

Heavy Metal Distribution in Soils near the Almalyk Mining and Smelting Industrial Area, Uzbekistan

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Abstract: The present study demonstrates distribution and chemical forms of heavy metals in soils of the Almalyk mining and smelting industrial area along five transects. The study area is located in Almalyk, Uzbekistan, where the intensification of industrial enterprises negatively impacts the environment. The distribution of 17 heavy metals (Cu, Zn, Pb, Sc, V, Cr, Co, Ni, Ga, Rb, Sr, Y, Zr, Nb, Ba, Th, and U) were studied in 21 sampling locations (21x3=63 soil samples) along five radial transects with a total length of 60 km downwind deposition gradient. Soil samples were collected from the upper layer (0-10 cm) at 4-6 km intervals. As a result of X-ray fluorescence spectrometry analyses by using X-ray fluorescence spectroscopy (XRF, Philips Analytical Ink, USA), a significant decrease in heavy metal (Cu, Zn, Pb) deposition was found going from the source in a downwind direction. Soil samples taken from the first location (near the pollution sources) showed higher concentrations of Cu, Zn and Pb, and lower concentrations with increasing distance from the source. Obtained data showed different impact of pollution sources to heavy metal deposition and distribution in soils. The Almalyk mining and smelting complex is the major source of Pb, Zn and Cu enrichment in soils. Distribution of other trace elements does not exceed background content and suggests lithogenic background. This allowed us to divide these elements into two groups: (1) technogenic (Cu, Zn and Pb); and (2) lithogenic (Sc, V, Cr, Co, Ni, Ga, Rb, Sr, Y, Zr, Nb, Ba, Th and U) origins.

Key words: heavy metals, mining and smelting industry, soil pollution

1 Introduction

The present research mainly describes the degree of soil pollution by heavy metals in the area of influence of the Almalyk Mining and Metallurgical Complex (AMMC) and other industrial enterprises located in the Angren river valley, Uzbekistan. In the area of research the main sources of pollution are mining and chemical industries. AMMC is one of the largest mining and metallurgical enterprises in the Republic of Uzbekistan. The composition of the mill includes eight mines, four dressing plants, two steel plants, sulfuric acid production and maintenance, mechanical and lime plants, motor control with four motors, rail management, management of the production of consumer goods, as well as more than 20 subsidiary shops. AMMC produces copper, gold, silver, lead, zinc and other products, and has the capacity for mining and processing of approximately 25 million tons of ore per year. Due to a lack of effective air-purifying devices, the Almalyk mining and metallurgical plant produces approximately 100 000 tons of

toxic compounds and heavy metals (sulfur dioxide, carbon, nitrogen oxides, sulfur oxides, Cu, Pb, Zn, Cd, Hg, and As) per year. This represents approximately 13% of the total atmospheric emissions from stationary sources in Uzbekistan (UNECE, 2000).

2 Materials and Methods

2.1 Study site and locations

The study site is a semi-arid area located between the mountain ranges of Qurama in the south and Chatkal in the north (Tien-Shan), extending into the southeast part of the Tashkent region of the Republic of Uzbekistan. The industrial complex includes a mining processing enterprise, and metallurgical and chemical plants located in the flat bottom of the Akhangaran River valley near the city of Almalyk (40°85'-69°69' E).

The research area represents a mountain valley area with a large variability of seasonal and daily air temperature and wind direction. Thermal inversions provide cyclic circulation of air masses and cause

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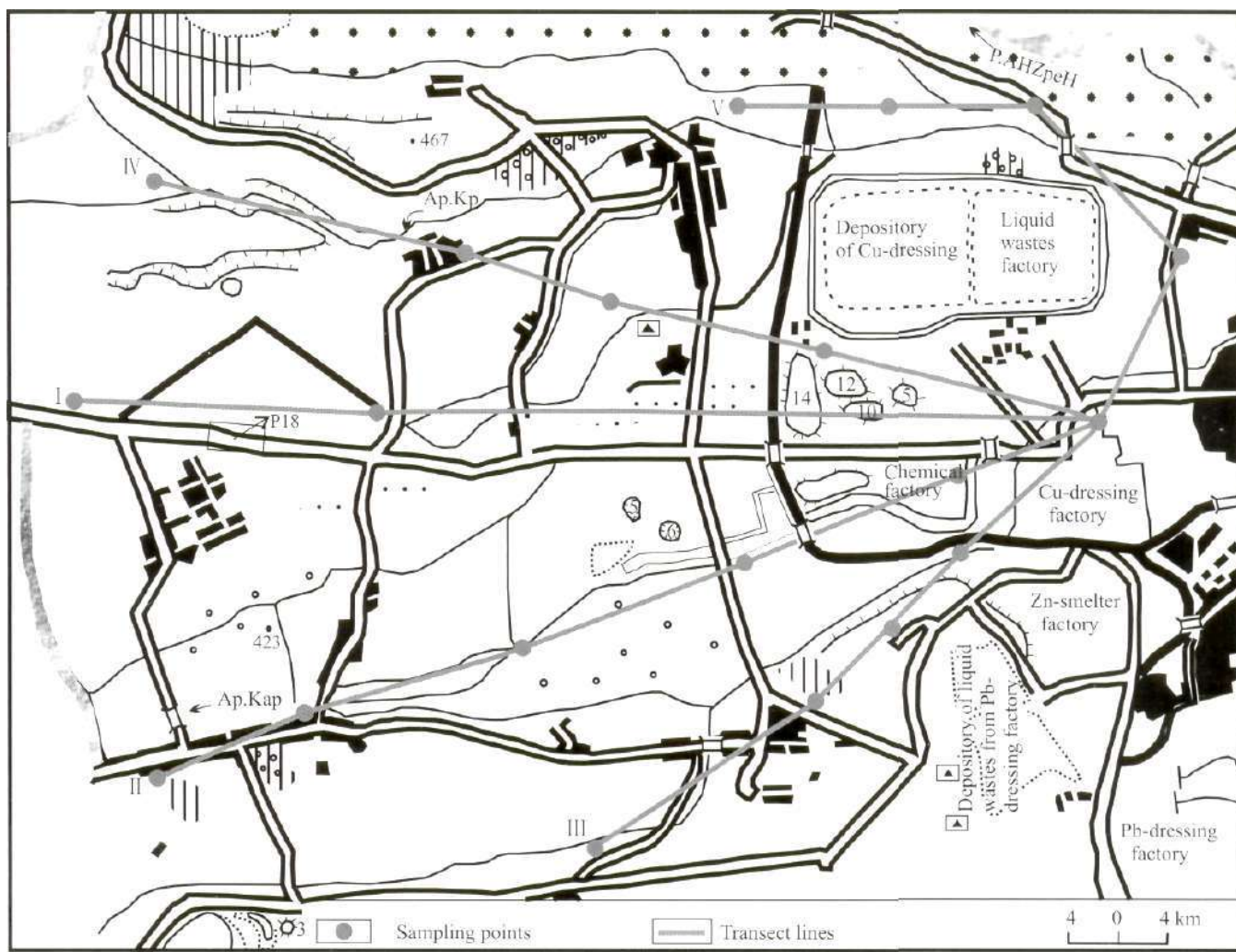


Fig. 1. Schematic map of Almalyk showing the locations of the selection of soil samples.

pendulum distributions of dust and gas smoke emissions from the industrial enterprises. The prevalent wind at the study site is in a western and south-western direction.

The climate is continental; minimal temperature measured between -25°C and -30°C in January and maximal temperature reached $42-47^{\circ}\text{C}$ in July. Annual rainfall at the study site ranged between 320 and 550 mm. Most of the precipitation fell in spring and winter (UNECE, 2001. Environmental Performance Review - Uzbekistan).

The vegetation cover along the study site is dominated by annual and perennial plants, the most common being astragalus, stipa, medicago and artemisa genera. The soils at the study area belong to the lithosols (FAO, 2003), with high levels of CaCO_3 contributing to a stable accumulation of heavy metals on top of the soil layer.

2.1 Soil samples and soil analyses

Examination of the distribution, accumulation and geochemical behaviour of heavy metals in surface soil layers with distance from sources of pollution were the main objectives of the present study. Distribution of heavy

metals in soils from the Almalyk mining area was studied in five geochemical profiles with radial-radiant direction (Fig. 1). Profile II stretches from east to west, with a distance of 15 km. Sections II-II and ИМИ have a NE-SW direction, with extents of 13 and 9 km, respectively. Profile IV-IV has a NW-SE direction (14 km). Profile V-V has a complex, slightly circular area (10 km) and is impossible to cross the tailings. These profiles cross the mine dumps, roads conveying ore mass, heap leaching area, enrichment plant, tailings, and metallurgical plants.

Distribution of heavy metals and trace elements (Cu, Zn, Pb, Sc, V, Cr, Co, Ni, Ga, Rb, Sr, Y, Zr, Nb, Ba, Th, and U) were studied at 21 sampling points ($21 \times 3 = 63$ soil samples) on five radial transects with a total length of 60 km downwind direction. Soil samples were collected from the upper layer (0-10 cm) at intervals of 4-6 km. From each point selected three random were samples and placed in individual plastic (polyethylene) bags weighing 6 g, and delivered to the laboratory to determine the chemical composition. Soils were screened through a 2-mm sieve before chemical analysis. In the laboratory, samples were dried and ground to powder ($<100\ \mu\text{m}$) through agate

Table 1 Trace element concentrations in soils of Almalyk (from the 21 sampling locations along the different transects I-I,II-II, III-III, IV-IV and V-V) (unit: g/t)

Sample	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Ba	Pb	Th	и	
XIV/1	1	24	149	43	13	16	1634	781	14	164	169	20	87	8	714	395	12,1	3,6
IX/1	2	18	120	28	13	20	1519	229	14	178	202	22	123	12	676	115	14,1	4,7
V/1	3	14	94	57	14	29	87	138	18	156	162	31	219	19	703	57	19,1	3,8
I/1	4	17	108	82	14	37	129	223	14	109	184	26	166	14	610	72	11,5	2,4
Sample	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Ba	Pb	Th	U	
XIV/1	1	24	149	43	13	16	1634	781	14	164	169	20	87	8	714	395	12,1	3,6
XI/9	2	12	90	58	13	28	125	138	17	159	154	32	196	18	698	60	18,7	5,5
VIII/9	3	11	78	46	10	22	83	111	17	157	183	29	197	18	719	52	18,2	3,5
VI/10	4	11	80	47	11	23	77	132	16	158	170	29	197	18	712	54	18,7	4,5
II/11	5	18	107	92	15	37	53	99	12	96	197	25	210	13	557	28	11,8	2,3
Sample	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Ba	Pb	Th	U	
XIV/1	1	24	149	43	13	16	1634	781	14	164	169	20	87	8	714	395	12,1	3,6
X/12	2	13	92	63	14	30	66	117	18	154	152	33	191	18	718	57	16,8	5,1
XVI/10	3	13	88	56	13	26	143	222	17	159	167	31	198	19	766	104	19,1	4,1
XIV/12	4	7	71	24	7	8	18	59	15	168	178	26	289	18	738	33	18,5	3,4
XII/12	5	8	77	41	10	20	48	104	18	167	172	28	198	18	756	49	18,7	2,9
Sample	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Ba	Pb	Th	U	
XIV/1	1	24	149	43	13	16	1634	781	14	164	169	20	87	8	714	395	12,1	3,6
XII/2	2	15	98	95	17	36	2946	1599	3	92	237	28	151	10	667	573	9,9	4
X/3	3	14	114	85	14	45	195	644	16	127	201	31	174	14	847	218	12,6	4,7
VII/4	4	11	89	56	10	21	187	664	15	116	212	22	173	12	792	367	9,1	4,8
IV/5	5	14	83	53	12	24	108	776	14	115	218	23	183	14	680	522	11,8	4
II/6	6	15	98	78	11	31	51	154	14	103	183	25	197	14	595	43	12,1	2,5
Sample	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Ba	Pb	Th	U	
XIV/1	1	24	149	43	13	16	1634	781	14	164	169	20	87	8	714	395	12,1	3,6
XIII/3	2	17	95	81	14	38	3137	1855	3	86	237	27	151	11	627	629	10	4,6
XII/4	3	13	93	60	13	29	127	684	16	134	202	25	187	13	813	115	14,1	3,3
XI/5	4	14	104	83	14	39	84	328	15	113	200	26	185	13	690	113	12,5	2,1
VIII/7	5	17	109	89	18	41	46	119	13	94	219	24	187	13	572	34	11	2,8

mortars and tablets were prepared using special glue (SCANDIPLEX, Fritsch Japan) for analysis at the X-ray fluorescent spectrometry (XRF, Philips Analytical Ink, USA).

Heavy metals were also fractionated using the sequential extraction procedure, in which the metal fractions were defined as exchangeable, carbonate-, Fe-Mn oxide-, and organic matter-bound and residual fractions. The sequential extraction scheme was developed from Tessier et al. (1979) and the same terminology is retained. As this method has given results for the possible bioavailability of the elements and their extractability or leachability, it is described in detail. Extraction was carried out progressively on an initial weight of 1 g of soil sample. The extractions were conducted in centrifuge tubes (polypropylene, 50 mL) to minimize losses of solid material. Between each extraction step, the tubes were centrifuged for 30 min at 4000 rpm. After decanting the extract the residue was washed by deionized water and centrifuged for 30 min, and this supernatant was discarded. The volume of rinse water used was kept to a minimum to avoid excessive solubilization of solid material. All extracts were stored in the dark at 2°C until analysis. The concentration of heavy metals was determined using the flame atomic absorption spectrometry method.

3 Results and Discussion

The results show that the heavy metal content always increases with the approach to the source of pollution, and decreases as distance increases from the source. The total content of heavy metals in soil samples are distributed on a number of Cu > Pb > Zn. Soil samples taken from the first point (near the pollution source) showed a high concentration of Cu, Zn and Pb, and decreased with increasing distance from the source (Fig. 2).

The maximum content of heavy metals was found in soil samples around the selected copper processing plant and the copper smelting factory: Cu (3137 g/t), Zn (1855 g/t) and Pb (637 g/t). Although the average concentration of Rb (134 g/t) and Th (15 g/t), relatively less than the above mentioned heavy metals, significant higher than background values, which demonstrating their technogenic origin (Fig. 3). Gross contents of these metals in soil samples are distributed on a number of Cu > Zn > Pb > Rb > Th.

The concentration of other metals did not exceed the background content (Table 1) and were distributed almost evenly (Fig. 3.) in all sampling points (Ba > Sr > Zr > V > Cr > Ni > Y > Nb > So Ga > Co > U).

The distribution of these metals in soils and their non-relative nature to the pollution sources demonstrates their

Table 2 Trace element concentrations in soils of Almalyk from the sampling locations along the transect II-II (unit: g/t)

Sample	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Ba	Pb	Th	U	
XVI/1	1	12	82	43	11	21	284	232	15	163	174	27	213	17	752	115	18.9	4.2
XI11/2	2	15	98	95	17	36	2946	1599	3	92	237	28	151	10	667	573	9.9	4
X/3	3	14	114	85	14	45	195	644	16	127	201	31	174	14	847	218	12.6	4.7
VII/4	4	11	89	56	10	21	187	664	15	116	212	22	173	12	792	367	9.1	4.8
IV/5	5	14	83	53	12	24	108	776	14	115	218	23	183	14	680	522	11.8	4
II/6	6	15	98	78	11	31	51	154	14	103	183	25	197	14	595	43	12.1	2.5

Table 3 Heavy metals concentration in Almalyk soils (%)

Distance	Depth	Fl	F2	F3	F4	F5	
100 m	0-10 cm	0.3	22.6	56.4	10.3	10.5	100
4 km	0-10 cm	0.6	20.3	48.6	10.5	19.9	100
8 km	0-10 cm	1.0	18.2	43.7	13.5	23.6	100
12 km	0-10 cm	1.8	10.6	42.4	13.3	31.9	100
16 km	0-10 cm	1.4	13.6	47.0	7.5	30.5	100
20 km	0-10 cm	1.0	11.4	43.9	6.9	36.8	100
Distance	Depth	Fl	F2	F3	F4	F5	
100 m	0-10 cm	0.5	13.2	8.1	60.4	17.8	100.0
4 km	0-10 cm	0.3	13.4	8.9	60.5	16.9	100.0
8 km	0-10 cm	0.9	10.2	21.7	33.0	34.2	100.0
12 km	0-10 cm	0.8	3.3	15.9	25.0	55.0	100.0
16 km	0-10 cm	0.6	2.9	22.5	5.0	69.0	100.0
20 km	0-10 cm	0.9	4.6	23.9	7.2	63.4	100.0
Distance	Depth	Fl	F2	F3	F4	F5	
100 m	0-10 cm	0.1	18.0	53.0	16.6	12.4	100.0
4 km	0-10 cm	0.1	20.3	36.1	25.5	18.0	100.0
8 km	0-10 cm	0.1	14.1	35.4	13.0	37.5	100.0
12 km	0-10 cm	0.1	7.1	44.9	9.1	38.7	100.0
16 km	0-10 cm	0.1	2.1	37.6	4.5	55.7	100.0
20 km	0-10 cm	0.0	5.1	34.7	5.3	54.9	100.0
Distance	Depth	Fl	F2	F3	F4	F5	
100 m	0-10 cm	3.0	38.7	32.0	13.9	12.4	100.0
4 km	0-10 cm	8.0	51.0	26.8	6.4	8.0	100.0
8 km	0-10 cm	12.7	27.8	25.3	20.3	13.9	100.0
12 km	0-10 cm	11.1	44.4	31.7	3.2	9.5	100.0
16 km	0-10 cm	14.3	42.9	32.1	3.6	7.1	100.0
20 km	0-10 cm	21.8	41.8	21.8	0.0	14.5	100.0
Distance	Depth	Fl	F2	F3	F4	F5	
100 m	0-10 cm	0.2	1.0	61.7	3.9	33.2	100.0
4 km	0-10 cm	0.1	2.7	22.1	2.7	72.4	100.0
8 km	0-10 cm	0.1	2.6	18.7	2.4	76.3	100.0
12 km	0-10 cm	0.2	1.7	21.0	3.0	74.0	100.0
16 km	0-10 cm	0.0	1.4	24.2	2.8	71.6	100.0
20 km	0-10 cm	0.2	1.5	21.4	2.2	74.7	100.0
Distance	Depth	Fl	F2	F3	F4	F5	
100 m	0-10 cm	1.2	7.1	29.5	8.5	53.6	100.0
4 km	0-10 cm	1.7	6.7	28.6	8.1	54.9	100.0
8 km	0-10 cm	1.6	3.4	22.5	8.9	63.5	100.0
12 km	0-10 cm	1.4	6.9	28.6	8.4	54.7	100.0
16 km	0-10 cm	0.9	6.9	30.4	7.3	54.5	100.0
20 km	0-10 cm	1.1	7.1	27.4	9.7	54.8	100.0

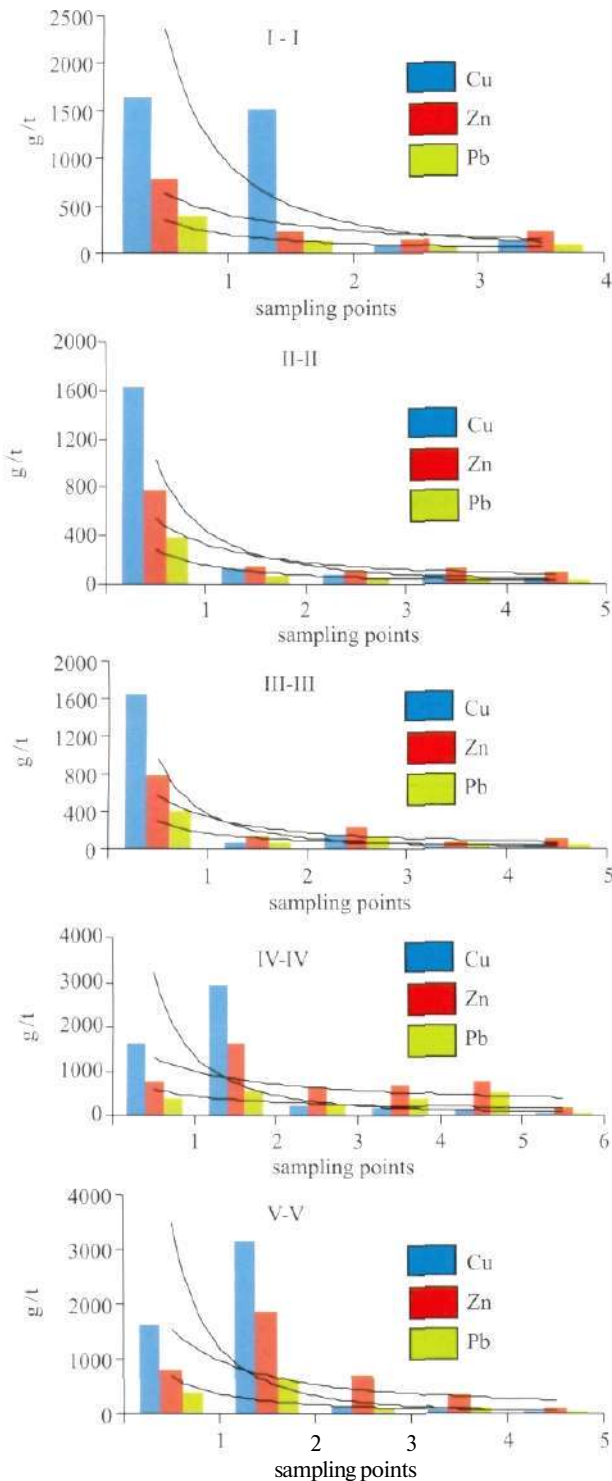


Fig. 2. Distribution of Cu, Zn and Pb removal from the source (along transects I-I, II-II, III-III, IV-IV and V-V).

lithogenic origin (Table 2 and Table 3).

The complementary use of a sequential method demonstrates that in the contaminated soils, most of the Zn, Pb, Cu and Cd concentrations were associated with inorganic and organic forms from which they can be relatively easily removed. Ni, Co and Cr mainly associated with inorganic residual forms, presumably of sulphide and oxide nature. Therefore, there is a much greater risk of Zn, Pb, Cu and Cd mobilization from these soils than for Ni,

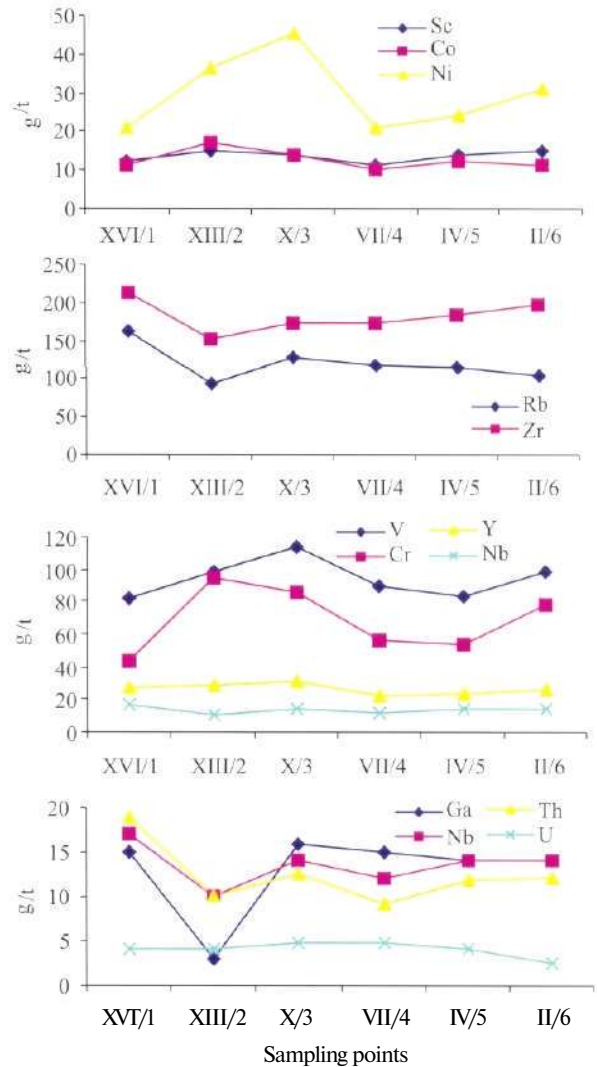


Fig. 3. Distribution of Sc, V, Cr, Co, Ni, Ga, Rb, Sr, Y, Zr, Nb, Ba and Th along transect II-II.

Co and Cr. The first two steps of the sequential extraction, which represent the more mobile metal forms, removed an appreciably larger average proportion of Cd (44%), Pb (24%), Zn (19%), and Cu (17%), than that of Cr (2%) and Ni (8%). The third and fourth fractions, which are under oxidizing conditions, may be released into solution, and contain twice the average amount of Cu (68%), Cd (44%), Pb (64%) and Zn (70%) than that of Ni (31%). In the residual (i.e. chemically inert) form, the total average proportion of Ni (56%) and Cr (76%) is more than twice that of other metals; Cd (12%), Pb (10%), Zn (13%), and Cu (19%) (Fig. 4).

4 Conclusions

The distribution of heavy metals in the present study was found to be strongly correlated to heavy metal physicochemical properties, as reported in other studies. This distribution yielded two different distribution patterns: (1) a gradual, continuous decrease from the

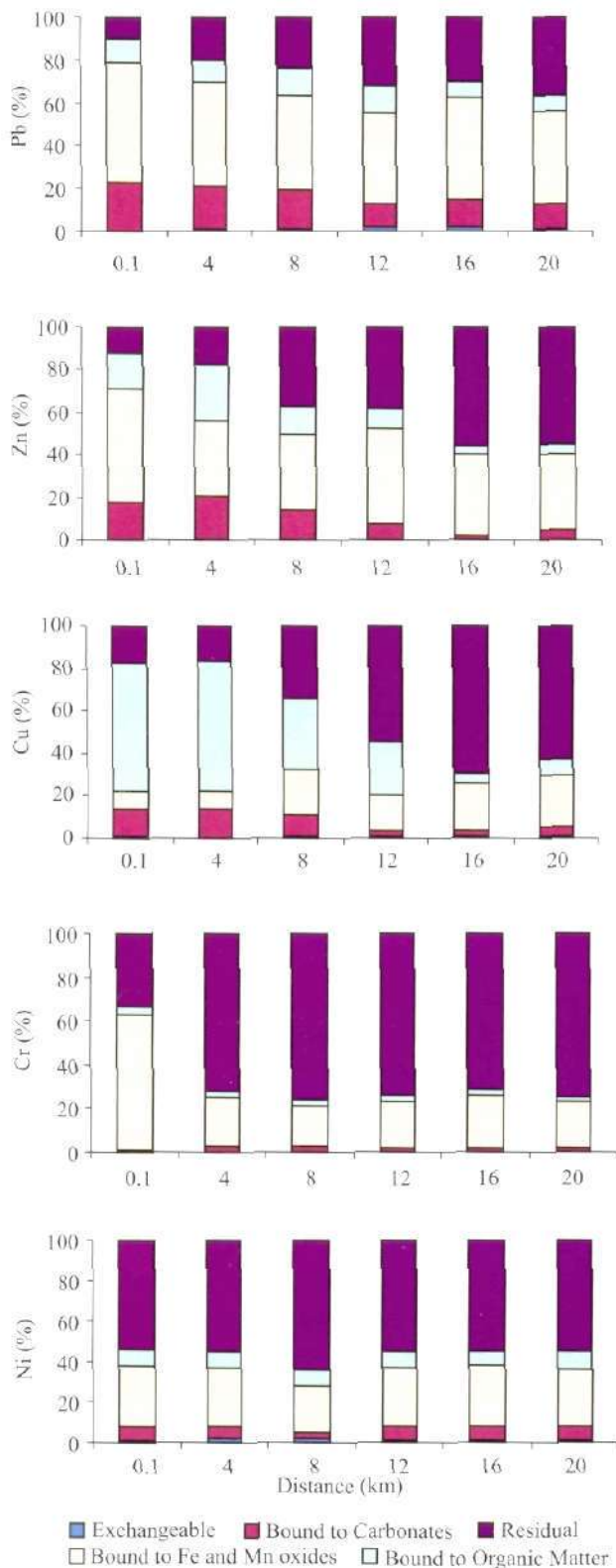


Fig. 4. Results of sequential extraction procedure (percentage of the five metal fractions of total concentration).

the source). Both distribution patterns are defined by both the abiotic components and the physicochemical properties of the pollutant. A high level of carbonate (CO_3^{2-}) content in the studied soils might reduce heavy metal mobility in soils by increasing chemisorptions. Earlier studies by Hutchinson and Whitby (1974) support our findings that Cu, Pb, Zn and Cd contamination accumulates mainly in the top soil layer and that a rapid and gradual decrease occurs with increasing distance from the smelter.

The primary results on the distribution of metals in Almalyk soil samples allows us to divide them into two groups: (1) technogenic (Cu, Zn, Pb, Rb and Th); and (2) lithogenic (Ba, Sr, Zr, V, Cr, Ni, Y, Nb, Sc, Ga, Co and U).

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pollution source along the downwind direction; and (2) a relatively low level of contamination at the source, with a gradual increase moving away from the source (in some cases a gradual decrease occurs at a certain distance from