant	Well depth 7 m near River Lebnitsa	River Lebnitsa near to the landfill	River Bistritsa beneath Ruen Mine	River Bistritsa after River Lebnitsa flow	River Bistri- tsa at Garlyano village	River Lebni-tsa beneath Ruen Plant	Well depth 7 m near River Lebnitsa	River Lebni-tsa near to the landfill
Active reaction pH	6,0-8,5	6,0-9,0	7,6	8	7	7,8	7,1	7,8	7,8	7,3	7,3	7,6	6,9	7,6
Soluble O2	>4	>2	7,1	7,4	7,3	7,4	6,4	6,8	6,8	7,6	8,2	7,7	8,2	8,6
BPC component 5	15	25	5,5	4,2	4,9	6,3	4,9	4,9	2,4	2,7	2,8	1,9	3	3,3
Oxidity (perm.)	30	40	1,12	0,88	1,12	1,52	0,8	1,6	0,88	1,36	2,32	2	1,12	2,08
HPC (bio-chromatic)	70	100	40	20	30	70	20	60	30	20	30	10	30	20
Soluble chemicals	1000	1500	432	64,4	70	109,6	135,4	140,4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Insolub. chemicals	50	100	20	10	10	10	20	10	20	10	10	20	50	20
Chlorine ions	300	400	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4	7	5	15	12	11
Sulphate ions	300	400	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	30	5	20	150	45	130
Nitrogen (ammonium)	2	5	0,03	0,01	0,02	0,03	0,01	0,01	0,02	0,01	0,012	0,01	0,014	0,01
Nitrogenous nitrite	0,04	0,06	0,01	0,001	0,002	0,005	0,005	0,001	0,001	0,001	0,01	0,12	0,008	0,04
Nitrogenous nitrate	10	20	0,6	1,18	0,8	0,8	1,7	8,16	1,34	0,3	0,56	1,66	3,29	0,54
Phosphate (PO4)	1	2	0,007	0,005	0,003	0,12	1,16	0,006	0,03	0,01	0,02	0,05	0,014	0,02
Cyanides (easily soluble)	0,05	0,1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,01	0,001	0,001	0,001	0,002	0,004
Iron (Total)	1,5	5	0,02	0,02	0,04	0,14	0,02	0,08	0,12	0,002	0,004	0,008	0,004	0,002
Manganese (Total)	0,3	0,8	0,081	0	0	0,48	0	0,34	0,05	0	0	0,04	0,01	0,15
Cadmium	0,01	0,02	0,008	0,01	0,008	0,,01	0,004	0,008	0,001	0,001	0,002	0,004	0,002	0,02
Lead	0,05	0,2	0,02	0,01	0,01	0,03	0,03	0,04	0,02	0,005	0,002	0,04	0,02	0,04
Copper	0,1	0,5	0,07	0,04	0,06	0,05	0,04	0,1	0,04	0,03	0,04	0,2	0,02	0,03
Zinc	5	10	0,1	0,22	0,24	0,48	0,24	0,15	0,008	0,08	0,01	0,08	0,08	0,06
INDICATORS	Permissible concentrations		December 1999 Macedonia						August 2000 Macedonia					
	II categ.	III categ.	River Toranitsa by the mine fields	River Banchilo before its flow in the River Toranitsa	River Yarets before its flow in the River Toranitsa	River Toranitsa by the enrichment plant	River Kriva reka 1 km from the landfill	River Kriva reka at Jidlovo village	River Toranitsa by the mine fields	River Banchilo before its flow in the River Toranitsa	River Yarets before its flow in the River Toranitsa	River Toranitsa by the enrichment plant	River Kriva reka 1 km from the landfill	River Kriva reka at Jidlovo village
Active reaction pH	6,0-8,5	6,0-9,0	6,78	6,8	7,01	7,25	7,36	7,26	6,6	6,8	8,1	7,4	7,8	7
Soluble O2	>4	>2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7,7	7,4	8,3	7,5	8,9	8,2
BPC component 5	15	25	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3,1	3,4	4	4,3	3,7	3,5
Oxidity (perm.)	30	40	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3,2	2,56	1,12	75,2	1,12	0,32
HPC (bio-chromatic)	70	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	60	10	10	112	10	20
Insolub. chemicals	50	100	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	20	80	50	60	20	40
Chlorine ions	300	400	7	7	27	9	7	7	7	7	6	5	4	10
Sulphate ions	300	400	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	80	60	20	70	40	30
Nitrogen (ammonium)	2	5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,05	0,08	0,08	0,64	0,1	0,08
Nitrogenous nitrite	0,04	0,06	0,009	0,002	0,036	0,001	0,002	0,002	0,04	0,02	0,02	0,12	0,08	0,04
Nitrogenous nitrate	10	20	0,879	0,11	1,175	0,677	0,518	0,464	1,13	0,55	0,5	230	1,5	1,5
Phosphate (PO4)	1	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,01	0,012	0,002	0,001	0,08	0,005
Cyanides (easily soluble)	0,05	0,1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,02	0,005	0,03	0,008	0,002	0,01
Iron (Total)	1,5	5	0,159	0,017	0,044	0,076	0,018	0,021	0,04	0,002	0,001	0,001	0,002	0,008
Manganese (Total)	0,3	0,8	0,25	n.d.	n.d.	0,15	n.d.	n.d.	0,14	0,02	0,01	0,02	0,08	0,06
Cadmium	0,01	0,02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,003	0,001	0,002	0,001	0,001	0,002
Lead	0,05	0,2	0,04	0,04	0,03	0,08	0,05	0,03	0,02	0,005	0,005	0,001	0,005	0,01
Arsenic	0,05	0,2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,001	0,001	0,002	0,003	0,001	0
Copper	0,1	0,5	0,04	n.d.	n.d.	n.d.	n.d.	n.d.	0,13	0,02	0,01	0,03	0,01	0,01
Nickel	0,2	0,5	0,04	0,02	0,02	0,02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zinc	5	10	0,28	0,1	0,1	0,2	0,14	0,07	0,08	0,03	0,08	0,02	0,01	0,01

established contamination with lead and zinc is definitely a result from the activity of the lead-zinc ore mines in that areas, like Velikov and Drenovski (1994) described copper contamination in the copper ore mining areas around the towns of Zlatitsa and Pirdop.

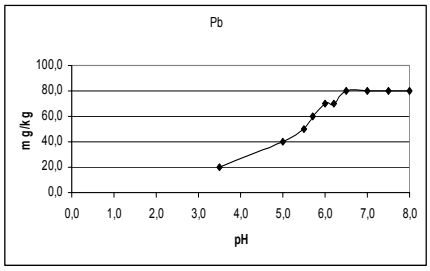
Lead causes many diseases as leucemia, kidney disorders, brain damage, early death, gastrointestinal distress, encephalopathy, and etc. High concentrations of zinc in the environment may cause growth depression, sexual immaturity, skin lesions, immunocompetence. Cadmium causes hypertension, giddiness, vomiting, respiratory difficulties, kidney disorders, cancer, and many others. Many of the above-mentioned diseases are widespread in the studied areas, as the kidney disorders and cancer, as well as the respiratory difficulties of the inhabitants. However, we should point out that the natural litho-geochemical background of the studied hazardous elements is high in Osogovo Mountain. For example, it was established that the coal near Osogovo granite massif is rich in lead, zinc and cadmium as their ash contains cadmium, which concentration exceeding 22 times the permissible breaking concentrations for soil (PBC) (Kortenski, Sotirov, 2002).



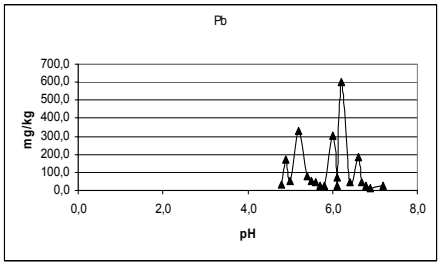
a) Permissible concentrations of copper in soils.



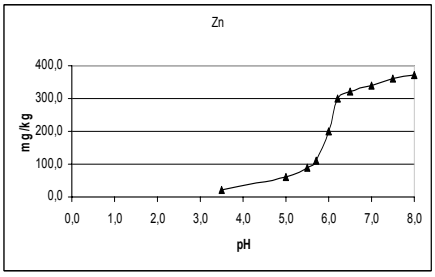
b) Concentrations of copper in the studied soils.



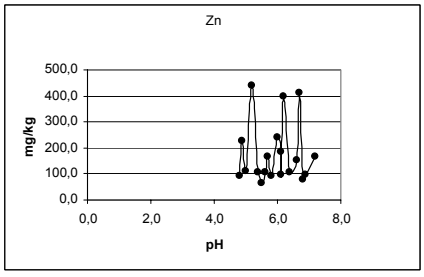
c) Permissible concentrations of lead in soils.



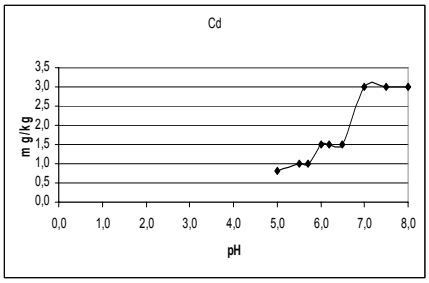
d) Concentrations of lead in the studied soils.



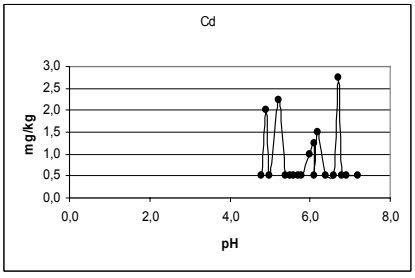
e) Permissible concentrations of zinc in soils.



f) Concentrations of zinc in the studied soils.



g) Permissible concentrations of cadmium in soils.



f) Concentrations of cadmium in the studied soils.

Fig. 1. Comparative diagrams between the permissible concentrations (State newspaper №54/1997) and the established concentrations of the studied elements in the soils.

References

Velikov, V., I. Drenovski. 1994. Contamination of the soils and drinking water in the areas around the towns Zlatitsa and Pirdop. – In: *Proceedings National Science-Practical Conference of Geography "Geoecology '94",* 86-91.

Bell, F. G. 1998. *Environmental Geology. Principle and Practice.* Cambridge, Blackwell Science, 594 pp.

Kortenski, J., A. Sotirov. (2002). Occurrence and distribution of environmentally hazardous elements in the Katrishte lignite bed, Strouma-Mesta province, Bulgaria. - *Environmental Geosciences Journal, DEG-AAPG, 9*, 4, 191-199.