AN INVESTIGATION OF THE SPATIAL VARIABILITY OF HEAVY METAL CONCENTRATIONS IN FLOODPLAIN SEDIMENTS AROUND THE METALLURGICAL COMBINE OF ELBASANI, ALBANIA

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Abstract: *Heavy metal contamination in the soil/water/flora is of great concern because of possible influence on the food chain. Surveys and monitoring of trace metal background levels are required to assess heavy metal contamination in soils (compared with natural concentration variations of heavy metals in soils). Based on those considerations, an immediate action is required to ameliorate the situation, since the natural resources (soil, water, and air) have been contaminated. 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. This study aimed to determine the degree of soil contamination by Cu, Zn, and Cd, with respect to distance from the metallurgical complex and determine various metal fractions for selected soil samples. Soil samples (80) from surface (0-20 cm) were collected at 1, 2, 3, 4, 5, 6 and 7 km distance from the metallurgical plant. Total content of heavy metals were determined by the mineralization of soil samples and a sequential fractionation procedure was used to partition the heavy metals into fractions using standard methodology. The data indicated that the soils around the plant are highly polluted up to 15 Km away from the plant with Cd, Zn and Cu (50 to 159; 86 to 147; 0.76 to 2.25 mg/kg soil, respectively). 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. Results from this study would help to implement appropriate soil-management techniques to limit mobility and plant availability of heavy metals minimizing their transfer into the food chain. 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 contamination, sequential extraction,*

INTRODUCTION

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. Elbasan district is one of the major agricultural areas of the country and possible contamination by heavy metals such as cadmium, nickel, chromium, lead, and copper would lead to vegetables and other crops grown in this area and therefore present a serious health risk for consumers. The pollution emitted from this complex has caused many problems to the microenvironment (SHALLARI, S., et al, 1998) and expected to have adverse effects on the public health and especially pregnant, lactating mothers and children. Heavy metal contamination in the soil/water/flora is of great concern because of possible influence on the food chain. Surveys and monitoring of trace metal background levels are required to assess heavy metal contamination in soils (compared with natural concentration variations of heavy metals in soils). Additionally, it is important to be able to understand their biogeochemical behaviors, and to examine their migration and distribution during pedogenesis process. Since sedimentation of particulate material is one of the most important fluxes in the aquatic system, a knowledge of trace metal concentration in sediment and soils can play a key role in detecting sources, evaluating the degree of pollution, and distribution mechanisms, especially in protected areas.

Heavy metal contamination has adverse effects on the agrosystems such as: loss of high quality farmland and pollution of soil and groundwater, enhanced demand for clean water, contamination of urban areas and increased public health problems, and low grazing quality and reduced crop yields and livestock production (SHALLARI, S., et al). Recent studies by several investigators have shown that atmospheric fallout from smelters can contribute significantly to soil contamination with heavy metals (PACES T. 1998). Metal deposition patterns, though depending to a considerable extent on climatic conditions (i.e. wind and rainfall distribution), (ELSOKKARY AND LAG 1978), generally decline exponentially with distance from the smelter. Consequently, metal concentrations in soils near the smelter may be elevated significantly and may pose a significant health hazard. The total soil metals concentration can be used to estimate the degree of soil exposure to heavy metal contamination, but they are not generally well correlated with plant uptake of metals. Such metals as Cu and Zn may exist in soils or sediments in various fractions (exchangeable, carbonate-bound, oxide-bound, organic matter-bound, or incorporated in crystal lattices) (MCLAREN AND CRAWFORD 1973, TESSIER et al., 1979). The distribution of metals with various forms depends on the existing chemical and mineral environment. The dominant forms of the metals that are present will control the relative impact of elevated metals on soil-plant systems. Availability to plants may be governed in turn by dynamic equilibrium involving these metal fractions, rather than by total metal contents per se (ELSOKKARY AND LAG 1978). Investigation of various metal fractions in contaminated soils should be of importance for estimating the amounts of metals potentially available to plants within relatively short span of time. Based on those considerations, an immediate action is required to ameliorate the situation, since the natural resources (soil, water, and air) have been contaminated. Sustainable development of this area would increase the income of the associated communities, increase their property values, and improve the health situation. 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.

MATERIALS AND METHODS

Sampling site: 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. Soil sampling, preparation, and analyses: 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

Soil pH was determined in 1:2.5 soil to $CaCl_2$, CEC (MEHLICH. A 1984**)**, organic C by elementary analysis, $CaCO_3$, and particle-size distribution by the combination of pipette and sieving method. Total content of heavy metals were determined by the mineralization of soil samples in the solution of aqua regia (HCl and HNO_3) in the ratio (3:1), (SPARKS, D.L., Ed. 1996).

Fractionation procedure: The sequential extraction procedure to partition Cu, Zn and Cd to fractions was as follows: **1.** Exchangeable (EX), in 1 M $Mg(NO_3)_2$, 10:40 g soil/ml solution (TESSIER et al. 1979); **2.** Carbonate (CARB), in 1 M NaOAC (pH5.0, CH_3COOH), 10:40 g soil/ml solution (TESSIER et al. 1979) ; **3.** Organic(OM), in 0.7 M NaOCl (pH 8.5), 10:20 g soil/ml solution (SHUMAN 1985); **4.**Mn Oxides(MnOX), in 0.1 M NH_2OH. HCl (pH2, HNO_3, 5:50 g soil/ml solution (CHAO 1972); **5.** Amorphous Fe oxides (AFeOX), in 0.25 M NH_2OH.HCl + 0.25 M HCl, 5:50 g soil/ml solution (CHAO AND ZHOU 1983); **6.** Crystalline Fe oxides (CFeOX), in 0.2 M $(NH_4)_2$ C_2O_4 + 0.2 M $H_2C_2O_4$ (pH3) + 0.1 M ascorbic acid, 5:50 g soil/ml solution (SHUMAN 1985); **7.** Residual (RES), in Conc. HF, Conc. $HClO_4$ and conc. HCl in sequence (TESSIER et al. 1979). All tests were carried out at the Institute of Soil Science & Conservation, Gieesen Germany.

RESULTS AND DISCUSSIONS

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. 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).

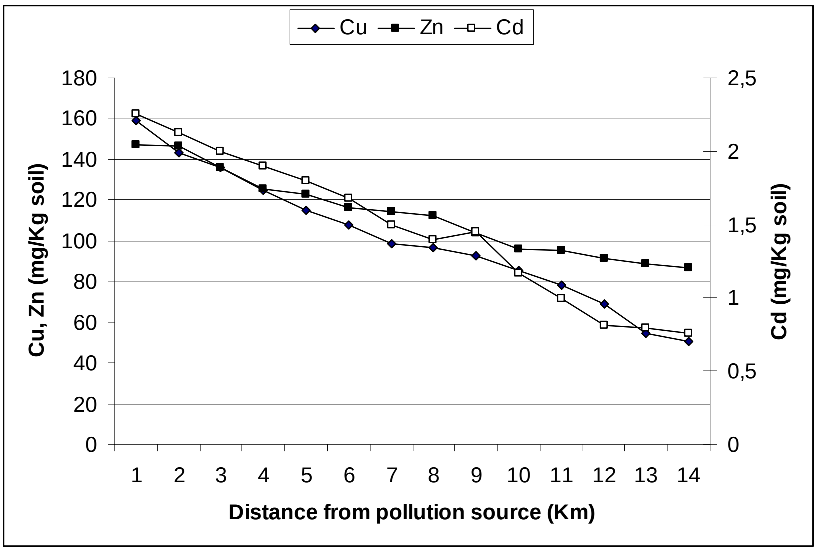

Figure 1. Distribution of total Cu, Zn and Cd in relation to distance from the Metallurgical plant of Elbasan

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.

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 Number	**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

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

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. 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.

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