

## ASSESSMENTS OF HEAVY METALS IN SURFACE URBAN SOILS: A STUDY FROM ELBASANI, ALBANIA

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### Abstract

Soil is a complex and heterogeneous mixture of organic and inorganic matter, as well as different components that determine the physical, chemical and biological properties of the soil. There are at least 68 trace elements in soil, representing only about 0.6% of their total composition, while 12 minor and major elements —Si, Al, O, Ca, Fe, K, Ti, Mg, Mn, Na, Cr, Ni— account for the rest. However, significant local or regional imbalances (relative to gross pedological averages) may occur in the soil composition. In contrast to soils in agricultural areas, soils in urban environments, particularly in parks and gardens, have a direct influence on public health that is unrelated to production of food because they easily come into contact with humans and are transferred to them, either as suspended dust or by direct contact. Furthermore, even though urban soils are rarely used for food production, they receive higher than normal loads of contaminants from traffic and industrial activities in heavily industrialized cities. Heavy metals in soils can also generate airborne particles and dusts, which may affect the environmental air quality. Heavy metal enrichment factors have been proposed as indicators for diffuse soil contamination.

**Key words:** Heavy metals, contamination, distribution, sequential extraction

### 1. Introduction

It is known that serious systemic health problems can develop as a result of excessive accumulation of dietary heavy metals such as Cd, Cr, and Pb in the human body. Heavy metals are extremely persistent in the environment; they are nonbiodegradable and nonthermodegradable and thus readily accumulate to toxic levels. Viewed from the standpoint of environmental pollution, metals may be classified according to three criteria: (i) noncritical (Na, Mg, Fe, K, Ca, Al, Sr, Li, Rb); (ii) toxic but very insoluble or very rare (Ti, Hf, Zr, W, Ta, Ga, La, Os, Ir, Ru, Ba, Rh), and (iii) very toxic and relatively accessible (Be, Co, Ni, Cu, Zn, Sn, Cr, As, Se, Te, Ag, Cd, Hg, Tl, Pb, Sb, Bi).

Environmental pollution with toxic metals is becoming a global phenomenon. As a result of the increasing concern with the potential effects of the metallic contaminants on human health and the environment, the research on fundamental, applied and health aspects of trace metals in the environment is increasing. Industrial processes that release a variety of metals into waterways include mining, smelting and refining. Almost all industrial processes

that produce waste discharges are potential sources of heavy metals to the aquatic environment. Domestic wastewater, sewage sludge, urban runoff, and leachate from solid waste disposal sites are also obvious sources of heavy metals into rivers, estuaries and coastal waters [4, 5]. Various analytical techniques are used to measure heavy metal concentration in soils using different geochemical mapping programs. One of these methods is through determinations of enrichment factor. The enrichment factor can be dependent on the analytical method applied. The behavior of a given element in soil (that is, the determination of its accumulation or leaching) may be established by comparing concentrations of a trace element with a reference element [11]. The obtained result is described as an enrichment factor (EF), given by the following equation:

$$EF = \frac{(C_n / C_{ref})}{(B_n / B_{ref})}$$

in which  $C_n$  is content of the examined element in the soil;  $C_{ref}$  is content of the examined element in the earth's crust,  $B_n$  is content of the reference element in the soil, and  $B_{ref}$  is content of the reference element in the earth's crust.

A reference element is “conservative” (that is, one in which the content in samples originates almost exclusively from the earth’s crust). The most common reference elements in the literature are aluminum (Al), zirconium (Zr), iron (Fe), scandium (Sc), and titanium (Ti), although there are also attempts to use other elements such as manganese (Mn), chromium (Cr) and lithium (Li). In the present study, the zones around the metallurgical combine were chosen for sampling because their soils have usually not been cultivated for a long time and thus, they could be expected to reflect the long-term accumulation of metals in the urban environment [6, 7, 12]. The main objectives of this paper are 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.

## 2. Material and methods

### 2.1 Sampling site

The Metallurgical combine is located in Elbasan, in the centre of Albania, near the Shkumbini river, about 60-km south-east from Tirana. The population of the city accounts for about 120,000 inhabitants. The metallurgical complex is located in the south-western part of the Elbasan city roughly 2-3 km far from the city. The climate is Mediterranean type with hot and dry summers and mild and wet winters. The average

rainfall is about 1,300 mm per year, however the majority of rains happen during the fall and winter season. The temperature varies from as low as in the winter to 35°C during the summer time.

### 2.2 Soil sampling, preparation, and analyses

In 2010, approximately 120 surface soil samples (0-20 cm) were collected from the different locations according to the distance from the metallurgical plant. The distance of these sites from plant was approximately 1, 2, 3, 4, 5, 6 and 7 km. 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. Soil pH was determined in 1:2.5 soils to CaCl<sub>2</sub>, CEC by Mehlich method, and organic C by elementary analysis, and CaCO<sub>3</sub> by the Scheibler method 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<sub>3</sub>) in the ratio 3:1). The pH of the soil was close to 8 at all sites. The alkaline range of soil is known to restrict the mobilization of heavy metals, thus reducing their uptake. However, the high nutrient input from irrigation water at these sites could result in relatively high growth rates and relatively high uptake of heavy metals as a result.

**Table 1:** Physical and chemical characteristics of soil samples used

Soil Number	pH (1:2.5)	CEC C mol (+)kg <sup>-1</sup>	Organic matter gkg <sup>-1</sup>	CaCO <sub>3</sub> %	Sand gkg <sup>-1</sup>	Silt gkg <sup>-1</sup>	clay gkg <sup>-1</sup>
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

Organic materials can affect metal species solubilization by complexing the metal ions, but they can also take metal ions out from the solution and contribute to the soils [4]. Decomposition of organic material produces organic ligands that may extract metals from the soil which can effectively mobilize metals by increasing their concentration. Biological oxidation of metabolisable forms of organic carbon has been recognized as the most important factor in early diagenesis. In the surface sediments, organic matter is decomposed by organisms in the presence of oxygen. In finer sediments such as clay, with the exception of coarse sediments and other high-energy areas where there is rapid advection of oxygenated water, this decomposition uses up oxygen in the sediment quickly. The decomposition occurs faster than the rate of diffusion of oxygen into the sediments and, as a result, most sediment is anaerobic just below the surface. The decomposition of organic matter proceeds under anoxic conditions using alternative electron acceptors to oxygen, such as nitrate, manganese and iron oxides, and sulphate to oxidize organic carbon. This oxidation, together with the resulting anoxic conditions, produces large changes to the form of iron, manganese and sulphur, which

are important in binding trace metals in sediment and releasing them to the overlying water.

### 2.3 Fractionation procedure

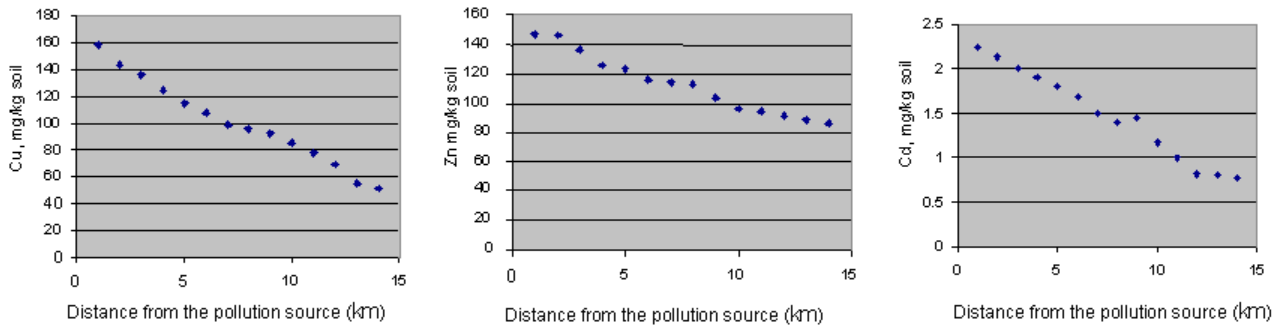
A sequential fractionation procedure was used to partition Cu, Zn and Cd into exchangeable (EX), carbonates (CARB), organic matter (OM), Mn oxide (MnOX), amorphous Fe oxide (AFeOX), crystalline Fe oxide (CFeOX), and residual (RES) fractions. Reagents used in the fractionation scheme were selected from those cited in the literature as being selective for the specific chemical form in soils and all analyses are carried out near the UNESCO-IHE Institute for Water Education (UNESCO-IHE), Netherlands. The sequential extraction procedure is given in Table 2.

## 3. Results and discussions

The concentration of metals (mean, ranges) and the contamination ratios in agricultural soil samples of the various sites and the control site are shown in Figure 1. Copper, Zn and Cd are commonly found in the urban but also in the agricultural area. Clearly, industrial emissions of metals may cause substantial pollution of dusts. The findings in the present study (50 to 159 mg/kg soil, 86 to 147 mg/kg

Table 2: Sequential extraction procedure for Copper, Zinc and Cadmium in soil.

Fraction	Solution	g soil/ml solution	Condition	Reference
Exchangeable (EX)	1 M Mg(NO <sub>3</sub> ) <sub>2</sub>	10:40	Shake 2 h	
Carbonate (CARB)	1 M NaOAc (pH5.0, CH <sub>3</sub> COOH)	10:40	Shake 5 h	[13]
Organic(OM)	0.7 M NaOCl (pH 8.5)	10:20	30 min in boiling water bath. Stir occasionally. Repeat extraction	[9].
Mn Oxides(MnOX)	0.1 M NH <sub>2</sub> OH. HCl (pH2, HNO <sub>3</sub> )	5:50	Shake 30min	[2].
Amorphous Fe oxides (AFeOX)	0.25 M NH <sub>2</sub> OH.HCl + 0.25 M HCl	5:50	Shake 30 min at 50°C in water bath	[3]
Crystalline Fe oxides (CFeOX)	0.2 M (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> + 0.2 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> (pH3) + 0.1 M ascorbic acid	5:50	30 min in boiling water bath. Stir occasionally	[10]
Residual (RES)	Conc. HF, Conc. HClO <sub>4</sub> and conc. HCl in sequence			[13].



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

**Table 3.** Distribution of Cd in different fractions for 14 soil samples collected from the vicinity of a metallurgical complex of Elbasan (mg kg<sup>-1</sup>)

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

soil and 0.76 to 2.25 mg/kg soil are the mean values for urban and agricultural area of Cu, Zn and Cd respectively) could indicate that motor vehicles and materials used in the manufacturing area, around the major refining processes, leaks of oil products during loading of tankers but also car abrasion and car lubricants for Cu and Zn are main sources of these heavy metals. Figures 2a, 2b and 2c 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 to a 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 [8, 10].

The fractionation data presented in Tables 3, 4 and 5 are averages of metal concentrations in each fraction, expressed in mg kg<sup>-1</sup> 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 5). The organic Cd fraction in these soils was significantly smaller compared to other fractions. The Cd associated with crystalline Mn and Fe oxides was

**Table 4.** Distribution of Zn in different fractions for 14 soil samples collected from the vicinity of a metallurgical complex of Elbasan (mg kg<sup>-1</sup>)

<i>Soil Nr</i>	<i>EX</i>	<i>CARB</i>	<i>OM</i>	<i>MnOX</i>	<i>AFeOX</i>	<i>CFeOX</i>	<i>RES</i>	<i>Sum</i>	<i>Total</i>
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 5.** Distribution of Cu in different fractions for 14 soil samples collected from the vicinity of a metallurgical complex of Elbasan (mg kg<sup>-1</sup>)

<i>Soil Nr</i>	<i>Ex</i>	<i>CARB</i>	<i>OM</i>	<i>MnOx</i>	<i>AFeOX</i>	<i>CFeOX</i>	<i>RES</i>	<i>Sum</i>	<i>Total</i>
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

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 distribution of Zn and Cu (Table 4 and 5) was similar to Cd, but with a reduced amount of exchangeable metal, and increased organically bound and residual fraction. Different studies of Zn fractions [7, 9, 12], 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 5).

#### 4. Conclusions

From this work can be concluded that significant contamination of soil samples was observed in the Elbasani region. Two major uses of soils analyses, especially on heavy metals, can be defined as: (i) the identification, monitoring, and control of pollution sources and (ii) the evaluation of the environmental

impact of polluted soils. The contamination is relatively similar or lower than that of other high populated regions in Albania or worldwide. The distribution of the metal concentration of the soil samples in the study area indicated that the industrial activity together with the traffic were mainly responsible for metal pollution, as the highest metal concentrations were found in the urban and in the agricultural zone [1, 2, 6]. Heavy metal contamination in the soils samples in the study area was higher as compared to the background levels for all metals investigated in this work. Anthropogenically impacted and background soils on major zones were assessed using different factors, contamination factors, pollution load index and geoaccumulation index for Zn, Cd and Cu. The contamination factor showed that generally there is high and moderate contamination of the heavy metals across the different agricultural areas. The geoaccumulation index showed that zones closed to the Metallurgical combine are very contaminated, whereas some zones far to the pollution zones are uncontaminated. 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.

An important issue is that the contamination levels were frequently higher than permissible limits in the plant tissue, at the same sites as water and soil samples that comply with established safe standards. This has important implications for policy in that

programmes aimed at monitoring and controlling heavy metal concentrations in irrigation water sources will not necessarily result in acceptable levels in vegetables. Policies and programs need to be adapted so that local edaphic conditions and agricultural practices are taken into account, and appropriate local measures developed for ameliorating heavy metal uptake by crops for a given set of local conditions. These measures need to be regularly reviewed to take into account factors such as the accumulation of heavy metals in the topsoil over time.

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