Fractionation of metals in street sediment samples by using the BCR sequential extraction procedure and multivariate statistical elucidation of the data

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Abstract

The concentrations of metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in street sediment samples were determined by flame atomic absorption spectrometry (FAAS) using the modified BCR (the European Community Bureau of Reference) sequential extraction procedure. According to the BCR protocol for extracting the metals from the relevant target phases, 1.0 g of specimen of the sample was treated with 0.11 M acetic acid (exchangeable and bound to carbonates), 0.5 M hydroxylamine hydrochloride (bound to iron- and manganese-oxides), and 8.8 M hydrogen peroxide plus 1 M ammonium acetate (bound to sulphides and organics), sequentially. The residue was treated with aqua regia solution for recovery studies, although this step is not part of the BCR procedure. The mobility sequence based on the sum of the BCR sequential extraction stages was: Cd $\approx$ Zn ($\sim$90%) > Pb ($\sim$84%) > Cu ($\sim$75%) > Mn ($\sim$70%) > Co ($\sim$57%) > Ni ($\sim$43%) > Cr ($\sim$40%) > Fe ($\sim$17%). Enrichment factors as the criteria for examining the impact of the anthropogenic emission sources of heavy metals were calculated, and it was observed that the highest enriched elements were Cd, Pb, and Zn in the dust samples, average 190, 111, and 20, respectively. Correlation analysis (CA) and principal component analysis (PCA) were applied to the data matrix to evaluate the analytical results and to identify the possible pollution sources of metals. PCA revealed that the sampling area was mainly influenced from three pollution sources, namely; traffic, industrial, and natural sources. The results show that chemical sequential extraction is a precious operational tool. Validation of the analytical results was checked by both recovery studies and analysis of the standard reference material (NIST SRM 2711 Montana Soil).
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1. Introduction

Sequential extraction procedures are commonly applied to assess sediment and soil-associated metals in environmental studies. Valuable information is obtained about the mobility and bioavailability of metals to living organisms, using sequential procedures. This information is not available from a total digestion procedure, which can easily provide a general perspective on metal contamination in the environment. Over the last two decades, a number of studies were conducted to determine the metals at different oxidation states, chemical speciation, and in different physicochemical forms, fractionation or partitioning, in environmental matrices.

To assess the behavior of metals present in soils and sediments, various sequential extraction procedures have been applied [1–8]. However, results acquired by using different sequential extraction methods were not comparable. This lead the Community Bureau of Reference (now called the Standards, Measurements and Testing Programme, SM&T) to develop a standardized/harmonized three-step sequential extraction protocol for metals in soil and sediment samples [3–5,9–14]. The BCR protocol fractionates the metals into target phases; namely, exchangeable and bound to carbonates, reducible (bound to Fe- and Mn-oxides), and oxidizable (bound to organic matter and sulphides). The residue contains the residual metals bound to the mineral matrix and they are only soluble in the mixtures of strong acids, i.e., aqua regia (pseudototal metal), $HNO_3 + HClO_4 + HF$ (total metal), etc.

Various analytical techniques have been used to quantify metals following a sequential extraction. For example, flame atomic absorption spectrometry (FAAS) [2–6], electrothermal atomic absorption spectrometry (ETAAS) [12,15], inductively coupled plasma atomic emission spectrometry (ICP-AES) [13,14,16], and inductively coupled plasma mass spectrometry (ICP-MS) [17–19].

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One of the major sources of outdoor air pollutants is the street sediment [20]. Metals may come from many different sources in urbanized areas, including vehicle emissions, industrial discharges and other activities. Metals can accumulate in topsoil from atmospheric deposition by sedimentation, impaction and interception, and therefore, atmospheric pollution is one of the major sources of heavy metal contamination in urban areas. For this reason, topsoil and street-deposited sediments in urban areas are sinks for potentially toxic metals [16].

A few studies have determined metals in street sediment samples using single weak acid leach procedures (e.g., 0.5 M HCl, 2 M HNO$_3$, etc.) [21]. Sequential extraction procedures applied to solid environmental matrices, have typically used the Tessier et al. procedure for street dusts [16,22–24], river sediment [2], soil and/or roadside soils [14,16,23,25–27], or more recently the original BCR for lake, river and/or road deposited sediments [2–7,9,13,28,29], soils [12,13,28–31] and modified BCR protocols for sediment and soil reference materials [32] and, later, to a variety of matrices including road deposited sediments [23,33–35], soils [23,36,37], reference materials [38–41], and sediments [37]. Because of the problems such as poor reproducibility, lack of phase sensitivity, redistribution of analytes between phases, and variability between operators for the original BCR sequential extraction protocol, especially in the second step (reducible phase), it has been optimized by Rauret et al. [32] to improve the overall reproducibility. Sutherland examined the relationship between the sum of three steps of the modified BCR protocol and those liberated from a single dilute HCl (0.5 M) leach for soil and road deposited sediment samples and found good correlations with r^2 values $\geq 92\%$ for the elements Al, Co, Cu, Mn, Pb, and Zn [34]. Kubová et al. [36] applied the modified BCR procedure to naturally acidified soils and they found that the most extractable Pb occurred in the reducible phase. Li et al. [23] reported the elevated concentrations of Cd, Cu, Pb, and Zn in urban soils and street dusts in Hong Kong, mainly originated from vehicle exhaust emissions and component wearing. Street sediments often include high concentrations of toxic metals and concerns have been expressed about the consequences for both environmental quality and human health [22].

The main objectives of the present study are: (a) to determine the metal concentrations (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) using the revised BCR sequential extraction protocol in street dusts collected from the streets of Kayseri (Turkey) and hence to ascertain their mobilities; (b) to define their natural and/or anthropogenic origin, e.g., source apportionment by using principal component analysis (PCA) and correlation analysis (CA). For this purpose, 33 street sediment samples were collected and analysed.

2. Material and methods

2.1. Apparatus and chemicals

A Perkin-Elmer 3110 model FAAS, a Clifton model shaker, a centrifuge of MLTW 54 model and a Jenco 672 model pH-meter were used throughout the analyses. The measurement of metals was carried out using an air/acetylene flame. The operating parameters for the studied metals were set as recommended in the operation manual of the manufacturer. In the determination of analyte elements, the following wavelengths (nm) were used: Cd 228.8, Co 232.0, Cr 359.3, Cu 324.8, Fe 248.3, Mn 279.6, Ni 232.0, Pb 283.3, and Zn 213.8.

All chemicals were of analytical reagent grade unless otherwise indicated. Double-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 metals or the corresponding pure metals (Merck, Darmstadt, Germany). The working solutions of metals were used by diluting these stock solutions prior to use. Acetic acid, CH$_3$COOH; hydroxylammonium chloride, H$_2$NOH·HCl; hydrogen peroxide, H$_2$O$_2$; ammonium acetate, CH$_3$COONH$_4$; HCl and HNO$_3$ acids were of reagent grade (Merck, Darmstadt, Germany). All the glassware and plastic vessels were treated by dilute (1:1) HNO$_3$ acid for 24 h and then rinsed with distilled water before the use.

2.2. Collection and preparation of samples

The street sediment samples ($n = 33$) were collected by sweeping using a plastic sweep from the main streets of Kay-

Table 1
Results in percentage for street sediment samples using modified BCR sequential extraction procedure on a grain size basis ($n = 3$)

Particle size (μm)	Step	Metals								
		Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
74–149	F1	28.4	20.5	12.7	3.5	0.5	18.2	4.8	4.7	23.2
	F2	26.2	17.4	10.5	17.3	7.8	38.1	13.7	22.2	35.7
	F3	32.2	19.1	4.7	76.3	2.2	10.4	21.7	46.0	17.8
	R	13.2	42.9	72.1	2.9	89.6	33.5	59.8	27.0	23.4
53–74	F1	29.7	18.0	15.2	4.9	0.5	17.5	3.5	5.2	23.5
	F2	26.6	18.8	9.3	11.5	5.8	38.8	12.8	20.7	38.0
	F3	31.0	16.3	1.4	80.0	2.0	11.5	18.2	45.8	15.9
	R	12.7	47.0	74.2	3.6	91.7	32.2	65.6	28.4	22.6
<53	F1	32.3	25.5	16.9	6.1	0.2	22.7	6.3	6.0	24.7
	F2	28.0	16.3	8.6	14.2	7.5	41.5	12.5	28.4	42.5
	F3	26.2	14.1	6.6	76.8	3.2	10.0	21.2	41.4	12.4
	R	13.5	44.1	67.9	3.0	89.0	25.8	60.0	24.2	20.4

Table 2
The modified BCR sequential extraction scheme used for operational speciation of metals

Step	Soil phases	Extractant	Shaking time and temperature
F1	Water and acid soluble, and exchangeable	40 mL of 0.11 M CH_3COOH	16 h at room temperature
F2	Reducible	40 mL of 0.5 M $HONH_2 \cdot HCl$ (pH 2)	16 h at room temperature
F3	Oxidisable	10 mL of 8.8 M H_2O_2 (pH 2) then 10 mL of 8.8 M H_2O_2 (pH 2) cool, add 50 mL of 1 M NH_4OAc (pH 2)	1 h at room temperature and 1 h at 85 °C 1 h at 85 °C 16 h at room temperature
R	Residual[a]	15 mL and then 10 mL of aqua regia	Heating on hot plate to dryness

[a] Digestion of the residual material is not a step of the BCR protocol.

seri (Turkey) in November 2000, at intervals of $\sim$250 m, and stored in the mouth-closed polyethylene bags. All samples were sieved through 53, 74, and 149 μm sieves, for investigating the effect of particle size on the fractionation of the metals using the BCR sequential extraction protocol. Grain size fractions were oven-dried at 105 °C for 2 h. The results are given in Table 1. As can be seen from Table 1, it was not observed any meaningful difference between the metal concentrations obtained by using the modified BCR procedure based on the particle size basis. Because of this, all the experiments were then performed using the samples having grain size fraction <74 μm.

2.3. The modified BCR sequential extraction procedure

The BCR sequential extraction procedure was applied, in triplicate, to 1.00 g of dried specimen (<74 μm) of the samples, using the reagents and experimental conditions given in Table 2 as a brief summary. Details of the modified BCR extraction procedure can be found elsewhere [32–34,37,38,41].

The only difference of the BCR procedure applied in this study from the standard protocol was that the extraction solutions obtained from each step of the BCR scheme were firstly evaporated to incipient dryness and then completed to 5 mL with 2 M HNO_3.

In addition, in order to check the validation of the method a certified soil reference material, e.g., NIST SRM 2711 Montana soil, was analysed by using the same procedure.

2.4. Detection limits

The calculation of the detection limits for each step and also residual phase of the BCR sequential extraction method are based on the usual definition as the concentration of the analyte yielding a net signal equivalent to three times the standard deviation of the background signal ($3s/b$, $n = 24$), where s is the standard deviation of the blank and b is the slope of the calibration graph. Since it is difficult to obtain a blank soil, the signal obtained using the reagents for each extraction stage was treated as the blank. Correlation coefficients (r) of the calibration curves were better than 0.998 for all elements studied.

2.5. Quality control of the analytical data

A standard reference material (SRM 2711 Montana soil from NIST) was used to validate the BCR sequential extraction pro-

cedure and for quality control of the analytical data. To further validate the method, we quantified the recovery of analyte spikes to the extracts obtained from the BCR procedure. In addition, blank determinations were performed in triplicate as well as sequential extractions of samples throughout all the experiments.

2.6. Enrichment factors (EF)

To determine the relative degree of metal contamination, comparisons are made to background concentrations in the Earth's crust [25,31,42,43]. Enrichment factors are commonly determined to characterize the magnitude of metal contamination in environmental samples [25,28,44]. The enrichment factors (EF) were calculated with respect to Fe according to the following equation:

$$EF = \frac{(C_x/C_{Fe})_{sediment}}{(C_x/C_{Fe})_{Earth's\ crust}}$$

where $(C_x/C_{Fe})_{sediment}$ is the ratio of concentration of the element being determined (C_x) to that of Fe (C_{Fe}) in the sediment sample and $(C_x/C_{Fe})_{Earth's\ crust}$ is the ratio in the reference Earth's crust [43]. Generally, EF values less than 5.0 are not considered significant, because such small enrichments may arise from differences in the composition of local soil material and reference soil used in EF calculations [43,44]. However, there is no accepted pollution ranking system or categorization of degree of pollution on the enrichment ratio and/or factor methodology, Sutherland firstly proposed a five-category system [45]. According to this approach: EF < 2 states deficiency to minimal enrichment, EF = 2–5 moderate enrichment, EF = 5–20 significant enrichment, EF = 20–40 very high enrichment, and EF > 40 extremely high enrichment [45,46]. In addition, Reimann and de Caritat states that EFs should be used in a much more careful manner and they cannot provide a reliable indication of the degree of human interference with the global environment [47].

2.7. Statistical analysis

To evaluate the analytical data, correlation analysis (CA) and principal component analysis (PCA) were used. The Pearson correlation coefficient, r, measures the strength of a linear relationship between two quantitative variables. Principal components analyses is often used in exploratory data analysis to: (i) study the correlations among a large number of interrelated

quantitative variables by grouping the variables into a few factors; after grouping, the variables within each factor are more highly correlated with variables in that factor than with variables in other factors, (ii) interpret each factor according to the meaning of the variables, and (iii) summarize many variables by a few factors [48]. These statistical techniques were widely applied to various environmental solid and/or liquid matrices such as street dust [20], soils [26,27,30,49,50], sediments [15,29], and water [51]. Statistical calculations were performed by using a software package, e.g., SPSS version 10.0.

In this study, PCA was used to elucidate the data with the aim for finding out the latent relationships between variables and/or samples, and for investigating pollutants (variables) sources. The PCA was applied to the data matrix (33 cases × 9 metals) of pseudototal metal concentrations (the sum of F1 + F2 + F3 + R) to ascertain the possible contributing factors towards the metal concentrations and thereby determine which metals have a common origin [22].

3. Results and discussion

3.1. Detection limits

Detection limits of the elements studied in each extraction stage were determined from the standard calibration curves of each element. Detection limits estimated from the standard calibration curves were found in the range of 0.003 (F2)–0.041 (F3) for Cd, 0.017 (F2)–0.050 (R) for Co, 0.21 (F1)–0.56 (F3) for

Cr, 0.010 (F3)–0.021 (R) for Cu, 0.002 (F1)–0.089 (R) for Fe, 0.003 (F1)–0.024 (F3) for Mn, 0.017 (F3)–0.034 (F1) for Ni, 0.68 (F2)–0.82 (R) for Pb, and 0.001 (F3)–0.002 μg/mL (F2) for Zn.

3.2. Validation of the method

To validate the BCR sequential extraction procedure, concentrations of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were determined in the standard reference material (SRM 2711 Montana soil). The results of the fractionation of the certified reference materials by optimized BCR sequential extraction protocol are presented in Table 3, in the form of the mean values and their standard deviations. The total concentrations, the sums of the four sequential extraction steps including the residual, of the metals by the BCR method were in good agreement with the certified values, except for Mn that had somewhat higher recovery value (about 170%), also similar value obtained by Sutherland and Tack (about 179%) [38]. The application of the optimized BCR protocol to the SRM 2711 shows that good interlaboratory comparability was obtained for three steps of the protocol for Cd, Cu, Fe, Pb, Zn, and to some extent for Mn.

To further validate the method, we quantified the recovery of analyte spikes to the extracts obtained from the BCR procedure. The recovery results for the each extraction step are shown in Table 4. As can be seen from Table 4, all recoveries were acceptable, between 92.7 and 100.0%, with precision values less than 6%.

Table 3
Indicative values for the content of various extractable metals (mean ± S.D. in μg g^{-1}) in SRM 2711 Montana soil

Element	Source of data	Fraction 1	Fraction 2	Fraction 3	Residual	Sum of (F1 + F2 + F3 + R)	Certified value	Recovery (%)
Cd	This work (n = 3)	24.9 ± 0.9	10.4 ± 0.6	1.10 ± 0.04	1.92 ± 0.10	38.3 ± 1.1	41.7 ± 0.3	91.9
	Ho and Evans [40]	28.6 ± 1.1	9.3 ± 0.6	2.4 ± 0.9	<1	40.2 ± 0.8		96.5
Cu	This work	3.11 ± 0.11	19.3 ± 1.6	11.9 ± 0.8	64.8 ± 2.7	99.1 ± 3.2	114 ± 2	87.0
	Kubová et al. [36]	5 ± 0.04	38 ± 0.1	10 ± 0.7	58 ± 0.6	111 ± 1		97.4
	Sutherland and Tack [38]	5 ± 0.3	27 ± 0.4	11 ± 0.2	63 ± 0.5	106 ± 0.7		93.0
	Sutherland and Tack [39]	5 ± 0.3	27 ± 0.4	11 ± 0.2	63 ± 0.5	105 ± 1		92.0
	Ho and Evans [40]	6.1 ± 1.6	12.4 ± 10.0	13.8 ± 7.2	90.8 ± 17.4	123 ± 18		108.1
Fe	This work	50.9 ± 1.6	1357 ± 0.4	191 ± 9	24769 ± 182	26368 ± 182	28900 ± 600	91.2
	Kubová et al. [36]	17 ± 1	1617 ± 9	279 ± 10	24845 ± 431	26758 ± 431		92.6
	Sutherland and Tack [38]	19 ± 1	1390 ± 29	298 ± 8	26200 ± 430	27907 ± 431		96.6
Mn	This work	531 ± 8	197 ± 6	30.7 ± 0.2	338 ± 7	1096 ± 13	638 ± 28	172
	Kubová et al. [36]	246 ± 1	87 ± 2	19 ± 1	277 ± 6	629 ± 6		98.6
	Sutherland and Tack [38]	577 ± 3	204 ± 1	43 ± 1	317 ± 7	1141 ± 7.7		178.8
Pb	This work	270 ± 8	788 ± 39	87.8 ± 3.8	54.2 ± 2.0	1200 ± 40	1162 ± 31	103.3
	Kubová et al. [36]	279 ± 1	771 ± 7	70 ± 3	48 ± 0.74	1168 ± 8		100.5
	Sutherland and Tack [38]	280 ± 4	774 ± 7	108 ± 3	51 ± 1	1213 ± 8.7		104.4
	Sutherland and Tack [39]	280 ± 4	774 ± 7	108 ± 3	51 ± 1	1210 ± 6		104.0
	Ho and Evans [40]	302 ± 27	349 ± 32	356 ± 85	97.9 ± 19.7	1100 ± 100		95.0
Zn	This work	40.4 ± 1.0	67.2 ± 2.8	27.4 ± 1.2	172 ± 2	307 ± 4	350.4 ± 4.8	87.5
	Kubová et al. [36]	37 ± 0.2	87 ± 0.6	38 ± 2.2	176 ± 1.5	338 ± 2.7		96.4
	Sutherland and Tack [38]	38 ± 1	78 ± 1	40 ± 0.4	172 ± 2	328 ± 2.5		93.7
	Sutherland and Tack [39]	38 ± 1	78 ± 1	40 ± 0.4	172 ± 2	328 ± 3		94.0
	Ho and Evans [40]	41.8 ± 1.2	62.2 ± 7.1	37.1 ± 13.3	206 ± 33	347 ± 34		99.0

Table 4
The results of recovery (%) and their standard deviations ($n = 3$) for each extraction step of the BCR protocol for the metals interested

Fraction	Recovery (%) values of the determined metals for the each extraction step							
	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
F1	94.6 ± 0.8	96.6 ± 3.3	95.3 ± 8.3	98.0 ± 1.8	93.9 ± 0.2	96.4 ± 0.3	97.0 ± 5.0	94.3 ± 0.1
F2	99.0 ± 1.8	96.7 ± 5.8	100.0 ± 0.0	96.0 ± 3.9	92.7 ± 1.5	97.2 ± 4.8	95.6 ± 3.9	94.7 ± 4.6
F3	93.8 ± 2.1	93.5 ± 0.2	96.7 ± 5.8	96.9 ± 3.1	97.2 ± 4.8	97.1 ± 2.5	100.0 ± 0.0	97.6 ± 0.8
R	98.3 ± 1.6	94.3 ± 2.6	94.5 ± 4.8	97.8 ± 3.9	95.8 ± 0.9	96.6 ± 0.1	95.6 ± 3.9	96.9 ± 1.5
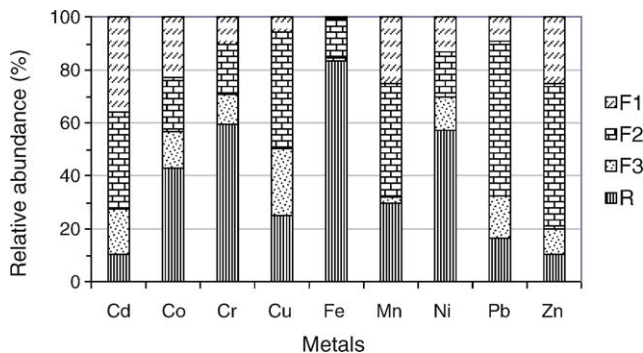
Fig. 1. Distribution of the metals in the four defined solid fractions, according to the mean values of the proportion of each metal in each fraction of the street sediments (<74 μm, $n = 33$).

3.3. Partitioning of metals

The average fractionation pattern of the metals in the street sediment samples, are given in Fig. 1. The concentrations of the metals as relative abundance in mobile phases of the samples (based on the sums of the first three fractions) are in the following order:

- Cd (89.9) > Zn (89.8) > Pb (83.6) > Cu (75.1) > Mn (70.4) > Co (57.1) > Ni (42.9) > Cr (40.8) > Fe (16.7).

The Cd contents, based on the mean values, in the first two fractions, 4.11 and 4.12 μg/g, respectively, were found to be very higher than the third fraction and the residual phase. At stage 1, Cd is the most mobilisable element ($\sim$36 ± 8%) and, therefore, probably the most bioavailable species. When each of the three mobile phases was examined separately, the results showed that the distributions of metals were somewhat different for each fraction, i.e.,

- Cd (36.4) > Zn (25.1) > Mn (25.0) > Co (22.6) > Ni (13.3) > Cr (10.1) > Pb (8.9) > Cu (6.0) > Fe (0.62), for F1.
- Pb (58.3) > Zn (55.1) > Cu (43.6) > Mn (43.1) > Cd (36.5) > Co (20.8) > Cr (19.1) > Ni (16.8) > Fe (15.0), for F2.
- Cu (25.6) > Cd (17.1) > Pb (16.4) > Co (13.7) > Ni (12.8) > Cr (11.6) > Zn (9.6) > Mn (2.4) > Fe (1.1), for F3.

When it is examined these three extractability order (sum of F1 + F2 + F3), it seems that probably the most mobilisable elements are Cd, Zn, Pb, Cu, Mn, and Co. The highest concentrations (%, in average) were observed for Pb ($\sim$58%), Zn ($\sim$55%), Cu ($\sim$44%), and Mn ($\sim$43%) at fraction 2. The results indicate that the metals probably occur in the forms bound to Fe/Mn oxides.

The Fe, Cr and Ni are generally lithogenic, associated with the silicate matrix, and the order for the studied elements are as follows:

- Fe (83.3) > Cr (59.2) > Ni (57.1) > Co (42.9) > Mn (29.6) > Cu (24.9) > Pb (16.4) > Zn (10.2) > Cd (10.1), for R.

The most non-mobilisable metals were Fe ($\sim$83%), Cr ($\sim$59%), and Ni ($\sim$57%) at the residual fraction (R). The high contents in the residual fraction expecially for Fe showed that these metals are strongly bound to minerals and resistant components of the solid matrix.

This behavior of these metals may be related to their occurrences in the silicate matrix structure of the samples but also occur in several common metallic alloys, especially for iron

Table 5
The mean contents and standard deviations of metals in different chemical pools in street sediments ($n = 33$), acquired by the modified BCR sequential extraction protocol (μg/g by dry mass)

Metal	Sequential extraction steps			R (Residual)	Mean total metal levels (F1 + F2 + F3 + R)
	F1 (bound to carbonates)	F2 (reducible)	F3 (oxidisable)		
Cd	4.11 ± 2.21	4.12 ± 2.86	1.93 ± 0.92	1.17 ± 0.44	11.29 ± 4.80
Co	4.44 ± 1.13	4.09 ± 1.40	2.69 ± 0.98	8.44 ± 6.53	19.66 ± 6.41
Cr	2.82 ± 1.14	5.32 ± 3.96	3.24 ± 1.87	16.70 ± 7.96	27.91 ± 12.00
Cu	5.02 ± 2.15	36.7 ± 38.8	21.5 ± 21.9	20.94 ± 8.66	84.2 ± 37.5
Fe	102 ± 70	2488 ± 2500	179 ± 114	13773 ± 2834	16542 ± 3846
Mn	69 ± 32	119 ± 97	6.52 ± 2.76	82 ± 30	276 ± 117
Ni	5.65 ± 0.95	7.12 ± 3.52	5.42 ± 0.93	24.24 ± 6.12	42.42 ± 7.25
Pb	36.8 ± 18.2	242 ± 201	68 ± 61	68 ± 55	415 ± 196
Zn	111 ± 87	244 ± 387	42.4 ± 38.1	45.2 ± 20.3	443 ± 474

because it can exist at high levels changing about from 0.5 to 10% (w/w) in soils and in similar matrices. The concentrations of Cd, Zn, Pb and Cu in the samples are much higher than the typical soil content values. This likely reflects an anthropogenic source, especially from traffic. For example, $\sim 84 \pm 12\%$ of Pb was in the mobilisable fractions, and this is an indicator of lead pollution from the vehicles. Turkey still uses leaded gasoline, in which tetra alkyl lead compounds are added to the gasoline to protect the engine against knocking.

The mean concentrations of the nine metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in the street dusts ($n = 33$) in each extraction stage of the BCR procedure are shown in Table 5. The highest concentrations for Zn (244 µg/g), Pb (242 µg/g), and Mn (119 µg/g) were found in the reducible fraction. These results, for Cd, Mn, Pb, and Zn, may indicate an anthropogenic source. For the other elements, the concentrations found in each extraction stage of the sequential extraction procedure used increase generally from stage 1 toward the residual phase, which shows they were less mobile and likely to be controlled by lithology.

Compared to percent concentrations in street sediments in the world (Table 6), the values of metals obtained from each extraction step of sequential extraction schemes seem comparable with each other in most cases. In spite of some differences being found at different extraction steps, there is good agreement between this work and other similar studies given in literature.

3.4. Enrichment factors

Enrichment factors were calculated for each sample relative to the abundance of the elements in the Earth's crust [51], choosing Fe as the reference element due to the crust-dominated element. The major assumptions underlying this method are that the iron of artificial origin is relatively small compared with iron of natural origin (in the Earth's crust, e.g., 0.5–10% w/w) and that the Earth's crust are a relevant basis for normalization [25]. An enrichment factor of approximately 1 would indicate that the relative concentration of a given metal is identical to which is present in unpolluted street sediment sample. If the EF_c values are greater than 5, they are considered to be contaminated

Table 6
Comparison of Tessier et al. [2] and modified BCR fractionation data for street sediments reported in the literature to those from this study, obtained using the modified BCR protocol

| Element	Source of data/scheme	Fraction 1	Fraction 2	Fraction 3	Residual
Cd	This work/modified BCR	36.4	36.5	17.1	10.4
	Li et al. [23]/Tessier et al.	55.2	27.3	21.5	–
	Banerjee [22]/Tessier et al.	49.5	8.9	2.9	38.8
	Lee [24]/Tessier et al.	24.0	24.9	23.7	28.3
Co	This work	22.6	20.8	13.7	42.9
	Sutherland et al. [33]/modified BCR	8.7	17.4	6.5	67.4
Cr	This work	10.1	19.1	11.6	59.8
	Banerjee [22]/Tessier et al.	2.3	7.5	2.14	88.1
	Lee [24]/Tessier et al.	1.4	24.7	11.1	65.3
Cu	This work	6.0	43.6	25.5	24.9
	Li et al. [23]/Tessier et al.	7.9	11.1	72.4	7.9
	Banerjee [22]/Tessier et al.	4.6	12.1	44.3	39.0
	Lee [24]/Tessier et al.	17.1	22.9	52.0	8.6
	Sutherland et al. [33]/modified BCR	6.4	27.0	25.2	41.7
Fe	This work	0.6	15.0	1.1	83.3
	Sutherland et al. [33]/modified BCR	0.05	6.2	3.8	90.0
Mn	This work	25.0	43.1	2.4	29.7
	Sutherland et al. [33]/modified BCR	19.1	26.1	5.2	49.6
Ni	This work	13.3	16.8	12.8	57.1
	Banerjee [22]/Tessier et al.	11.4	12.3	5.4	70.9
	Lee [24]/Tessier et al.	32.9	20.8	5.8	40.4
	Sutherland et al. [33]/modified BCR	2.6	9.7	9.2	78.5
Pb	This work	8.9	58.3	16.4	16.4
	Li et al. [23]/Tessier et al.	26.5	43.5	13.2	17.6
	Banerjee [22]/Tessier et al.	20.3	28.3	16.2	35.3
	Lee [24]/Tessier et al.	13.7	53.7	16.0	16.0
	Sutherland et al. [33]/modified BCR	3.0	68.4	20.3	8.3
Zn	This work	25.1	55.1	9.6	10.2
	Li et al. [23]/Tessier et al.	64.3	27.5	4.3	2.9
	Banerjee [22]/Tessier et al.	23.5	45.6	11.1	19.7
	Lee [24]/Tessier et al.	52.8	26.4	4.2	4.2
	Sutherland et al. [33]/modified BCR	34.0	37.2	8.1	20.8
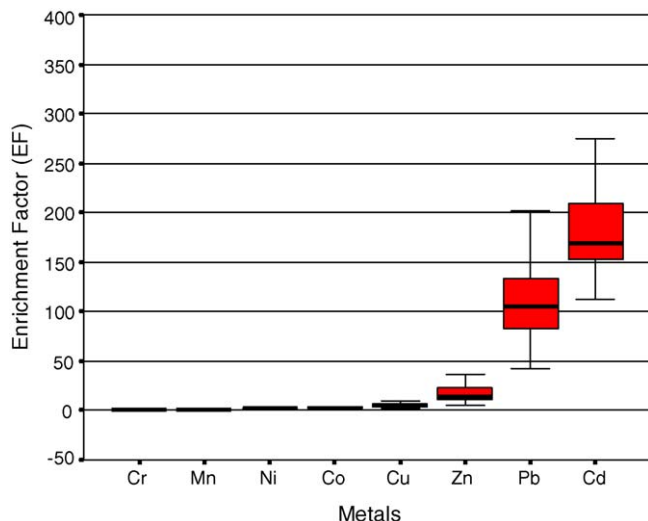
Fig. 2. Average crustal enrichment factor values in the street sediment samples ($n = 33$).

[43,45]. Mean EFs for Cr and Mn, are equal to unity, and values for Ni and Co are <5 (Fig. 2).

Cd, Pb, and Zn levels in the street sediment samples are characterized by very high EF values (average values and standard deviations are approximately 169 ± 69, 111 ± 39 and 20 ± 17 (31.5–380, 42.7–202, and 5.6–87), respectively, reflecting the strong contamination signals. The average EF for Cu was 5.2 ± 2.0. The EFs observed for Ni, Co and Cu may be not con-

sidered although they are an indicator of metal accumulation, because such small enrichments may arise from differences in the composition of local soil material and the reference Earth's crust used in EF$_c$ calculations [43].

The high EF values indicate that the source of accumulation of Cd, Pb, and Zn originates mainly from anthropogenic contributions. Anthropogenic sources of Cd are motor oils, car tyres, and zinc compounds [31]. The important contributors of Pb to street sediments are the parent geological materials from which soils are derived, smelters, coal combustion, and the widespread use of leaded petrol. The elevated contents of Cd and Pb in the street sediments, in average 11.3 ± 4.8 and $415 \pm 196 \, \mu g/g$, respectively, are in good agreement with the high EFs of these two metals.

Comparative results for EFs, which have similar matrices to street sediments, are given in Table 7. In the studies given in Table 7, the EF values are almost higher than 5 for elements Cd, Pb and Zn, only for Ni in Ref. [52] and for Cu in Ref. [18]. According to the ranking system proposed by Sutherland [45], Zn concentrations have significantly enriched and those of Pb and Cd have extremely high enriched in the street sediments investigated in this study.

3.5. Statistical analysis

3.5.1. Correlation analysis

To investigate inter-element relationships in the street sediment samples, correlation coefficients were calculated and the

Table 7
Literature summary of enrichment factors in urban soils and street sediments

Element	Reference/kind of sample						
	This study[a]	[49]/Urban soil	[31]/High-way soil	[25]/Roadside soil	[52]/Conta-minated soil	[18]/Road-way dust	[28]/Car park dust
Cd	190 ± 69	–[b]	57 ± 65	8.8	132 ± 7	4.0–10.0	187 ± 73
Co	2.8 ± 0.9	–	1.1 ± 0.2	–	4.6 ± 0.4	2.1	1.7–2.3
Cr	0.95 ± 0.4	–	1.0 ± 0.2	–	2.7 ± 0.3	7.2–17.8	0.6–0.8
Cu	5.2 ± 2.0	–	0.9 ± 0.1	–	3.3 ± 0.2	13.9–163.8	1.5–2.2
Mn	1.0 ± 0.3	–	1.0 ± 0.1	1.3	8.2 ± 1.0	1.5–2.9	1.0–1.4
Ni	2.0 ± 0.5	–	3.8 ± 1.5	–	31.2 ± 2.2	1.9–7.2	1.4–1.5
Pb	111 ± 39	3–16	6.2 ± 3.5	11.8	63.1 ± 6.4	72.0–100.0	27.5 ± 13.3
Zn	20 ± 17	0.75–3.2	3.5 ± 1.0	16.9	6.6 ± 1.4	16.4–43.94	5.1–6.9

[a] Based on the Earth crust's iron value as reference element (mean $\pm$ S.D., $n = 33$).
[b] Not available.

Table 8
Pearson correlation coefficients for the total metal concentrations based on the sum of the modified BCR sequential extraction fractions including residual phase ($\sum = F1 + F2 + F3 + R$)

	Cu	Fe	Ni	Co	Cd	Cr	Pb	Zn	Mn
Cu	1.000								
Fe	0.473	1.000							
Ni	0.110	0.424	1.000						
Co	0.302	0.261	0.244	1.000					
Cd	0.302	0.525	0.219	0.117	1.000				
Cr	0.069	0.495	0.713	0.408	0.097	1.000			
Pb	0.561	0.601	0.143	0.001	0.562	0.263	1.000		
Zn	0.338	0.521	0.210	0.172	0.983	0.085	0.538	1.000	
Mn	0.302	0.609	0.353	0.216	0.876	0.191	0.380	0.888	1.000

Correlation is significant at the 0.05 probability level ($r = 0.3345$, $n = 33$); 0.01 probability level ($r = 0.4304$, $n = 33$); 0.001 probability level ($r = 0.5330$, $n = 33$).

Table 9
The results of principal component anaysis ($n = 33$)

Component	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	Variance (%)	Cumulative %	Total	Variance (%)	Cumulative %	Total	Variance (%)	Cumulative %
1	4.23	47.01	47.01	4.23	47.01	47.01	3.02	33.55	33.55
2	1.75	19.48	66.49	1.75	19.48	66.49	1.99	22.07	55.62
3	1.10	12.27	78.75	1.10	12.27	78.75	1.88	20.86	76.49
4	0.90	10.00	88.76	0.90	10.00	88.76	1.10	12.27	88.76
5	0.44	4.85	93.61						
6	0.35	3.92	97.53						
7	0.14	1.50	99.04						
8	0.07	0.81	99.84						
9	0.01	0.16	100.00						

Extraction method: principal component analysis. Rotation method: Varimax with Kaiser normalization.

matrix is presented in Table 8. All the metal pairs showed positive relations but some of them were significant at 95% and/or higher confidence level [53]. The pairs of Cd–Mn, Zn–Mn, and Cd–Zn showed very high correlations (≥ 0.876) at 99.9% confidence level. The significant correlations between the three metals viz. Cd, Zn, and Mn, also indicate a common source for these metals. Although Mn is mainly of geochemical origin, it occurs as alloys with Fe. For example, stainless steel contains Fe, Cr, and Ni in varying amounts. Mn is the most frequent additive for steel [54]. Piña et al. showed close relations among Mn, Pb, and Cd varying from 0.54 to 0.74 in airborne particles [55]. On the other hand, the pairs of Cu–Pb, Fe–Pb, Fe–Mn, Ni–Cr, Cd–Pb, and Zn–Pb show good relations to each other at the same confidence level. While Fe shows moderate correlations with Cu, Cd, Cr, and Zn elements at 99% confidence level, the pairs of Cu–Zn, Ni–Fe, Ni–Mn, Co–Cr, and, Pb–Mn show weak correlations at 95% confidence level. Co and Pb no correlated to each other. In the case of correlations between the other metal pairs there were no significant linear associations, but only very weak correlations observed varying from 0.069 to 0.302.

3.5.2. Multi-element data elucidation: principal component analysis

By extracting the eigenvalues and eigenvectors from the correlation matrix, the number of significant factors, the percent of variance explained by each of them was calculated by using the

software package SPSS 10.0 and are given in Table 9. The results show that three eigenvalues >1 and explain $\approx 76\%$ of the total variance, the fourth eigenvalue explains about 10% of the variance, which is a significant contribution towards the explanation of cumulative variance. For this reason, the first four eigenvalues, which explain $\approx 89\%$ of the total variance, were selected for further analysis, and eigenvalues <0.9 were discarded for establishing a probable number of contributing source factors.

The four factor loadings extracted after performing the varimax rotation and communalities (h^2, square of loading) are given in Table 10. The first factor explains $\sim 34\%$ of the total variance and loads heavily on Zn, Cd, and Mn, and weak loadings on Pb and Fe. This factor sources may be attributed to traffic, especially Cd, and Zn, and weakly to soil (Mn). Factor 2 is loaded primarily by Cr and Ni, and also moderately Fe, which may be relevant to anthropogenic activities, mainly traffic (corrosion of steel parts of vehicles, etc.). Factor 3 is loaded primarily by Pb and Cu, and also Fe, and sources for this factor may be explained by contributions mainly from traffic, especially cars which consume the leaded gasoline, and also soil for the Fe contribution. In the first three principal components, Fe has increasing loading values from PC1 to PC3, that is, 0.427, 0.490, and 0.573, respectively. This explains the contribution of soil in the three factors, i.e., approximately 18, 24, and 33% contributions for each PC in the sequence above. The fourth factor is correlated very strongly with Co which has a high loading value, i.e., 0.941.

Table 10
Varimax rotated PC loadings and communalities for the street sediment samples ($n = 33$, only those larger than 0.1 are shown)

Metals	Principal component				Communalities (h^2)
	1	2	3	4	
Zn	0.95		0.24		0.97
Cd	0.95		0.236		0.97
Mn	0.92	0.20	0.13	0.12	0.92
Cr		0.92	0.13	0.18	0.89
Ni	0.18	0.88			0.82
Cu	0.13		0.85	0.33	0.85
Pb	0.34	0.17	0.82	−0.22	0.87
Fe	0.43	0.49	0.57		0.76
Co		0.23		0.94	0.95
Explained variance	33.55%	22.07%	20.86%	12.27%	88.77%

Extraction method: principal component analysis. Rotation method: Varimax with Kaiser normalization.
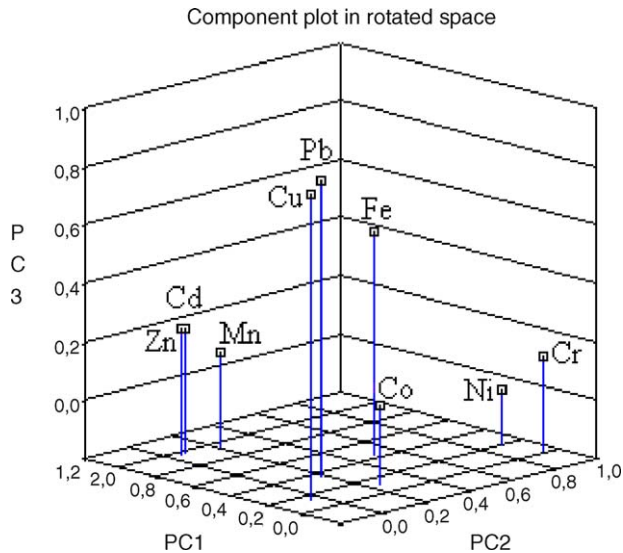
Fig. 3. PCA results in the three-dimensional space: plot of loadings of the three first principal components acquired in the analysis.

It is originated from the Earth's crust, because it is one of the elements not having enrichment in the street sediments. Also, the relations among the metals based on the first three principal components are illustrated in Fig. 3 in a three-dimensional space. There are high correlations among the elements Zn, Cd, and Mn on the PC1, between the Cr and Ni on the PC2, and among the Cu, Pb, and also Fe on the PC3, which means that the sources are different for each group of the elements.
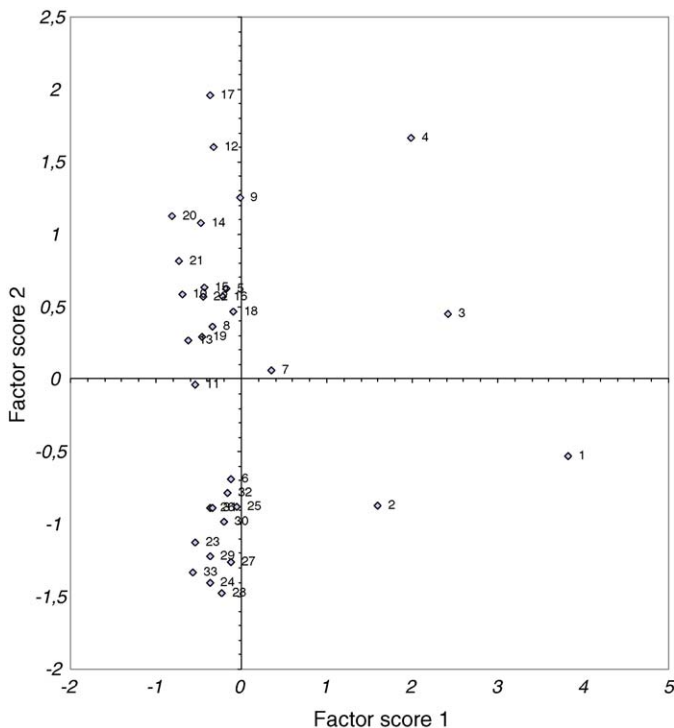

Fig. 4. Factor scores plot of the 33 samples with eight variables, excluding Co due to its low communality (0.377) at the initial run of the PCA. Communalities for the other metals were higher than 0.7. In this figure, the PC1 is represented by the horizontal axis and the PC2 by the vertical axis.

Relationships between individual samples ($n = 33$) can be visualized by utilizing scores plots. This includes plotting a graph of the scores of the samples against those for a different component; for example, PC1 versus PC2, and Fig. 4 illustrates a scores plot for all street sediments. There is a clear separation between the samples with a satisfactorily manner and is enough for this purpose. This plot provides better separation among the samples: 1–4, 5–22 except for 6, and 23–33. The samples with number 1–4 were taken from the sampling points, which are closed to an abandoned zinc smelter that is about 6 km far from the nearest sampling location, and these samples are therefore characterized with their high zinc contents. The samples 5–22, excluding no.6, were collected from the main streets of the city, and characterized by the same origin with high traffic density, while the others with no. 23–33 (including no. 6) were belonging to the sampling locations situated in the north and the south parts of the city having a lower traffic density with respect to the main streets.

4. Conclusion

The sediment samples collected from the streets in Kayseri, Turkey, show high concentrations of metals, especially Cd, Pb, and Zn, which may cause serious environmental impacts. The results of PCA and correlation analyses show that these statistical techniques were useful in interpreting a large data set, and for extracting structural information. The conclusions drawn from this study are as following:

1) The application of the modified BCR sequential extraction procedure to the street sediment samples indicated that metal mobility followed the sequence: Cd > Zn > Pb > Cu > Mn > Co > Ni > Cr > Fe.
2) The distribution of the metals in the target phases of the samples shows similar mobility behaviors, although some differences are present in each extraction stage.
3) Correlation analysis, principal component analysis and enrichment factor calculations showed supporting results to each other.
4) The metals Cd, Pb, and Zn (between ca. 20 and 200) were enriched substantially in the street sediment samples.
5) High pollution levels of the metals in these samples, especially for Cd, Pb, and Zn, can cause important environmental problems and/or risks for human health.

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