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Original Research

Determination of Heavy Metal Contamination in Roadside Surface Soil by Sequential Extraction

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Abstract

This paper investigated concentrations of heavy metals in roadside surface soil samples collected from the D-100 highway in Sakarya, Turkey. The sequential extraction procedure has been applied to 24 soil surface samples and heavy metals concentrations (Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, V, and Zn) determined by ICP-OES. The three-step BCR sequential extraction procedure was used in order to evaluate mobility, availability, and persistence of trace elements in roadside surface soil samples. Validation of the analytical results was checked by analysis of the BCR-701 certified reference material. The results showed good agreement between the obtained and the certified values for the heavy metals analyzed. The results show that Zn (229 µg/g), Pb (227 µg/g), Mn (129 µg/g), Fe (113 µg/g), and Cr (101 µg/g) are the most contaminated heavy metals in roadside surface soil samples.

Keywords: BCR sequential extraction, heavy metals, roadside soil, ICP-OES, Sakarya

Introduction

The presence of heavy metals in waters (lakes, rivers, sea), air, dusts, soils, and sediments plays an important role in human life [1-4]. Many separation and preconcentration techniques for the determination of heavy metals [5-7] and also the removal process for the purification of contaminated sources have been proposed [8-10]. Heavy metals are an important toxicity source for soils. Heavy metal contamination of soil is based on three main sources: road traffic (automobiles), industrial activities, and weathered materials [11, 12]. In terms of roadside soil the most effective contaminant source is vehicle traffic. Ward et al. [13] reported that heavy metal pollution from automotive emissions affects roadside surface soils. the D-100 highway is a commonly used road in Sakarya, Turkey.

The BCR (European Community Bureau of Reference) sequential extraction procedure was carried out for determining extractable heavy metals in roadside soils. This procedure identifies biological and physicochemical availability, mobilization, and transport of heavy metals [14]. The BCR method decreases errors in extracting the heavy metals from their substrates and also uses certified reference material to obtain comparative results for the accuracy of the methods [15]. BCR-701 certified reference material was used in this study.

The main objective of this study was to determine heavy metal concentrations in roadside surface soil samples collected from the D-100 highway. Similar studies about the heavy metal content of D-100 were evaluated in literature. Yetimoğlu and Ercan [16] reported multivariate analysis of metal contamination in street dusts on the upper side of D-100 as different from this study. Sisman et al. [17] reported heavy metals in roadside soil from the Sapanca area highway in 2002 and only nickel and lead contents were evaluated. Saltık and Altundag [18] reported similar study but only aqua regia digestion results evaluated. In this study contamination levels of soils evaluated by BCR sequential extraction procedure and the samples were analyzed for the distribution of Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, V, and Zn elements.

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Material and Methods

The roadside surface soil samples were collected from D-100 on the edge of Adapazari-Sapanca Lake in August 2010 from 20 different points (Fig. 1).

The samples were collected at 1 kilometer intervals along 12 km of highway with a small brush and stored in moisture-proof plastic bags. All the soil samples were dried in the open air in a laboratory for 2-3 days. Dried soil samples were passed through a sieve of 230 (63 µm pore diameter) mesh size. Sequential extraction method was performed by taking 1.0 g of dried soil samples. [14, 19, 20]. The samples were treated with 0.11 mol·L^{-1} acetic acid at pH 2.85 for 16 h and were shaken at 200 rpm (bound to carbonate phases – dissoluble in acids). After centrifugation at 4,000 rpm for 15 min the solid phases were shaken for 16 h at pH 2 with 0.1 mol·L^{-1} hydroxylamine hydrochloride and 0.1 mol·L^{-1} hydrochloride acid at 200 rpm (bound to Fe and Mn oxides phases – reducible). The solid phases were digested with 8.8 mol·L^{-1} hydrogen peroxide followed by 1.0 mol·L^{-1} ammonium acetate at pH 2 and were shaken for 16 h at 200 rpm (bound to sulphide and organic phases – oxidizable). At the last step the residues were digested with aqua regia (bound to mineral phases – residual).

The concentrations of heavy metals (Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, V, and Zn) in soil samples were measured by inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectro Arcos). Nuve SL 350 model shaker, Nuve NF 400 model centrifuge, and Sshott CG 840 model pH meter were used throughout the experiments. All used reagents were products of analytical grade quality (Merck, Germany). The ranges of the calibration curves (6 points) were selected to match the expected concentrations (10-320 ng/mL) for all the elements.

pH was measured in soil samples to determine acidity. For this purpose an ultra-pure water 1:5 (w/v) suspension was prepared. pH measurements were taken on this suspension by immersed pH probe.

Results

pH is an important parameter for plant growth due to the influence of dissolution of metals in soil. The measured pH values of surface soil samples are shown in Table 1. The values range 7.2-8.2.

The mean levels and abundance percentages of the metal concentrations in soil samples are shown in Table 2. The concentrations of metals in each fraction and residual in soil samples were in the following order:

Cd>Ni>Fe>Ba>Zn>Pb>Mn>Sr>Cr>Cu>V>Co	F1
Mn>Sr>Cd>Ba>Cd>Pb>Cr>Ni>Zn>Co>V>Cu	F2
Cu>Sr>Zn>Cr>Ba>Pb>Co>Mn>Cd>Fe>Ni>V	F3
Co>V>Cr>Ni>Pb>Fe>Cu>Ba>Mn>Sr>Cd>Zn	R

The results indicated that Cd, Sr, and Mn showed the highest mobility. The mobility of metals in soil samples were in the following order:
Cd>Sr>Mn>Ba>Cu>Fe>Zn>Pb>Ni>Cr>V>Co

In order to validate the sequential extraction method results, BCR-701 standard reference material was analyzed. The recoveries in each fraction are shown in Table 3. The results were in agreement with the certified values for all metals. The recoveries were in the range 94.25-99.16% for those bound to carbonates, 96.19-101.36% for those bound to iron and manganese oxide, and 94.28-99.45% for those bound to sulfide and organic matter fractions.

Discussion

The highest concentrations of Pb, Zn, Cr, Mn and the lowest abundance of Cd in soil samples were found in all the fractions and residual. The highest percentages of Fe, Ni, and Cd in soil samples were found in those bound to carbonate fractions, indicating that these metals would be released into the environment if environmental conditions became more acidic [20]. Co, Cr, and Pb were present at the lower level under acidic conditions. The lowest release of

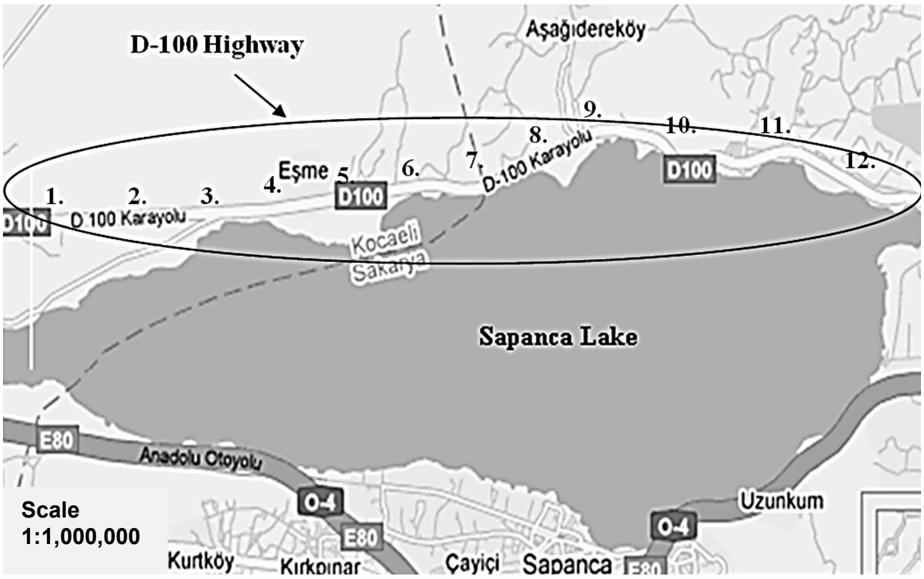

Fig. 1. Map of sampling area. (From Google Maps).

Table 1. The measured pH values of surface soil samples.

Sampling Point	1	2	3	4	5	6	7	8	9	10	11	12
pH	8.2	7.8	7.9	7.2	8.1	7.8	8.2	8.3	7.4	7.3	8.1	8.2

Table 2. The results of determined values for surface soil samples, mean (µg/g±RSD%) N=3.

Metals	Fractions								
	F1		F2		F3		Residual		(F1+F2+F3+ Residual)
	Mean± RSD%	Ratio %	Mean± RSD%	Ratio %	Mean± RSD%	Ratio %	Mean± RSD%	Ratio %	Total
Pb	38.10±0.14	16.73	65.35±1.98	28.71	48.21 ±2.02	21.18	75.6±2.04	33.21	227.60
Ba	11.02±1.10	26.64	13.08±1.23	31.62	9.57±1.65	23.13	7.66±0.86	18.52	41.36
Sr	4.50±1.84	12.83	12.41±1.34	34.85	14.05±2.12	39.46	4.10±1.54	11.51	35.60
Cu	7.34±0.15	10.57	4.21±0.15	6.30	40.12±1.22	57.79	17.90±1.76	25.78	69.42
V	2.10±0.06	10.13	3.50±0.20	16.89	3.07±0.34	6.75	12.50±0.19	60.32	20.72
Mn	20.04±1.60	15.81	67.02 ±2.02	51.87	24.40±0.67	18.88	17.20±1.34	13.31	129.20
Co	1.21±0.50	5.50	2.10±1.10	9.50	3.20±2.10	14.50	15.42±1.20	70.34	21.92
Fe	41.20±0.90	36.20	23.2±1.02	20.38	14.60±0.80	12.82	34.80±0.45	30.57	113.80
Ni	18.02±1.54	37.77	7.10±1.01	14.88	5.04±0.12	9.46	17.00±1.23	35.63	47.70
Cr	11.57±0.89	11.92	18.05±2.23	18.83	24.05±1.03	24.04	47.70±1.98	47.00	101.37
Cd	2.87±0.64	43.15	1.93±0.18	29.02	1.10±0.43	16.54	0.75±0.09	8.86	6.65
Zn	58.06±1.34	25.34	34.31±0.67	14.97	63.05±1.98	27.52	73.04±1.27	3.13	229.07

Cu in soil samples was found in reducible fraction. Mn was the most abundant metal in reducible fractions, indicating those bound to iron and manganese oxides. The mean concentrations of Pb, Ba, Sr, V, Co, and Cr in the reducible fraction were higher, and Zn, Cd, Ni, Fe concentrations were lower than those bound to carbonates fraction. Cu was dominant in oxidizable fraction, indicating bound-to-sulfide and organic matter in soil samples. The lowest level of V, Fe, and Ni were found in the oxidizable fraction. Sr was present at the higher level in the oxidizable fraction than other fractions. The results indicated that Co was the most abundant metal in residual, indicating bound-to-mineral structures (aluminosilicates) [21].

Yalçın and Sevinç [22] investigated Fe, Zn, and Pb content in water of Sapanca Lake at the 1990-91 time intervals. Duman et al. [23] reported Pb, Cr, Cu, Mn, Ni, Zn, and Cd concentrations in surface sediments of Sapanca Lake at 2003-04 time intervals. Both of them reported that the motorway was the major heavy metal pollution source for lake water and sediment. According to the results, the most contaminated heavy metals in water and sediments were Fe, Zn, Pb, Mn, and Zn. Similarly, these heavy metals were found to be the most contaminated elements in roadside surface soil in this study.

The obtained results in this study were compared to the literature values in major cities around the world (Table 4). The results obtained for the upper side of D-100 [16], higher from this study except Ni and Cd values. Pb values were lower and Ni values were higher in this study compared to the Sapanca area highway study [17]. The results showed that Pb contamination has increased since 2002. The concentration of the elements in the Sakarya D-100 highway was lower than in India [24]. The values of Pb, Zn, and Cu in this study were lower than the studies carried out in Paris [25], Madrid [26], and London [27]. The study results carried out in China [28] were close to the values in this study, except from Cd and Pb. The values of the works on the Istanbul E-5 highway [29] were higher except for Cd and Ni.

Conclusions

Sequential extraction is a powerful method for determining different binding forms and mobility of trace elements. It also gives more information about metal diffusion and toxicity. The results show that Zn, Pb, Mn, Fe, and Cr are the most contaminated heavy metals in roadside surface

Table 3. The Certificate and found results for BCR 701 (μg/g).

Standard Reference Material	Found	Certified	Recovery (%)
BCR-701			
F 1			
Cr	2.13±0.12	2.26±0.16	94.25
Cu	47.59±1.21	49.30±1.70	96.54
Pb	3.04±0.36	3.18±0.21	95.67
Zn	203.30±2.31	205.00±6.00	99.16
Ni	14.98±1.30	15.4±0.90	97.25
Cd	7.02±0.51	7.34±0.35	95.68
F 2			
Cr	46.32±1.16	45.70±2.00	101.36
Cu	122.30±2.14	124.00±3.00	98.61
Pb	121.31±1.98	126±3.00	96.28
Zn	109.66±3.46	114.00±5.00	96.19
Ni	25.95±0.80	26.6±1.30	97.54
Cd	3.65±0.69	3.77±0.28	96.76
Cr	139.64±4.65	143.00±7.00	97.65
Cu	54.44±2.35	55.20±4.00	98.62
Pb	8.77±1.56	9.30±2.00	94.28
Zn	45.45±1.67	45.70±4.00	99.45
Ni	15.07±0.3	15.30±0.90	98.51
Cd	0.26±0.1	0.27±0.06	96.30

soil samples. Automotive emissions are the most effected contaminant source for heavy metal pollution for roadside surface soils. Sapanca Lake, which is the one of the biggest natural drinking water sources in Turkey, is near the D-100 highway. The highway soil is a pollution source for the lake. The heavy metal content of surface soil is transported to lake water by the rain. This study shows that the heavy metal contamination of highway surface soil can be dangerous for Lake Sapanca.

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Table 4. Heavy metal concentrations in street dust in major cities worldwide (μg/g).

Cd	Cr	Cu	Ni	Pb	Zn	Reference
0.3	-	191.1	27.1	368.3	431.2	[16]
-	-	-	58.7	47.5	-	[17]
15.8	700	230	130	205	330	[24]
-	-	360	-	2000	2900	[25]
-	61	188	44	1927	476	[26]
-	-	342	-	1120	2119	[27]
0.73	80.8	107.7	36.1	71.7	238.6	[28]
0.3	-	191.1	27.1	368.3	431.2	[29]
6.65	101.4	69.4	47.7	227.6	229.1	This study

"-" - Not detected

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