RESIDUES AND TRACE ELEMENTS

Extractable Trace Metals Content of Dust from Vehicle Air Filters as Determined by Sequential Extraction and Flame Atomic Absorption Spectrometry

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A modified four-step sequential extraction procedure developed within the Standards, Measurement, and Testing Program (formally the Community Bureau of Reference) of the European Commission was applied to determine the distribution of Cd, Cu, Fe, and Mn in air filter dust samples collected from vehicles. The four fractions were acid-soluble, reducible, oxidizable, and residual. These fractions have the advantage of providing better insight into the mechanism of association of metals in the dust. The determination of trace metals in dust samples was performed by flame atomic absorption spectrometry. The results obtained after applying the sequential extraction scheme indicated that Cu was the most abundant metal in the organic and residual fractions of the dust matrix. Fe was found mainly in the residual fraction, and the major amounts of Mn and Cd were present in the acid-soluble and bound-to-carbonate fraction. The mean values of Cd, Cu, Fe, and Mn were found to be 15.58, 33.54, 1625, and 180 g/g, respectively. The results obtained are in agreement with data reported in the literature.

Some trace elements (e.g., Cu, Se, and Zn) are essential to maintain the metabolism of the human body. However, at higher concentrations, they can lead to health problems (1, 2). They enter human bodies via food, drinking water, and air. Urban dusts are important carriers of hazardous substances, including toxic metals that are introduced into the atmosphere by industrial activities, cars, train engines, etc. Toxic elements transported to humans from the environment can affect their health (3), so the analysis of the trace element content of environmental samples is important (4–6). To date, strong acid digestion has been widely applied for sample

treatment or preparation before determination of total trace metals in environmental samples. However, this approach can be misleading when assessing environmental effects because of overestimation of the concentration of trace elements. Trace metal speciation in environmental media using sequential extraction techniques offers a more realistic estimate of actual environmental impact. For many years, sequential extraction procedures have been developed and applied to extract elements from samples under different conditions. The principle of this method is based on the fractionation of a material into different fractions that can be selectively destroyed by extraction (7). Fractionation is the process of classification of an analyte or a group of analytes into a certain matrix, according to their physical size, solubility, chemical bonding, and reactivity properties. A general goal of selective chemical leaching is the accurate determination of the partitioning of elements among different discrete phases of a sample. Fractionation is usually performed by a sequence of selective chemicals and extraction techniques, which include the successive removal, or dissolution, of these phases and their associated metals (8).

The use of sequential extraction furnishes detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization, and transport of trace metals. The mobility of metals in the environment depends strongly on their chemical forms or type of binding of the element. The determination of total concentrations in the sample does not give sufficient information about the mobility and biological and physicochemical properties of metals. In many instances, biological toxicity of the elements is related more closely to the concentrations of particular physicochemical forms (9, 10).

Many different schemes were developed in the past 20 years, as illustrated by a huge number of publications in the international scientific literature. The Community Bureau of Reference (BCR), now the Standards, Measurements, and Testing Program, proposed a modified three-step extraction procedure (11) based on acetic acid extraction (Step 1: exchangeable and acid-soluble fraction); hydroxylamine hydrochloride extraction at high concentration and low
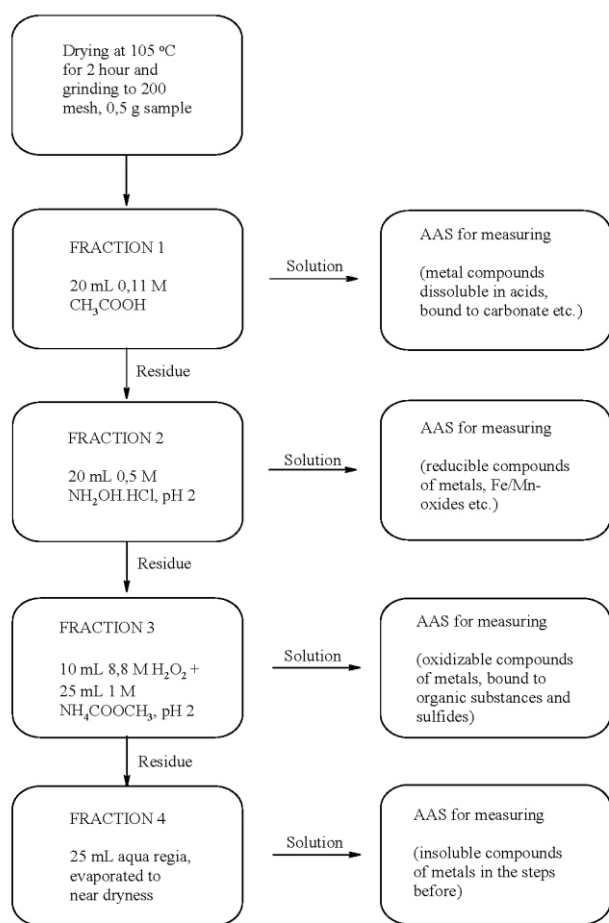
Figure 1. Modified BCR sequential extraction procedure.

pH (Step 2: reducible fraction); and hydrogen peroxide–ammonium acetate extraction (Step 3: oxidizable fraction). One of the main limitations of the BCR sequential extraction procedure is that it is extremely time-consuming.

Sequential extraction procedures have been modified by many researchers in order to optimize the sequential extraction of metals, and they are widely used to determine specific chemical forms of trace metals in a range of environmental media, including sediments, soil, solid waste, etc. (3, 7–23).

In this study, a sequential, four-step extraction procedure modified by the BCR was applied to fractionate the Cu, Fe, Mn, and Cd contents in dust samples collected from air filters of different vehicles. The fractions extracted were acid-soluble (extraction Step 1); reducible-iron/manganese oxides (extraction Step 2); oxidizable-organic matter and sulfides (extraction Step 3); and residual (extraction Step 4). The determination of trace metal ions in dust samples was performed by flame atomic absorption spectrometry (FAAS). The main objectives of the present study were to determine the metal concentrations (Cd, Cu, Fe, and Mn) using the modified BCR sequential extraction procedure in air filter dust samples collected from vehicles; to understand the mobility,

availability, and persistence of trace metals; and to evaluate the results with the data reported from other countries.

Reagents

All chemicals used were of analytical reagent grade unless otherwise stated. Double-distilled deionized water was used for preparing the solutions and all dilutions. All stock solutions of the metals (1000 mg/L) were prepared from the nitrate salts of Cd, Cu, Fe, and Mn. The working solutions of metals were prepared by diluting these stock solutions prior to use. All glassware and plastic vessels were treated with diluted (1:1) HNO_3 (Riedel de Haen, Seelze, Germany) for 24 h and then rinsed with distilled water before use. Acetic acid (CH_3COOH; Riedel de Haen); hydroxylammonium chloride ($NH_2OH \cdot HCl$; Merck, Darmstadt, Germany); hydrogen peroxide (Riedel de Haen); ammonium acetate (Carlo Erba, Rodano, Italy); and hydrochloric and nitric acids (Riedel de Haen) were of analytical reagent grade. Solutions of 1 M nitric acid, 0.11 M acetic acid, 0.5 M hydroxylammonium chloride (pH 2, with 1 M HNO_3), 8.8 M hydrogen peroxide (pH 2, with 1 M HNO_3), and 1 ammonium acetate (pH 2, with 1 M HNO_3) were prepared in distilled water.

Apparatus

A Nüve (Ankara, Turkey) Model ST 402 shaker, a Nüve Model NF 800 centrifuge, and a Hanna (Padova, Italy) Model HI 8314 pH meter were used throughout the analyses. The determination of the metals in the dust samples were performed with a PerkinElmer (Norwalk, CT) Model 3110 flame atomic absorption spectrometer. The air/acetylene flame was used to atomize the metal atoms. All instrumental settings were those recommended in the manufacturer's manual. The wavelengths (nm) used for the determination of the analytes were as follows: Cd 228.8, Cu 324.8, Fe 248.3, and Mn 279.6.

Sampling

A total of nine dust samples were collected from the air filter of different vehicles in August 2006 and stored in closed polyethylene bags. Samples were homogenized using an agate homogenizer (Ankara, Turkey), passed through a 200 mesh sieve, oven-dried at 105 C for 2 h, and stored in a glass container until analysis.

Modified BCR Sequential Extraction Procedure

In order to assess the binding forms of heavy metals in air filter dust samples, the sequential extraction scheme was applied to all samples. The modified BCR extraction procedure can be found elsewhere (20, 24–29). A detailed flow diagram of the sequential extraction procedure is given in Figure 1. The details of the analysis procedure used are as follows:

(**a**) *Fraction 1 (acid-soluble and bound-to-carbonate phase).*—For each dust sample, three replicates (0.5 g) were introduced into a 50 mL PTFE centrifuge tube. A 20 mL portion of 0.11 M CH_3COOH was added to the tube containing the sample, and the tube was shaken for 16 h at

Table 1. BCR sequential extraction partitioning of Cu in dust samples

Sample No.	Acid-soluble[a]	Reducible[a]	Oxidizable[a]	Residual[a]	Sum[b]
1	2.95 ± 0.01	1.08 ± 0.004	6.36 ± 0.24	7.85 ± 0.34	18.2 ± 0.4
2	11.0 ± 0.4	5.50 ± 0.06	21.2 ± 0.5	17.9 ± 0.7	55.6 ± 0.9
3	4.47 ± 0.06	1.45 ± 0.02	10.3 ± 0.8	10.3 ± 0.3	26.6 ± 0.9
4	15.1 ± 0.5	3.61 ± 0.12	12.8 ± 0.3	11.0 ± 0.3	42.5 ± 0.7
5	0.48 ± 0.01	2.52 ± 0.12	3.73 ± 0.35	9.71 ± 0.17	16.4 ± 0.4
6	8.44 ± 0.84	3.31 ± 0.03	10.5 ± 0.1	14.7 ± 1.1	37.0 ± 1.4
7	3.73 ± 0.18	1.28 ± 0.09	9.96 ± 0.51	15.1 ± 0.7	30.1 ± 0.9
8	10.8 ± 0.5	8.93 ± 0.45	15.8 ± 1.4	7.24 ± 0.12	42.7 ± 1.5
9	3.84 ± 0.07	7.91 ± 0.47	12.2 ± 0.3	8.79 ± 0.51	32.7 ± 0.8
Mean value	6.75 (20.13)[c]	3.95 (11.8)	11.4 (34.1)	11.4 (34.0)	33.5
Dust sample (30)	5.82	2.40	13.5	15.1	36.9

[a] Mean, g/g, ± standard deviation (SD).
[b] Total concentration of the four fractions ± SD.
[c] The values given in parentheses are percentage ratio.

room temperature. The extract was subsequently separated from the solid phase by centrifugation at 3000 rpm for 20 min. The supernatant liquid was decanted into a 50 mL beaker and covered by a watchglass. The extract was analyzed immediately or stored at 4 C. The residue was shaken in 10 mL of distilled water for 15 min and then centrifuged for the same amount of time. The second supernatant liquid was discharged without any loss of the solid residue and treated as in Step 2.

(b) *Fraction 2 (reducing conditions).*—A 20 mL portion of hydroxylammonium chloride solution (0.5 M) adjusted to pH 2 with nitric acid was added to the solid residue remaining

from the first extraction step. After shaking the extract for 16 h at room temperature, it was centrifuged for 20 min and then decanted carefully into a beaker. The residue was washed with water, shaken, and centrifuged in preparation for the third step.

(c) *Fraction 3 (oxidizing conditions).*—A 5 mL portion of hydrogen peroxide (8.8 M) was carefully added to the solid residue in a centrifuge tube. After closing the tube with a stopper, it was occasionally shaken by hand at room temperature for 1 h. It was placed in a sand bath to heat at 85 C for 1 h. The solution was evaporated to near dryness, and, after cooling, another 5 mL of hydrogen peroxide

Table 2. BCR sequential extraction partitioning of Fe in dust samples

Sample No.	Acid-soluble[a]	Reducible[a]	Oxidizable[a]	Residual[a]	Sum[b]
1	29.2 ± 2.0	156 ± 16	378 ± 18	537 ± 20	1101 ± 31
2	91.7 ± 2.1	152 ± 5	320 ± 26	1219 ± 44	1783 ± 52
3	11.9 ± 0.9	94.6 ± 2.9	631 ± 41	1193 ± 7	1930 ± 42
4	17.8 ± 1.3	120 ± 4	598 ± 10	1063 ± 43	1799 ± 45
5	44.3 ± 1.0	53.5 ± 1.2	244 ± 6	1100 ± 5	1442 ± 7
6	35.7 ± 1.5	160 ± 6	344 ± 20	1078 ± 45	1618 ± 49
7	46.7 ± 3.7	76.5 ± 4.2	298 ± 24	1073 ± 45	1495 ± 51
8	39.6 ± 0.6	250 ± 3	525 ± 33	871 ± 14	1685 ± 36
9	16.8 ± 0.8	286 ± 19	526 ± 12	943 ± 26	1772 ± 34
Mean value	37.1 (2.28)[c]	150 (9.22)	430 (26.4)	1008 (62.1)	1625
Soil sample (25)	0.2–62	2380–8580	630–4660	9400–152600	—
Sediment sample (10)	19	271	928	2508	3726

[a] Mean, g/g, ± SD.
[b] Total concentration of the four fractions ± SD.
[c] The values given in parentheses are percentage ratio.

Table 3.   BCR sequential extraction partitioning of Mn in dust samples

Sample No.	Acid-soluble[a]	Reducible[a]	Oxidizable[a]	Residual[a]	Sum[b]
1	94.2 ± 5.1	45.8 ± 2.1	29.1 ± 0.4	30.5 ± 0.4	200 ± 6
2	105 ± 3	36.5 ± 1.3	17.5 ± 0.8	37.7 ± 0.8	197 ± 4
3	86.0 ± 3.9	24.3 ± 1.0	22.9 ± 0.3	312.0 ± 0.5	165 ± 4
4	67.4 ± 0.6	19.0 ± 0.3	19.7 ± 0.4	22.8 ± 0.1	129 ± 1
5	71.3 ± 1.8	62.7 ± 2.3	13.5 ± 0.3	ND[c]	NC[d]
6	99.0 ± 4.3	29.7 ± 2.6	12.8 ± 0.6	ND	NC
7	94.9 ± 1.5	28.2 ± 1.2	14.6 ± 0.6	ND	NC
8	119 ± 5	28.3 ± 0.4	21.8 ± 0.4	28.9 ± 0.7	198 ± 5
9	100 ± 2	31.6 ± 0.3	16.7 ± 0.5	40.7 ± 1.8	189 ± 3
Mean value	95.3 (53.1)[e]	30.9 (17.2)	21.3 (11.9)	32.1 (17.9)	179
Dust sample (3)	550	127	86.7	652	1416
Dust sample (30)	71.0	66.6	35.7	64.0	237

[a] Mean, g/g, ± SD.

[b] Total concentration of the four fractions ± SD.

[c] ND = Not determined.

[d] NC = Not calculated.

[e] The values given in parentheses are percentage ratio.

solution was added to the residue. The tube was heated at 85 C for 1 h and again evaporated to near dryness. Then, 25 mL of ammonium acetate (1 M) adjusted to pH 2 with nitric acid was added to the residue. The extraction process was carried out as described in the first and second steps, and the extract was then poured into a beaker. After washing with deionized water, the solid residue was digested with aqua regia (Step 4).

(**d**) *Fraction 4 (remaining residue).*—In this step, 5 mL of doubly distilled water was added to the remaining residue, and then aqua regia solution volumes of 15 and 10 mL were introduced to the same residue in turn. After each addition, the solution was evaporated to near dryness. The residue was dissolved in 0.5 M HNO_3, filtered with a blue band filter paper (Macherey-Nagel, Düren, Germany), and diluted with deionized water to 5 mL. The resulting solution was then analyzed by FAAS.

Results and Discussion

The sequential extraction results for Cd, Cu, Fe, and Mn in air filter dust samples are shown in Tables 1–4, reported as mean value ± standard deviation for three replicate determinations. The precision obtained for the four individual fractions of the modified BCR sequential extraction procedure was less than 10% for all elements. This excellent precision may be attributed to the fine grinding and good homogeneity of the samples during preparation of the dust, and careful handling and analysis in the subsequent steps.

The results obtained after applying the sequential extraction scheme indicate that Cu was most abundant metal in the organic and residual fractions of the dust matrix. Fe was found mainly in the residual fraction, and the major amount of Mn and Cd were present mainly in the acid-soluble and bound-to-carbonate fraction.

The chemical association of copper within the air filter dusts was dominated by the residual fraction (43.0, 59.1, 39.8, and 50.3%) for samples numbered 1, 5, 6, and 7, respectively, and by the oxidizable fraction (38.2, 38.9, 30.1, 36.9, and 37.3%) for samples numbered 2, 3, 4, 8, and 9, respectively. Although the proportions of Cu present in different fractions varied considerably, its association in the acid soluble and bound to carbonate fraction (Step 1) and Fe-Mn oxides fraction (Step 2) was dominated by the bound to carbonate fraction (12.4–35.5%) in six of nine samples. The percentages of copper in reducible fractions in dust samples were in the range of 4.2–24.2%, and concentrations were in the range of 16.4–55.6 g/g. The highest copper value was found in Sample 2. Copper was mainly bound to organic matter and sulfides in most of the dust samples, where the highest percentage was found in the oxidizable fraction. The chalcopfilic element Cu is mainly present in the sulfide form in nature. It has been shown in other studies that an increase in the solubility of copper is due to its oxidation states (8–10). This explains the high percentage of Cu in Step 3. The results agree with others studies in which a large proportion of Cu in various samples was associated with the organic fraction (7, 10, 23, 30, 31).

Fe in all samples was found mainly in association with the residual fraction of the dust matrix (48.8–76.3% of total Fe). Iron concentrations were in the range of 1100–1930 g/g in the dust samples. Iron in the nonresidual fractions of the air filter dusts showed in order of association: oxidizable (16.9–34.4%) > reducible (3.7–16.1%) > acid-soluble and

Table 4.   BCR sequential extraction partitioning of Cd in dust samples

Sample No.	Acid-soluble[a]	Reducible[a]	Oxidizable[a]	Residual[a]	Sum[b]
1	2.26 ± 0.01	0.84 ± 0.003	0.61 ± 0.002	0.21 ± 0.001	3.92 ± 0.01
2	2.79 ± 0.15	1.00 ± 0.04	ND[c]	0.19 ± 0.01	NC[d]
3	1.65 ± 0.02	0.51 ± 0.01	ND	0.20 ± 0.003	NC
4	4.11 ± 0.23	0.49 ± 0.02	ND	0.18 ± 0.01	NC
5	5.47 ± 0.23	6.60 ± 0.24	5.75 ± 0.13	2.45 ± 0.19	20.3 ± 0.4
6	6.46 ± 0.28	4.07 ± 0.17	5.43 ± 0.07	2.22 ± 0.13	18.2 ± 0.4
7	6.37 ± 0.29	4.64 ± 0.18	6.46 ± 0.16	2.48 ± 0.03	20.0 ± 0.4
Mean value	5.14 (33.0)[e]	4.04 (25.9)	4.56 (29.3)	1.84 (11.8)	15.6
Dust sample (3)	3.69	2.36	<0.5	3.26	—
Dust sample (30)	1.40	0.72	0.23	0.17	2.53
Soil sample (29)	114	81.2	18.7	3.81	218

[a] Mean ± g/g, ± SD.

[b] Total concentration of the four fractions ± SD.

[c] ND = Not determined.

[d] NC = Not calculated.

[e] The values given in parentheses are percentage ratio.

bound-to-carbonate fraction (0.62–5.14%). The proportion of Fe in the acid-soluble fractions was fairly low. In this case, the chemical forms of the Fe probably consisted of sulfides that bind to organic substances, and the species soluble in aqua regia. Tüzen (10) used the four-step BCR sequential extraction procedure for sediment samples. He reported that the highest concentration value (67%) for iron was observed in residual fraction. Similar results were found in this study. High percentages of Fe in the residual fraction have also been reported for urban soil samples by Davidson et al. (12) and Sutherland and Tack (25) and for lake sediment samples by Tokalioğlu et al. (31; Table 2).

The Mn in the dust samples is strongly associated with the acid-soluble and bound-to-carbonate fraction (47.2–60.1%). Mn partitioned almost equally between the reducible and residual fractions, with percentages in the range of 14.3–22.9% (average 17.20%) and 14.6–21.5% (average 17.9%), respectively. The Mn percentage of the oxidizable fraction averaged 11.9%. The Mn concentrations were in the range of 129–200 g/g in air filter dust samples (Table 3), and these values were lower than those of urban soils of Sevilla, Torino, and Glasgow reported by Madrid et al. (32); in urban dust samples of two Prague tunnels reported by Sysalova and Szakova (3); and in urban soil samples from five European cities reported by Davidson et al. (12).

The mean Cd levels in the first three fractions were 2.3–6.5, 0.84–6.6, and 0.61–6.5 g/g, respectively. These values were higher than those in the residual fraction. Cd was identified as potentially the most bioavailable element, since it had the highest percentage bound to the acid-soluble and bound-to-carbonate fraction, accounting for approximately 33% of total Cd. The results agreed with the other studies, in which a large proportion of Cd in a simulated air filter sample was associated with

Fraction 1 (30, 33). In air filter dusts, the first three fractions contained more than 88% of the total Cd.

Comparing the metal concentrations in dust, soil, and sediment samples from around the world (Tables 1–4), the results obtained from each extraction step of sequential extraction schemes seem comparable with each other in most cases (3, 10, 25, 29, 30). In spite of some differences for different extraction steps, there is a good agreement, in general, between this work and other similar studies reported in the literature.

The average fractionation pattern of the metals in the air filter dust samples is shown in Figure 2. The concentrations of the metals as relative abundance in mobile phases of the samples (based on the first three fractions) were in the following order: Cd (88.2%) > Mn (82.1%) > Cu (66.0%) > Fe (37.9%). When each of the four steps was examined separately, the results showed that the distributions of metals were somewhat different for each fraction. Among
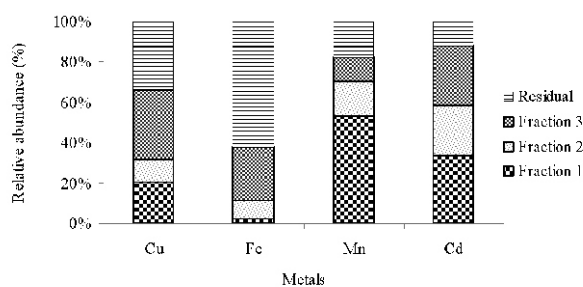

Figure 2.   Relative abundance in each fraction of Cu, Fe, Mn, and Cd in the air filter dust samples.

Table 5.   Levels of investigated metals in standard reference materials (BCR 141 R Calcareous Loam soil and CRM025-050 soil) found after application of the sequential extraction procedure

Element	Fraction	Certified value (BCR 141 R), g/g	Found value (BCR 141 R)[a]	Certified value (CRM025-050), g/g	Found value (CRM025-050)[a]
Cadmium	Fraction 1	—	7.27 ± 0.07	—	302.09 ± 5.90
	Fraction 2	—	4.89 ± 0.42	—	35.20 ± 0.94
	Fraction 3	—	ND[b]	—	0.79 ± 0.01
	Residual	—	2.75 ± 0.03	—	2.68 ± 0.04
	Sum	14.0	14.91 ± 0.43[c]	369	340.76 ± 5.97[c]
Manganese	Fraction 1	—	335 ± 7	—	100 ± 2
	Fraction 2	—	237 ± 4	—	79 ± 3
	Fraction 3	—	34 ± 1	—	ND
	Residual	—	83 ± 3	—	30 ± 2
	Sum	653	689 ± 9[c]	173	209 ± 4[c]

[a] Mean, g/g, ± SD.

[b] ND = Not determined.

[c] Total concentration of the four fractions ± SD.

all determined metals, Mn was found to be the dominant element in air filter dust, followed by Cd, Cu, and Fe, at Step 1. The extracted percent of Cd was higher than other metals in dusts at Step 2. The distributions of Cu, Cd, Fe, and Mn at Step 3 were found to be 34.1, 29.3, 26.4, and 11.9%, respectively. The highest amount of extracted metal was found to be Fe (62.1%), followed by Cu, Mn, and Cd in the residual fraction (Tables 1–4).

When the extractability order was studied (sum of Fractions 1–3), it seemed that the most mobile elements were Mn, Cd, and Cu. The mobility of Mn, Cd, and Cu indicates that the metals originated from anthropogenic (man-made) sources. The most nonmobile metal was Fe (about 62%) in the residual fraction. The high contents in the residual fraction, especially for Fe, showed that these metals are strongly bound to minerals and resistant components of the solid matrix. Many factors, including pH, organic content, presence of sulfides, etc., significantly affect the distribution and redistribution of trace metals in the environment (34, 35).

Validation of the analytical results was performed by analysis of the CRM025-050 soil and BCR 141 R Calcareous Loam soil certified reference materials (Table 5). The amounts found were in agreement with the certified values for Cd and Mn ions at the 95% confidence level. The RSD values were 10% for the elements investigated.

Conclusions

If the concentration levels of the most common matrix constituents of the reference standard materials analyzed and the accuracy of the presented methods are considered together, it can be concluded that the proposed method is free from interferences from the various constituents. The proposed BCR method provided easy, rapid, reliable, and inexpensive determination of trace metals in the dust samples. Cu and Fe were found mainly in the acid-soluble residue and bound to organic matter/sulfide fractions. The low percentage of Fe in the acid-soluble fraction suggests weak bioavailability of the metal in the environment. Cd and Mn were mobile elements and, therefore, probably bioavailable in this environment. It may be concluded that the bioavailability of any metal is related to its chemical forms in the sediment structure rather than its total concentration.

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