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DETERMINATION OF HEAVY METALS IN SOIL EXTRACTS AND PLANT TISSUES AT AROUND OF A ZINC SMELTER

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Extractable contents of heavy metals such as Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and Bi in soil and plant tissue samples (fruit, leaf, twig and root) collected, along a distance of 1100 m to the West, from the surroundings of a metallurgical factory producing mainly zinc, cadmium and lead were determined by flame atomic absorption spectrometry (FAAS). In addition, the determinations of Ca and Mg, macro nutrient elements for plants, were also performed. Three extractant solutions were used for dissolution of soil samples, namely aqua regia (1 HNO₃+ 3 HCl) for total metal analysis, 1 mol L⁻¹ ammonium acetate for exchangeable metal contents, and a dilute acid mixture (0.1 M HCl in 0.025 M H₂SO₄) for acid soluble metal contents. A mixture of HNO₃ and HClO₄ was used to analyze the fruit samples. The analyses of the leaf, the twig, and the root tissue samples were made by dry ashing method. The detection limits of the metals were in the range of 0.04 to 0.45 µg/mL for all soil extracts and 0.01 to 1.50 µg/mL for the fruit samples. The recovery values for all the determinations were higher than 95 %. The results obtained from the analyses of plant tissue and soil samples were evaluated using linear correlation analysis and concentration factors to identify the effect of the factory near the grape-vine area.

Keywords: Soil extracts; plant tissues; toxic heavy metals; concentration factor; flame atomic absorption spectrometry

INTRODUCTION

The sources of heavy metal pollution in soils and surface waters are mainly raised from industrial, traffic and municipal wastes such as solid, liquid and gaseous ones. Soil is both a principal source of trace elements entering the food chain and a major sink for pollutant elements.^[1] Both the inhalation of the dusts originated from soils and the intake of toxic metals-dust polluted being taken up

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by the plants have serious effects on the food-chain. The importance in the food chain of these toxic metals is due especially to the easy uptake by plants and their accumulation.^[2,3] The heavy metals arsenic, cadmium, chromium, cobalt, copper, lead, mercury, molybdenum, nickel, selenium and zinc are the most hazardous of these substances. Although many of these heavy metals are needed in small quantities by plants and animals, they may enter soils in great enough quantities to pose risks to the health of plants, animals, and humans. Heavy metals are persistent, and their negative effects in soil are long-lasting. Some non-essential toxic elements, especially Cd, Hg and Pb, have toxic effects on living organisms even at very low concentrations.^[4] Therefore, today, all of these are crucial environmental problems and they may also be kept of importance in the future. Soils consist of heterogeneous mixtures of organic and inorganic substances, and the binding mechanisms for metals vary with the composition of the soil. The ecological effects of heavy metals in soil are closely related to the species distribution in the solid and liquid phases of the soil. Chemical extractions of soils indicate a complicated relationship with the availability of particulate-associated forms of trace metals to flora and fauna. This is probably due to the effect of competition between adsorption sites in the solid substrate and selective mechanisms of metal uptake by the different organisms.^[5]

In plant nutrition, it is important to determine the metal levels which can be taken up by the plant rather than their total concentrations. In another way, even though any metal occurs in excess amount in soil if the metal cannot be taken up by the plant, this is no importance in the point of the plant. It is well known that a proportional relationship is obviously between the metal concentrations appropriate for taking up by the plant and their levels that can be passed into soil extracts.^[6,7]

Up to now, different methods including various acids and/or acid mixtures have widely been used for the determination of toxic heavy metals in soils^[8-12] and plant tissues.^[13-16] Five mineral acids (hydrofluoric, perchloric, sulfuric, nitric and hydrochloric), either separately or in a combination have been used for the simultaneous extraction of a large number of metals in soils. Such total metal contents only give a very approximate estimation of the plant-available trace element status of a soil. However, it is known that the environmental behavior of trace elements depends not only on the total amounts but also on their chemical forms.^[5] For this purpose, to assess the reactivity of species or binding forms of heavy metals in solid materials, extraction procedures have been applied, both as single leaching steps and combined in sequential extraction schemes.^[17-21] The aim of this study was (a) to investigate the metal levels in the soil and the plant tissue samples with respect to the distance from the factory (smelter); (b) to assess the relationship between metal concentrations found for these samples. In

the analysis of soil samples, three extractant solutions including ammonium acetate, a dilute acid mixture, and aqua regia were used. In the extraction method with ammonium acetate reagent, the extractable metal ions (mobile or plant-available contents) were introduced into solution by means of ion exchange. An aqua regia digestion is used for the determination of pseudo-total concentrations of heavy or toxic metal accumulations in soils.^[1] The fruit samples were dissolved by wet digestion and the other plant tissues by dry ashing.^[22] The determination of heavy metals in soils and plant tissues (fruit, leaf, twig, and root) was performed by flame atomic absorption spectrometry.

EXPERIMENTAL

Instrumentation and reagents

The determinations of metals in the soil and plant tissue samples were carried out by a Perkin Elmer Model 3110 flame atomic absorption spectrometer equipped with an air/acetylene burner. Hollow cathode lamps (Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Bi, Mg and Ca) were used as radiation source. The measurements were performed under the operating conditions suggested in the data processor of the manufacturer.^[22]

High purity reagents and doubly-distilled deionized water were used for all the experiments. Standard stock solutions containing 1000 $\mu\text{g/mL}$ of each metal in 0.5 M HNO_3 were prepared from nitrate salts for Cr, Mn, Co, Ni, Cd, Pb, Bi, Mg, and Ca, and from pure metal powders for Fe, Cu, and Zn. Working standards for calibration were prepared from the stock solutions by diluting prior to use. Solutions of 1 M HNO_3 , 0.1 M HCl in 0.025 M H_2SO_4 and 1 M $\text{CH}_3\text{COONH}_4$ (pH 7) were prepared in bidistilled water. A Clifton shaker, end-over-end type, and an electrical heater were used throughout all the experiments.

Collection and preparation of samples

Soil and plant samples were collected from different locations along 1100 m from the factory towards the West (Figure 1). Since plants take up lots of nutrient elements and micronutrients required from a depth of 15–20 cm by their roots, the soil samples were taken from this depth by a tool made of 18–10 Cr-Ni stainless steel. Also, the plant tissue samples were collected from the same points in which the soil samples were taken.

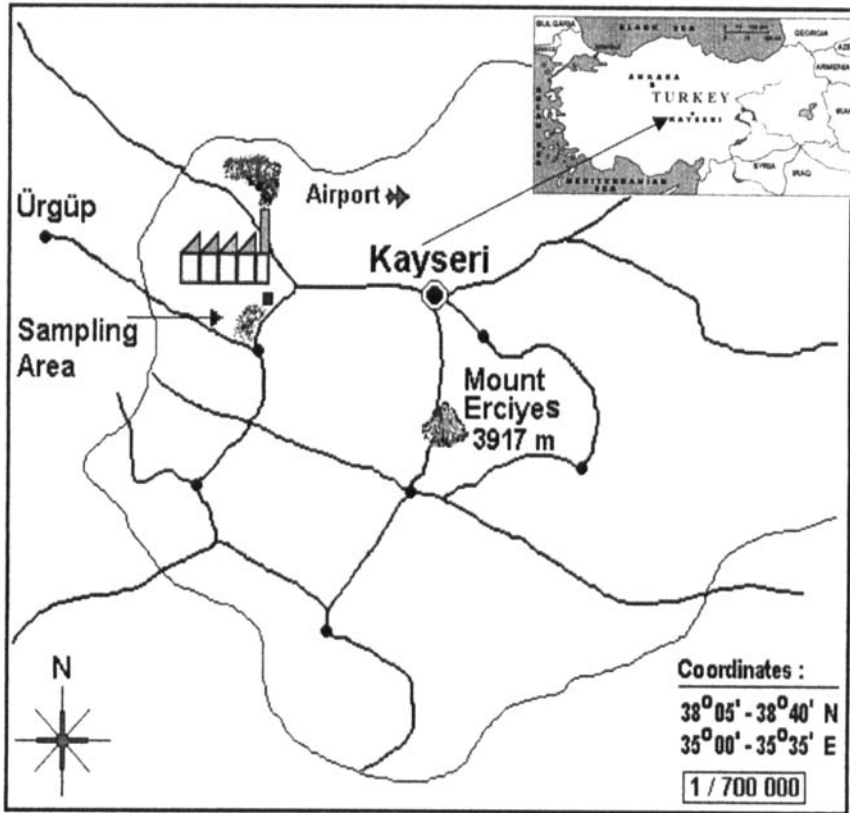


FIGURE 1 Map of Kayseri province and sampling area

To investigate the soil pollution level in view of heavy metals, control soil samples were collected from the Mountain of Alidağı, about 25 km South-East part of the City (Kayseri), and control fruit samples were taken from Ürgüp, approximately 60 km from the City towards the West. All the samples were put into polyethylene bags washed with tap water, 1:1 HNO₃ and distilled water, respectively.

Once in the laboratory, the soil samples were dried at 110°C in an electrical oven, ground with an agate mortar, and then passed through a sieve to separate the fractions of particle size less than 200 mesh. All the plant tissue samples (fruit, leaf, twig and root) were washed with distilled water and then dried in an oven at 80°C. The fruit and leaf samples were ground in an agate mortar. The twig and root samples were cut very finely by an unused surgeon knife sterilized. All the samples prepared were preserved in polyethylene bags until the analysis.

Description of the zinc smelter

In the zinc plant, about 170000 tonnes of zinc ore per year is processed as metal carbonate or oxide. Particulate matter emissions of the plants is nearly 1250 tons per year. The zinc ore with oxide and carbonate coming from the mine quarries to the smelter consists of 21 % Zn, 2–3 % Pb, 0.07 % Cd, 15 % Fe, 0.022 % F, 0.003 % Cl, 6 % Al₂O₃, 8 % SiO₂, 0.60 % MgO and 10–15 % CaO. Annual capacity of the smelter is 33650 tons of electrolytic ingot zinc, 6000 tons of metal lead, 124 tons of metal cadmium and 4.5 tons of silver.

Analysis of soil samples

To analyze the soil samples (n=22) collected from different locations along a distance of 1100 m to the West from the factory, three different extractants were used. Each sample and blank were analyzed in triplicate for the three extractant solutions.

Dissolution with diluted acid mixture, ammonium acetate and aqua regia

Weighing a 2.5 g of each soil sample pretreated was placed into 100 mL of beaker glass. A 5 mL of 0.1 M HCl in 0.025 M H₂SO₄ was added to the beaker and shaken on a shaker for 25 minutes. After shaking, the solutions were passed through a blue band filter paper and then the filtrates were taken into 10 mL of volumetric flasks by completing to the mark with distilled water. The determination of metals which are soluble in dilute acid mixture was performed by FAAS.

A 15 mL aliquot of 1 M ammonium acetate solution (pH 7) was added to 1.5 g of soil sample in a 100 mL of beaker glass and then the mixture obtained was shaken for 15 minutes. The suspension was filtered through a blue band filter paper and the filtrate was taken into a volume of 15 mL with some distilled water. The determinations of the exchangeable cations in a medium of 1 M CH₃COONH₄ were made by FAAS.

A 10 mL of aqua regia was added to 1 g of soil sample in a beaker glass. The soil sample solution was evaporated to incipient dryness on a sand bath at 80°C. After adding a 5 mL of concentrated HClO₄ to each one, the solutions were heated again at 50°C. A second 10-mL of aqua regia was added to the samples and the solutions were evaporated near to dryness. The residue was dissolved with some dilute nitric acid and passed through the filter, and then completed with distilled water to 10 mL. The metal contents of these solutions were determined by FAAS. For the determinations of the elements Ca, Mg, Mn, Ni, Fe and Zn 100, 400, 1000 and 2000-fold dilutions were made, when required.

TABLE I Recovery and detection limit values for fruit and soil samples

Element	Sample											
	Fruit			Dilute acid			Ammonium acetate			Aqua regia		
	Recovery (%) ^a	Detection limit ^b (µg/mL)	Recovery (%)	Detection limit (µg/mL)	Recovery (%)	Detection limit (µg/mL)	Recovery (%)	Detection limit (µg/mL)	Recovery (%)	Detection limit (µg/mL)	Recovery (%)	Detection limit (µg/mL)
Pb	95.7 ± 0.9	0.17	97.0 ± 0.9	0.14	97.6 ± 0.1	0.29	97.7 ± 0.9	0.23				
Cd	96.8 ± 0.6	0.02	98.1 ± 0.6	0.15	98.5 ± 0.6	0.02	98.6 ± 0.4	0.02				
Zn	97.0 ± 0.9	0.09	95.6 ± 0.4	0.03	96.7 ± 0.7	0.03	96.9 ± 0.8	0.11				
Fe	96.1 ± 0.5	0.45	96.1 ± 0.6	0.40	97.6 ± 0.6	0.29	97.0 ± 0.7	1.08				
Ni	96.0 ± 0.5	0.43	96.1 ± 0.8	0.34	95.6 ± 0.9	0.37	97.0 ± 0.5	0.29				
Cu	96.2 ± 0.8	0.17	95.1 ± 0.5	0.10	96.9 ± 0.8	0.35	97.5 ± 0.9	0.13				
Cr	97.0 ± 0.8	0.34	96.1 ± 0.9	0.14	97.8 ± 0.6	0.10	97.6 ± 0.6	0.19				
Mn	97.5 ± 0.6	0.11	96.2 ± 0.6	0.17	96.0 ± 0.9	0.20	96.9 ± 0.5	0.14				
Co	95.4 ± 0.5	0.20	97.6 ± 0.7	0.12	96.8 ± 0.5	0.26	96.0 ± 0.7	0.16				
Bi	95.0 ± 0.5	0.39	96.8 ± 0.9	0.61	96.1 ± 1.0	0.37	97.3 ± 0.7	1.02				
Ca	97.8 ± 0.6	0.39	97.0 ± 1.0	0.24	96.8 ± 0.8	0.32	97.8 ± 0.8	1.50				
Mg	96.8 ± 0.9	0.04	97.5 ± 0.7	0.01	95.3 ± 0.8	0.04	97.7 ± 0.6	0.03				

a. Average of 10 determinations with 95% confidence level for recoveries, $R \pm t \times s / \sqrt{n}$.

b. n=20.

TABLE II The mean metal contents obtained from different soil extractants ($\mu\text{g/g}$ dry weight, $n = 22$)

Element	Soil samples (Dissolving medium)			Aqua regia (1 HNO ₃ + 3 HCl)	Typical soil contents ^[4]	Control sample ^a		
	0.1 M HCl in 0.025 M H ₂ SO ₄	1 M CH ₃ COONH ₄ (pH 7.0)	1 M CH ₃ COONH ₄ (pH 7.0)					
	Mean	Range	Mean	Range	Mean	Range		
Pb	7.9	3.2 - 13	12.0	8.6 - 16.8	104	87 - 122	2 - 20	8.0
Zn	5.0	1.8 - 8.8	5.4	2.5 - 8.1	63	31 - 88	20 - 300	54
Cd	0.3	0.04 - 0.5	0.3	0.1 - 0.6	3.5	2.4 - 4.6	0.03 - 0.3	nd
Fe	10.0	4.8 - 18.1	2.8	1.8 - 3.8	7484	5050 - 9670	0.5 - 10 %	nd
Ni	4.5	2.6 - 5.2	2.3	1.4 - 3.9	308	240 - 371	5 - 500	20
Cu	0.9	0.4 - 1.6	0.7	0.4 - 1.2	24	18 - 30	5 - 80	13
Co	2.5	1.6 - 3.4	4.4	2.4 - 8.2	15	12.3 - 18.3	1 - 50	nd
Cr	5.4	3.2 - 7.6	6.6	3.4 - 9.6	35	25.3 - 39.5	10-200	nd
Bi	9.4	8.8 - 10.6	15.6	11.0 - 19.0	26.4	23.4 - 30.0	nd ^b	nd
Mn	195	168 - 237	129	120 - 141	1014	888 - 1160	200 - 2000	264
Ca	2313	1576 - 2760	2904	2170 - 3635	10294	9020 - 11170	0.5 - 2 %	nd
Mg	30.2	20 - 46	12.2	10.0 - 14.0	323	240 - 390	0.2 - 2 %	nd

a. The control sample was dissolved in aqua regia.

b. Not determined.

Analysis of plant tissues

The plant tissue samples (n=22) collected from the same points with the soil samples were analyzed for the same elements mentioned above. Each sample analysis and blank determination, using the same reagents for each plant tissue, were run in triplicate.

Dissolution of fruit samples

Weighing a 2 g of each fruit sample was put into a graduated beaker glass of 100 mL. A 10-mL of concentrated HNO₃ (65 %) was added to each beaker and then covered with a watch glass. The beakers were placed onto a sand bath and then heated at 120°C until up going of NO_x gases was completed. After cooling, a 2 mL of concentrated HClO₄ (60 %) was added to beaker and evaporated to incipient dryness at 100°C. The beakers were washed with a little portion of 1 mol L⁻¹ HNO₃, and the washings were completed to 5 mL in graduated flasks. The metal contents (Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Bi, Mg and Ca) of these solutions were determined by FAAS. For the measurements of the elements of Fe, Zn, Ca, and Mg 20, 40, 500 and 1000-fold dilutions were made, respectively.

Dissolution of leaf, twig and root samples

Weighings of one g from each of the leaf, twig and root samples were put into porcelain crucibles separately. The samples weighted were ashed at 450°C in a muffle furnace for a night. After cooling, 5 mL of 20 % HCl was added to each residue and then they were evaporated near to dryness on a sand bath. After adding 5 mL of 1 M HCl, the sample solutions were centrifuged at 2500 rpm for 20 minutes. The solutions were taken into graduated flasks of 5 mL using 1 M HCl. The measurements of Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, and Bi elements were done by FAAS.

RESULTS AND DISCUSSION

Recovery and detection limit

To determine the accuracy of the methods used in the determination of the metals in both the soil extracts and plant tissues, known-amounts of the elements studied were added to the soil and fruit samples. The recovery values (%) were calculated by comparison with the concentrations of the metals with or without spiked

samples. The recovery values of the elements for both soil and fruit samples were quantitative ($\geq 95\%$). The relative standard deviations for all the elements in soil samples were found in the range of 0.3 to 1.8, 0.4 to 8.6 and 0.3 to 11.5 % in aqua regia, dilute acid mixture and ammonium acetate extractants, respectively.

The solvents and the reagents used in the analyses of soil and fruit samples were taken into consideration in the determination of detection limits of twelve elements. In calculating the detection limits, the Equation of $X_C = \bar{X}_{blank} + 3S_{blank}$ was used.^[23] The detection limit and recovery values of the elements determined for both soil and fruit extracts are shown in Table I.

Evaluation of the results of soil sample analysis

As can be seen from Table II, the concentrations found for all the elements using aqua regia were higher than those of both other soil extractants and control sample. The concentrations found using aqua regia for the Fe, Mn, Zn, Cu, Co, Ni and Cr elements were in the range of typical soil metal contents.^[24,25] The concentrations of Pb and Cd elements for aqua regia digestion were higher than the typical soil contents for these metals.

The mean concentrations of Fe, Ni, Cu, Zn, and Cd metals in the ammonium acetate extracts were lower than those of the plant tissues (fruit, leaf, twig and root) for the same elements. For Mn, this case is only valid for leaf samples. This explanation can also be acceptable for all the elements, in dilute acid mixture, except for Ni. The extractabilities of all the metals in dilute acid mixture and ammonium acetate solutions with respect to the contents in aqua regia extracts increase up to 36 % and 59 %, respectively. The greatness of percentage concentrations of the metals in the ammonium acetate extractant medium, which are related to their mobilities or bioavailabilities, may give an information about the extents taken up by plants.^[1]

In our previous study, the metal concentrations of soils collected from the vicinity of the same smelter for Zn (27–10500 $\mu\text{g/g}$), Pb (0.5–1648 $\mu\text{g/g}$), Cd (0.1–4.9 $\mu\text{g/g}$), Cu (5–47 $\mu\text{g/g}$), Ni (15–57 $\mu\text{g/g}$) and Mn (212–730 $\mu\text{g/g}$) had been determined by FAAS using aqua regia digestion at distances of 50, 100, 250, 500, 1000, 1500 and 2000 m for four main- and four sub-directions.^[26] The Mn concentration (1014 $\mu\text{g/g}$) obtained with the present study for aqua regia digestion was found to be higher than that mentioned just above, based on average values.

In order to investigate possible pollution effects on the surrounding of the solid wastes deposited within the smelter area in which the surroundings of the plant are generally agricultural lands, i.e., grape-vine and wheaten areas, the metal lev-

els in these wastes were determined in the same way of the soil samples. As can be seen from the results of analysis (Table III), the metal levels for the three extractant media were found more higher than the average values of the other 22 soil samples. In addition to the dust emissions of the smelter, these analytical results show that the open solid waste area may be a point source of pollution for its environment both today and in the future.

TABLE III The mean metal levels of waste area ($\mu\text{g/g}$ dry matter, $n = 4$)

Element	0.1 M HCl in 0.025 M H_2SO_4	1 M $\text{CH}_3\text{COONH}_4$ (pH 7.0)	Aqua regia (1 HNO_3 + 3 HCl)
Pb	6.0 ± 1.1^a	21.0 ± 1.6	168 ± 5
Zn	17.0 ± 0.1	32.0 ± 0.2	215 ± 2
Cd	0.80 ± 0.03	1.00 ± 0.08	9.0 ± 0.2
Fe	31.0 ± 0.8	8.0 ± 1.1	14000 ± 60
Ni	10.0 ± 1.1	5.0 ± 0.2	678 ± 3
Cu	3.50 ± 0.09	2.0 ± 0.1	48.0 ± 0.5
Co	6.50 ± 0.05	16.0 ± 0.3	23.0 ± 0.3
Cr	14.0 ± 0.3	19.0 ± 0.6	57.0 ± 0.6
Bi	19.0 ± 0.1	30.0 ± 0.3	57.0 ± 0.3
Mn	273 ± 6	197 ± 18	1502 ± 37
Ca	4113 ± 56	4290 ± 56	16150 ± 172
Mg	13.0 ± 0.03	21.0 ± 3.2	698 ± 46

a. $\bar{x} \pm t \cdot s/\sqrt{n}$, at 95% confidence level

Evaluation of the results of analysis of plant tissue samples

As can be seen from the Table IV, when the results of analysis of the fruit, leaf, twig and root samples were evaluated, it was observed that the mean concentrations of Pb, Cd, Cr and Co were higher than the typical plant tissue contents. If the concentration of any metal in soil is at a high level ($>$ typical soil metal content), this situation may also explain that the concentration of the metal in plant tissue will probably be high (e.g., Pb and Cd).

Pb, Cd, Cr and Co contents of the fruit samples indicate that a metal accumulation exists. The average concentrations of the Zn, Ni, Cu, Ca and Mg elements are in the range of threshold values.^[24] The concentrations of Mn and Fe, which are micronutrients in soils for plants, of the fruit samples are lower than those of

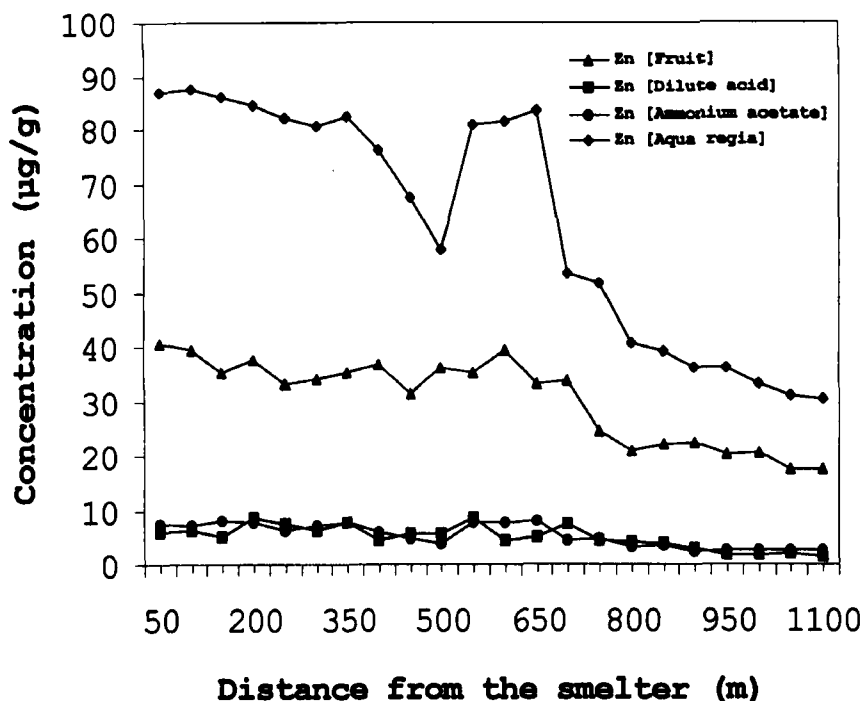


FIGURE 2 Concentration profile of Zn associated with different extractant media of fruit and soil samples according to the distance from the smelter

the threshold values. These low levels may be explained with the soil structure. The structure of soil is one of the most important factors of soil composition that affects the extents of the metals taken up by plants. Some elements can be more easily taken up by the plants because of their weak metal-chelate complexes. If the strong metal-chelate complexes can not be digested by the microorganisms, the elements can not be taken up by the plants. There is a competition, for example, among clays, ion-exchangers, organic ligands (i.e., humic acids, fulvic acids, etc.), and roots of plant during the uptake of the soil nutrients.^[6] On the other hand, the metal levels of fruit samples for Cr, Mn, Co, Ni, Cu, Zn, Cd, Pb, and Bi were observed higher than those of control samples; for example, ratios (metal concentration of fruit sample/metal concentration of control sample) were found to be 59, 6 and 7.4 for lead, cadmium and chromium, respectively. But, iron level of the control sample (181 µg/g) was greater than that of the fruit sample (6-fold). This difference in level may be related to mineral structure of the soil.

TABLE IV Mean concentrations of metals in plant tissue samples ($\mu\text{g/g}$ dry weight, $n = 22$)

Element	Fruit ^a			Leaf ^b			Twig ^b			Root ^b			Control fruit samples	Typical plant tissue contents ^[24]
	Mean	Range		Mean	Range		Mean	Range		Mean	Range			
Pb	7.1	4.7–11.0		100	21.7–284		11.2	3.1–29.3		52	2.88–196		0.12	0.05–3
Zn	30	17–40.7		292	49.4–724		54	5.16–119		184	6.46–1750		23.9	15–100
Cd	0.3	0.05–0.4		1.69	0.2–3.74		0.49	0.09–2.15		2.00	0.05–12.2		0.05	0.01–0.3
Fe	30	16–63		398	183–783		54	23.0–111		435	35.3–1667		181	40–500
Ni	3.2	1.8–4.8		5.75	1.72–11.8		2.34	0.27–6.88		3.98	0.20–14.8		0.40	0.5–5
Cu	4.2	2.7–6.0		6.39	1.9–17.4		6.62	1.62–27.2		5.84	2.18–13.1		2.72	2.5–25
Co	1.6	0.9–2.15		2.18	1.38–3.95		0.92	0.18–1.8		1.12	0.19–2.50		0.11	0.1–0.6
Cr	1.7	0.9–2.4		2.17	1.01–4.44		1.16	0.55–5.8		1.44	0.38–3.68		0.23	0.05–0.5
Bi	7.0	4.34–10.6		nd ^c	nd		nd	nd		nd	nd		2.09	nd
Mn	6.5	4.2–8.7		166	67–415		70	15.4–184		60	16.9–151		2.40	50–1000
Ca	3430	2845–4856		nd	nd		nd	nd		nd	nd		nd	0.3–2.5 %
Mg	1177	1025–1500		nd	nd		nd	nd		nd	nd		nd	0.1–0.5 %

a. Wet digestion ($\text{HNO}_3 + \text{HClO}_4$).

b. Dry ashing.

c. Not determined.

TABLE V Correlation matrix that gives the relationship between metal concentrations of soil ammonium acetate extract and fruit metal concentrations (n=22)

	Elements in fruit samples											
	Zn	Pb	Ni	Mn	Mg	Fe	Cu	Cr	Co	Cd	Ca	Bi
Zn	0.86 ^a	0.79	0.37	0.69	<0.33	0.46	0.45	<0.33	0.41	0.82	<0.33	0.73
Pb	0.86	0.70	0.36	0.56	<0.33	0.38	0.43	<0.33	0.38	0.78	0.39	0.65
Ni	0.75	0.44	<0.33	0.51	<0.33	0.46	0.55	<0.33	0.36	0.69	0.39	0.74
Mn	0.71	0.39	0.33	0.56	<0.33	0.58	0.40	<0.33	0.34	0.73	0.39	0.82
Mg	0.73	0.64	0.69	0.49	0.55	0.38	0.31	0.35	0.61	0.78	0.42	0.59
Fe	0.80	0.53	0.36	0.61	<0.33	0.62	0.46	<0.33	0.44	0.75	0.46	0.81
Cu	0.84	0.60	0.49	0.69	<0.33	0.55	0.44	<0.33	0.37	0.79	0.53	0.84
Cr	0.87	0.62	0.47	0.64	<0.33	0.56	0.39	<0.33	0.38	0.85	0.63	0.84
Co	0.75	0.49	0.45	0.52	0.35	0.37	0.45	<0.33	0.40	0.71	0.60	0.74
Cd	0.92	0.78	0.50	0.78	<0.33	0.54	0.36	<0.33	0.50	0.88	0.44	0.87
Ca	0.88	0.64	0.54	0.67	<0.33	0.55	0.46	<0.33	0.34	0.89	0.60	0.86
Bi	0.89	0.65	0.51	0.69	<0.33	0.61	0.37	<0.33	0.53	0.84	0.52	0.85

a. Correlation coefficients of ± 0.33 or better are shown only. $r_{\text{critical}}: 0.33$ (n = 22, at 90 % confidence level)^[30].

TABLE VI Concentration factors of the metals found in the plant tissues for three different soil extracts

Element ^a	Fruit			Leaf			Twig			Root			Control fruit samples, CF ₃
	CF ₁ ^b	CF ₂ ^c	CF ₃ ^d	CF ₁	CF ₂	CF ₃	CF ₁	CF ₂	CF ₃	CF ₁	CF ₂	CF ₃	
Pb	0.90	0.59	0.07	12.7	8.33	0.96	1.42	0.93	0.11	6.58	4.33	0.50	0.001
Zn	6.00	5.56	0.48	58.4	54.1	4.64	10.8	10.0	0.86	36.8	34.1	2.92	0.38
Cd	1.00	1.00	0.09	5.63	5.63	0.48	1.63	1.63	0.01	6.67	6.67	0.57	0.01
Fe	3.00	10.7	0.004	39.8	142.1	0.05	5.40	19.3	0.01	43.5	155.4	0.06	0.02
Ni	0.71	1.39	0.01	1.28	2.50	0.02	0.52	1.02	0.01	0.88	1.73	0.01	0.001
Cu	4.68	6.00	0.18	7.10	9.13	0.27	7.36	9.46	0.28	6.49	8.34	0.24	0.11
Co	0.64	0.36	0.11	0.87	0.49	0.14	0.37	0.21	0.06	0.45	0.26	0.08	0.01
Cr	0.32	0.26	0.05	0.40	0.33	0.06	0.22	0.18	0.03	0.27	0.22	0.41	0.01
Bi	0.74	0.45	0.26	nd ^e	nd	nd	nd	nd	nd	nd	nd	nd	nd
Mn	0.03	0.05	0.01	0.85	1.29	0.002	0.36	0.54	0.07	0.31	0.46	0.06	0.002

a. The CF₁, CF₂ and CF₃ values of Ca and Mg for fruit samples are 1.48, 1.18, 0.33 and 39.0, 96.5, 3.64, respectively.

b. CF₁ (dilute acid mixture).

c. CF₂ (ammonium acetate).

d. CF₃ (aqua regia).

e. Not determined.

In general, the metal levels of leaf samples were found to be higher than those of the fruit, twig and root samples. The high metal contents of the leaf samples with respect to the other plant tissues may be explained with the large surface of leaves that cause the uptake of metals by surface adsorption, because metal ions present in solution at the leaf surface can diffuse into leaf cells or may bind to the cuticle or cell wall.^[27] In addition, the leaf behaves as a bioaccumulator.^[28,29]

Metal levels of plant tissues increase usually in order of fruit, twig, root and leaf. The fruit, leaf and twig samples are annual plant tissues while the roots are per annual plants which may be a hundred years old or more. The metal contents of per annual roots being lower than that of the leaf tissues may be related to the roots, which are deeper, in which the metal contents may be lower than the surface soils.

In general, the more distant the concentrations of the elements in the soil and plant tissue samples are from the smelter, the more they decrease. The change in Zn levels, as an example, of both the soil samples for the three extractants and the fruit tissue samples related to the distance is shown in Figure 2.

Statistical evaluation

The correlation coefficients (r) among the metal concentrations of the fruit and soil ammonium acetate extracts are presented in Table V. For example, the correlation coefficients between fruit and soil metal contents for Cd, Zn, and Pb were very high (probably due to the smelter emissions) which were 0.88, 0.86 and 0.70, respectively. For Bi, a much high correlation coefficient (0.85) was also observed.^[30] The correlation coefficient values lower for Pb and much higher for Zn and Cd were also reported by Ross.^[27] In addition, the correlation coefficients of these four elements with the others were very high and changed in the range of 0.59–0.89, except for the r values of Pb with Mn, Ni, Fe and Co (see Table V). These results show that the smelter has a great pollution influence on its near environment. The table is self explanatory for the remaining correlation.

Most earlier studies of metal uptake by plants have assumed that the prime source of metals is the soil. This can be defined as the extent of metal that different plants could take up by calculating plant/soil metal ratios called as concentration factors (CF). As can be seen from Table VI, the calculated CFs of Zn, Cd and Pb for fruit, leaf, twig and root were much higher than those of other elements, which are in order of $Zn > Cd > Pb > Cu > Mn > Co > Cr > Fe > Ni$. However, the CFs of Cd and Pb for fruit and twig were slightly low compared to leaf and root. The much higher CF_{Zn} , CF_{Cd} and CF_{Pb} (to a certain degree) values are attributed to greater mobility or bioavailability of these metals in the soil. The

previous studies indicate a relative ease of uptake of Zn and Cd from soil, but not for Pb.^[27]

CONCLUSION

Extraction methods with the different extractants of soil and fruit samples (also dry ashing for leaf, twig and root samples) offer an information on the levels of heavy metals in these matrices. Especially, the analysis of soils with different extractants provides a crucial knowledge about mobilities, bioavailabilities and interactions between soils and plants of the metals. Recovery studies show that the extraction methods used in this study are satisfactory and reproducible for analysis of soil and plant tissues. The strong correlations were observed among the Zn, Cd, Bi and Pb concentrations determined in fruit samples and ammonium acetate extracts of soil samples. The concentration factors calculated for the Zn, Cd and Pb elements support the results of correlation analysis. The analytical results obtained for both soil and plant tissue analyses indicate that there is a potentially polluted area for the environment in vicinity of the zinc smelter. The pollution levels for both soil and plant samples decrease along the distance of 1100 m from the factory to the West. But at every distance from the smelter in the studied area, the concentration levels of metals in these samples are still higher than those of their control samples. At the same time, the high heavy metal contents of the soil affect the plant tissues, especially leaves, and the metals are accumulated in those parts more densely than the other plant tissues. Therefore, in future, more concentrated studies such as soil characteristics, speciation of metals and determination of pesticides may be necessary in the same region.

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