ASSESSMENT AND VARIABILITY OF SELECTED ELEMENTS IN SOIL SURROUNDING THE ELBASANI METALLURGICAL COMPLEX IN ALBANIA

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Abstract: *Heavy metals are among the pollutants that should be monitored in order to obtain a coherent and comprehensive overview of quality status for a certain soil system. Some contaminants are conserved as they pass from organism to organism in a food chain, possibly resulting in progressively higher concentrations at high content levels. In soil systems, plants take the heavy metal mainly by their root system, as a natural requirement for their growth. If the sediment is contaminated then the amount of metals available for the plants will be high. The metallurgical complex of Elbasan is the largest and most important one in the country but at the same time represents a source of significant heavy metal contamination in the wider watershed Shkumbini River. Numerous efforts have been made to establish protocols and standards for the determination of the heavy and toxic elements in plant and soils to study their distribution, and establish pollution levels as well as their derived risks for the ecosystem and environmental stability. The number of measurements is restricted by the number of samples which were collected from the study area and this number is primarily limited by the funding of the analysis. Moreover, the samples were typically taken from vertical sections, which is in general a soil profile or a catena of soil profiles. The objectives of this study were to: (i) determine the degree of soil contamination by Cu, Zn, and Cd, with respect to distance from the metallurgical complex of Elbasan, Albania, and (ii) determine various metal fractions for selected soil samples. The data gathered from this study will allow the evaluation of soil-management techniques to limit mobility and plant availability of heavy metals and to ultimately minimize their transfer into the food chain.*

Key words: *heavy metal, soil pollution, toxic element*

INTRODUCTION

One of the factors controlling the nutrients distribution and potentially harmful elements in soils is geological history. The element concentrations in soils are influenced by: atmospheric conditions, as precipitation and temperature, input of marine aerosols, differences in local topography, age of the soil, land use changes, agricultural practices and pollution. An extended interest in heavy metals research in the agricultural, environmental and life science became more prominent over last four past decades due to a number of environmental crises, mainly in the developed nations. The most important anthropogenic sources of heavy metals for soils include: atmospheric deposition from industrial, urban and road emissions, commercial fertilizers and agrochemicals and other wastes used as soil amendments, irrigation waters. All of these sources have its influence in elements concentration in soils in local zone around industry source. The metallurgical complex of Elbasan is the largest plant in the country with a treatment capacity of 800 thousand tons/year of iron-nickel and producing an estimated 44.8 tons of toxic dust/year with minor changes from the original technology installed in 1976. The contaminants emitted from this complex have the most effect on the Shkumbini River, the main watershed for the region. Smelters, whose emissions contain toxic gases and dusts rich in heavy metals like Pb, Cu, Zn Cr, Ni and Cd, caused particularly dangerous effects. Therefore, the Shkumbini is among the most polluted rivers in Albania.

Nevertheless, its waters are used to irrigate agricultural crops downstream.

During 1991-1998 demographic changes dominated by the negative rate of population increase, migration from the villages and from the remote areas towards the big cities and especially at the capital city of Tirana have created massive urbanization problems associated with pollution and contamination of their surroundings. The high growth rate of the population and its *migration to urban* areas has brought an uncontrolled increase of population in the largest cities and their suburbs. Besides other negative effects that are connected to environmental *damage and pollution*, this phenomen has caused damage of the landscape and tourists values, especially in the coastal areas, because of illegal constructions.

During last 20 years this metallurgical complex has been one of most polluting industrial plants, in connection with solid waste resulting from industrial processes applied there. The World Bank declared that the area located around this metallurgical complex is one of Albania's most important "hot spots". From 1991 this metallurgical plant released 44.8 tons of toxic dust/year. The pollution emitted from this complex has caused the most effect on the Shkumbini River (the main watershed in this region), has caused many problems to the microenvironment and adverse effects in the human health, especially pregnant and lactating mothers. They have been caused by the presence of toxic gases, vapours and dust. (SALLAKU F., *et al*. 2002).

The remainders of the elements in the periodic table are called "trace elements" and their individual concentrations do not normally exceed 1000 mg/kg (0.1%), in fact most have average concentrations of less than 100 mg/kg. And all remainder is made up of all the other elements, most of which are normally present at race levels, except where they are concentrated in localized mineral deposits. The original parent material from which all soils are derived by weathering is the igneous rock which still comprises 95% of the earth's crust. The remaining 5% of rocks is of secondary sedimentary origin and weathering particles of rock may pass through this intermediate stage before conversion to soil. The major components of the earth's crust are therefore igneous rocks, sedimentary and metamorphic rocks derived from igneous rocks weathering and soils derived by weathering from both kinds of rocks. .

MATERIAL AND METHODS

The Metallurgical plant is located in Elbasan, in the centre of Albania, near the Shkumbini river, about 60-km south-east from Tirana, located roughly 2-3 km far from the city. The population of the wider area accounts for about 120,000 inhabitants.

Figure 1. Metallurgical Combine in Elbasan

In 2007, 80 surface soil samples (0-20 cm) were collected from the different locations according to the distance (1, 2, 3, 4, 5, 6 and 7 km) from the metallurgical plant. Sub samples of each soil were air dried and ground to pass through a 2-mm stainless-steel sieve. The main characteristics of these soils are given in Table 1.

Table 1

Physical and chemical characteristics of soil samples used

Soil Number	**PH (1:2.5)**	**CEC C mol (+)kg^{-1}**	**Organic matter gkg^{-1}**	**$CaCO_3$ %**	**Sand gkg^{-1}**	**Silt gkg^{-1}**	**clay gkg^{-1}**
1	6.6	17.39	6.5	19.42	645.1	327.3	27.6
2	6.79	17.52	8.1	16.35	452.1	263.5	284.4
3	6.94	20.30	8.4	15.12	417.9	372.9	209.2
4	6.83	20.68	12.1	14.51	502.8	301.7	195.5
5	7.04	18.17	10.6	19.01	585.0	284.2	130.8
6	7.05	25.01	13.9	16.76	544.2	296.9	158.9
7	7.22	27.37	14.4	15.33	616.7	240.7	142.6
8	7.32	26.15	11.3	12.47	648.1	222.5	129.4
9	7.36	31.18	7.1	13.49	618.1	239.7	142.2
10	7.43	30.27	9.3	6.74	607.8	212.2	180.0
11	7.66	32.31	10.8	9.2	507.8	296.4	195.8
12	6.9	35.16	12.1	11.45	625.7	195.6	178.7

Metallurgical Combine in Elbasan has been the most important industrial metallurgy centre in the country. These metallurgical combine produced steel, coke, pig iron, and limited amount of nickel. The plant was closed in 1990, although there is still an electric scrap smelter working with obsolete equipment. Tailings and waste (about 1.5-2.0 million tons) from the metallurgical operation represent the major pollution source in Elbasan city.

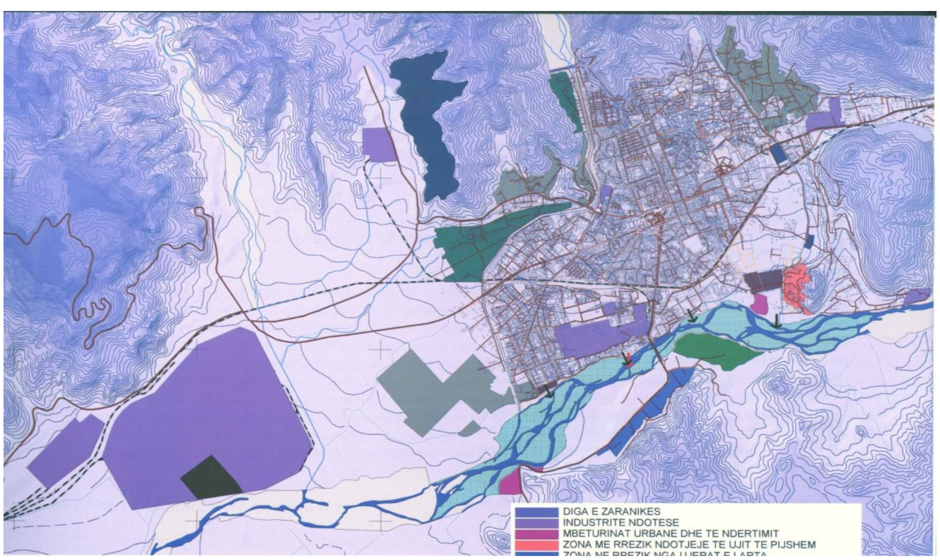

Figure 2. The soil sample site

They contaminate soil and groundwater with heavy metals (chromium, nickel and manganese). The former phenol containing waste water treatment plant is now out of functioning; consequently this metallurgical complex represents a source of significant heavy metal contamination and non-treated waste water continues to be discharged in the wider watershed Shkumbini River.

RESULTS AND DISCUSSIONS

The total metal content of soil is the result of inputs of metals from several sources-parent materials, atmospheric deposition, fertilizers, agrichemicals, organic wastes and other inorganic pollutants, minus losses in metals removed in crop material, leaching and volatilization. Heavy metals in soils have received increasing attention in recent years, partly because of the growing scientific and public awareness of environmental issues, and partly because of the development of analytical techniques to measure their concentrations accurately. Surveys carried out since 1960s have indicated that soils in many parts of the world, especially in urban and industrial areas, contain anomalously high concentrations of heavy metals. Although in most cases the levels are not (yet) high enough may cause acute toxicity problems, increased concentrations in the food chain may cause significant health effects in the long term (ALLOWAY B. J. 1990). However, recently polluted soil often have higher contents of the pollutant metals in the topsoil because the pedogenic processes have not been operating long enough to effect a redistribution within the profile.

The pollution caused mainly industrial activities, has caused critical environment damages. As consequence of the lack of accurate information on concentration of chemical another dangerous agents around the country, the risk they represent for the environment and for the health of people remain unclear. Urbanization of rural areas represents another environment threat. The fast and uncontrolled overpopulation of a limit area like Tirana, combined with the poor and inadequate social infrastructure, has caused the fast degradation and deterioration of the urban environment of the capital town. Figures 1a, 1b and 1c show the distribution of total Cu, Zn and Cd in soil samples (0-20 cm) with respect to distance from the metallurgical plant of Elbasan. Total metal concentrations of the soil samples (Figure 1) show a wide range of values, from background toa level considered to reflect gross contamination. For Cu the range is from 50 to 159 mg/kg soil, Zn 86 to 147 mg/kg soil and Cd 0.76 to 2.25- mg/kg soil.

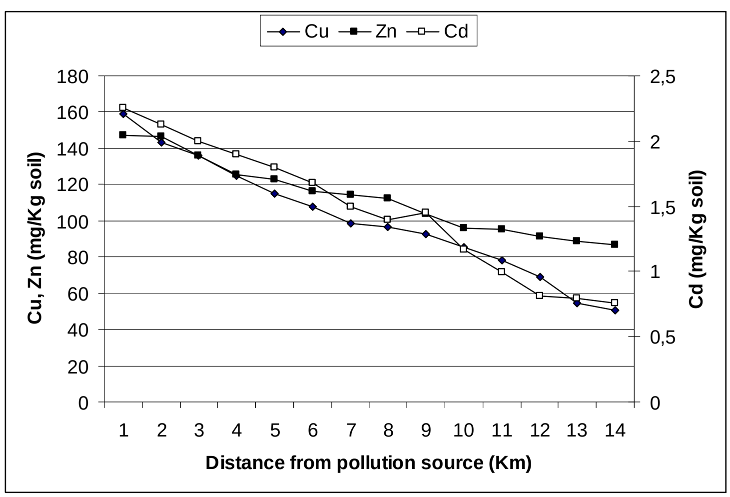

Figure 1. Distribution of total Cu, Zn and Cd in relation to distance from the Metallurgical plant of Elbasan

An intense reduction in concentrations of these metals with distance was observed. Our data shows high levels of heavy metal content within the 2 to 5 km distances from the Metallurgical complex. The same results are observed and from other authors in their studies about heavy metal concentration near this metallurgical plant (SHALLARI, *et al*, 1998).

Table 2.

Distribution of Cd in different fractions for 14 soil samples collected from the vicinity of a metallurgical complex of Elbasan (mg kg-1)

Soil number	**EX**	**CARB**	**OM**	**MnOX**	**AFeOX**	**CFeOX**	**RES**	**Sum**	**Total**
1	0.89	0.29	0.136	0.165	0.25	0.156	0.3	2.18	2.25
2	0.85	0.23	0.133	0.161	0.23	0.149	0.34	2.1	2.13
3	0.832	0.216	0.13	0.156	0.22	0.146	0.2	1.9	2.0
4	0.795	0.213	0.123	0.132	0.24	0.136	0.211	1.85	1.9
5	0.765	0.205	0.116	0.118	0.218	0.145	0.133	1.7	1.8
6	0.698	0.2	0.11	0.12	0.239	0.126	0.137	1.63	1.68
7	0.66	0.018	0.09	0.11	0.234	0.116	0.232	1.46	1.5
8	0.58	0.017	0.08	0.11	0.185	0.096	0.23	1.32	1.4
9	0.58	0.014	0.076	0.095	0.176	0.091	0.268	1.30	1.45
10	0.43	0.08	0.086	0.093	0.152	0.094	0.225	1.16	1.17
11	0.389	0.085	0.078	0.086	0.093	0.091	0.163	0.985	0.99
12	0.289	0.076	0.068	0.065	0.069	0.080	0.153	0.800	0.81
13	0.263	0.066	0.063	0.059	0.061	0.064	0.209	0.785	0.79
14	0.236	0.061	0.056	0.053	0.050	0.060	0.229	0.745	0.76
Mean	0.589	0.175	0.09	0.1	0.17	0.11	0.21	1.43	1.47

Table 3.

Distribution of Zn in different fractions for 14 soil samples collected from the vicinity of a metallurgical complex of Elbasan (mg kg-1)

Soil Numbe r	**EX**	**CARB**	**OM**	**MnOX**	**AFeOX**	**CFeOX**	**RES**	**Sum**	**Total**
1	2.6	3.5	1.9	3.8	5.2	6.8	121.9	145.7	146.5
2	2.5	3.4	1.9	3.7	5.6	7.1	120.6	144.8	147
3	2.4	3.3	1.8	3.6	5.4	7.3	110.9	134.7	136
4	2.2	3.1	1.6	3.5	5.1	6.2	102.1	123.8	125.5
5	2.3	3.0	1.5	3.4	5.2	6.8	99	121.2	123
6	2.1	3.1	1.7	3.6	5.1	6.4	92.8	114.8	116
7	2.2	3.0	1.8	3.7	5.3	6.1	91.8	113.9	114.5
8	2.1	2.9	1.6	3.5	5.2	5.8	89.3	110.4	112.3
9	2.0	3.3	1.8	3.2	4.4	5.6	81.4	101.7	103.5
10	2.1	3.6	1.9	3.4	5.2	5.3	73.3	94.8	96
11	2.0	3.5	1.8	3.2	6.2	6.1	70.9	93.7	95
12	1.8	3.1	1.7	3.0	5.9	6.0	68	89.5	91.5
13	1.7	3.0	1.5	3.2	6.1	6.3	67.5	88.6	89
14	1.6	2.9	1.2	3.1	5.9	6.1	64.6	85.4	86.5
Mean	2.1	3.1	1.6	3.4	5.4	6.2	80.9	102.7	113

The fractionation data presented in Tables 2, 3 and 4 are averages of metal concentrations in each fraction, expressed in mg kg $^{-1}$ for each fraction. These data show the various fractions of Cd, Zn and Cu for the soil samples examined. From our data, an average of nearly 65-70 % of the total Cd in these soils was present in exchangeable, carbonates, and residual form (Table 4). The organic Cd fraction in these soils was significantly smaller compared to other fractions. The Cd associated with crystalline Mn and Fe oxides was very low in the soils, in contrast to the data presented from different authors, who hypothesized that these oxides are major trace metal sinks.

Table 4

Distribution of Cu in different fractions for 14 soil samples collected from the vicinity of a metallurgical complex of Elbasan (mg kg-1)

Soil number	**Ex**	**CARB**	**OM**	**MnOx**	**AFeOX**	**CFeOX**	**RES**	**Sum**	**Total**
1	4.3	3.5	1.5	1.2	18.8	26.2	101.7	157.9	159
2	4.9	7.8	1.45	ND	17.3	25.3	79.6	135.6	136
3	4.1	7.8	1.45	ND	17.3	25.3	79.6	135.6	136
4	5.2	6.3	1.3	1.18	18.2	27.1	65.2	124.5	125
5	3.3	5.2	1.5	1.26	16.2	23.3	62.2	113	115
6	3.5	9.6	1.4	ND	15.2	22.3	53.5	105.5	108
7	3.4	3.2	1.3	ND	13.9	20.5	53.7	96	98.5
8	2.3	5.2	1.2	ND	12.4	17.6	53.8	92.5	96.3
9	2.1	2.3	1.5	1.2	12.9	17.5	53	90.5	92.4
10	2.9	6.3	1.4	1.2	11.8	16.8	49.9	84.3	85.5
11	2.9	3.2	1.5	1.15	8.9	13.5	46.3	77.5	78
12	2.8	2.9	1.4	1.18	5.6	11.8	39.3	65	69
13	2.8	2.6	1.4	1.3	5.2	11.6	27.1	52	54.6
14	2.5	2.5	1.3	ND	4.8	10.2	26.9	48.2	50.4
Mean	3.3	4.6	1.3	1.1	12.2	19.2	56.9	98.6	101

The residual Cd is also likely to be composed of a range of bonding tapes. This fraction may include resistant Cd oxide minerals, organically deposited on the soil from aerial sources. The distribution of Zn and Cu (Table 3 and 4) was similar to Cd, but with a reduced amount of exchangeable metal, and increased organically bound and residual fraction. Different studies of Zn fractions (Shuman, 1979), have found up to 70% of Zn in agricultural soils in the residual fraction, and nearly all the remainder associated with Fe oxides. The high organic content and low amount of Fe and Mn appear to determine the Zn distribution found in the soils analyzed in this study. Residual, organically bound, carbonate/crystalline Fe fraction were nearly equal and accounting for most of the Cu in these soils (Table 2).

CONCLUSIONS

The data presented in this study indicated that the soils around the Metallurgical plant of Elbasan are highly polluted with Cd, Zn and Cu, and that the extent of contamination is limited to the immediate industrialized region (within 20 km from the industrial centre). A sequential extraction technique used to characterize bonding of metals to the soils showed that organic matter, carbonates and poorly crystalline Fe oxides, and tightly bound residual fractions contained > 60 % of the total Cd, Zn and Cu. Exchangeable Cd was a significant fraction, averaging from 30 to 40 % of the total present. Although amounts of organic matter and Fe oxides were of obvious importance in influencing this distribution, there was little variation in different fractions found in this study.

BIBLIOGRAPHY

1. ANDERSEN, A. M., A. H. JOHNSON, and T. G. SICCAMA. 1990. Levels of lead, copper, and zinc in the forest floor in the northeastern United States. J. Environ. Qual. 9:293-296
2. ELSOKKARY and LAG 1978, Distribution of different fractions of Cd, Pb, Zn and Cu in industrially polluted and nonpolluted soils of Odda Region, Norway. Act Agric.Scand. 28: 262-268
3. GUPTA, S.K., and K.Y. CHEN. 1975. Partitioning of trace metal in selective chemical fractions of near shore sediments. Environ. Lett. 10: 129-158
4. MCLAREN, R. G., and D.V.CRAWFORD. 1993. Studies on soil copper: The fractionation of copper in soils. J. Soil Sci. 24: 172-181
5. MILLER, W. P., and W.W.MCFEE. 1983. Distribution of cadmium, zinc, copper and lead in soils of industrial north western Indiana. J Environ. Qual. 12: 29-33
6. MEHLICH A. 1984. Mehlich No.3 soil test extractant: A modification of Mehlich No.2 Commun. Soil Science.Plant Anal., 15: 1409-1416
7. PACES T. 1998, Critical loads of trace metals in soils: A method of calculation. Water, Air, and Soil Pollution 105: 451-458
8. SALLAKU, F., S. SHALLARI**,** H.-R. Wegener and P.F. Henningsen. 1999. Heavy metals in industrial area of Elbasan. Bull. Agric. Sci. (in Albanian) 3:85-92
9. SPARKS, D.L., ED. 1996, Methods of Soil Analyses, Soil Science Society of America, 1996, Madison, WI
10. SHALLARI, S., C. SCHWARTZ, A. HASKO and J.L. MOREL. 1998. Heavy metals in soils and plants of serpentine and industrial sites of Albania. Sci. Total Environ. 209:133-142.
11. TESSIER, A., P. G. C. CAMPBELL, and M. BISSON. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem.51: 844-851