Advances in Environmental Research, *Vol. 3, No. 4 (2014) 321-335*
DOI: http://dx.doi.org/10.12989/aer.2014.3.4.321

Accumulation of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in urban soil and their mobility characteristics

Krishna G. Bhattacharyya* and Mayur J. Mahanta

Department of Chemistry, Gauhati University, Guwahati 781014, Assam, India

(*Received January 12, 2014, Revised June 16, 2014, Accepted August 12, 2014*)

Abstract. Eight trace metals, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn, were measured in the urban soil of Guwahati City, Assam, India from 31 sites representing five different types of land use, residential, commercial, industrial, public utilities, and roadside. Cd and Co occurred in very low concentrations (Cd << Co) in all types of land use without any significant variation from one type of land use to another. Ni concentrations were more than those of Co, and the concentrations depended on land use pattern. Average Cr and Cu concentrations were ≥ 100 mg/kg, but Cr had a significantly higher presence in industrial land use. Pb concentrations showed similar trends. The two metals, Mn and Zn, were present in much larger amounts compared to the others with values ≥ 300 mg/kg. Industrial and roadside soil contained much more Mn while commercial soil was enriched with Zn. Toxicity Characteristic Leaching Procedure (TCLP) was used for elucidating the mobility characteristics of the eight heavy metals. Mn suffered the highest leaching from commercial land (9.9 mg/kg on average) and also from other types of land. Co, Cu and Pb showed higher leachability from commercial soils but the leached concentrations were less than those of Mn. The two metals, Zn and Ni, were leached from residential land in considerable amounts. The TCLP showed Mn to be the most leachable metal and Cr the least.

Keywords: heavy metal accumulation; TCLP; leaching; urban soil; Cd; Co; Cr; Cu; Mn; Ni; Pb; Zn

1. Introduction

Soils of urban areas are often degraded in quality compared to agricultural or natural soils. Intense human activities associated with construction, transport, import of materials, etc., disturb the heterogeneity of urban and suburban soils, sometimes producing young soils with unpredictable layering (Tiller 1992, Linde *et al*. 2001). The urban soil is the receptor of significant quantities of pollutants accumulating from traffic and industry related emissions and deposition, and dumping of wastes. These modify soil properties and increase pollutant contents, especially of the potentially toxic trace elements (Bullock and Gregory 1991, Adriano 2001, Moller *et al*. 2005, Ruiz-Cortés *et al*. 2005, Lu *et al*. 2007). Urbanization has altered the physical, chemical and biological properties of soils (Thornton 1991) throughout the world, the degree of such modification being dependent on the relative level of human disturbance.

Hu *et al*. (2013) analyzed 227 surface soil samples from Guangdong Province, China for As,

*Corresponding author, Professor, E-mail: kgbhattacharyya@gmail.com

http://www.techno-press.org/?journal=aer&subpage=7 ISSN: 2234-1722 (Print), 2234-1730 (Online)

Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn and found that the surface soils had mean Cd, Cu, Zn, and As contents over two times higher than the background values and that soil pollution by Pb was more widespread than the other heavy metals. In a detailed work on metals in topsoil in Dublin, Ireland, it was shown that the concentrations of lead, copper, zinc and mercury were strongly influenced by human activities, with elevated concentrations in the city docklands, inner city and heavy industry areas (Glennon *et al*. 2014). In another recent study on metal contamination of the road side dusty soil Dhaka, Bangladesh, significant positive correlation was found among pairs of heavy metals like Pb/Zn, Pb/Cr, Pb/Cu, Zn/Cr and Cr/Cu, etc. Anthropogenic input and upward industrial growth have been shown to be the main cause of soil contamination (Rakib *et al*. 2014).

The bioavailability and toxicity of metals to the biota depends on soil chemistry and is location specific, yet standards wherever available are commonly expressed as a single value for all soils (Stephen *et al*. 2004). Heavy metals enter soils through the routes of some parent materials (Ross 1994). The quantum of damage likely to be caused by the presence of these metals in soil is always determined by how much of the same is released to the environment and is bioavailable (Chlopecka *et al*. 1996, Temminghoff *et al*. 1997, Govil *et al*. 2008).

Heavy metal behavior in soil and their entry into the food web is usually investigated by treating the soil with various extractants (Rauret 1998, Kaminski and Landsberger 2000, Abollino *et al*. 2002, Herreweghe *et al*. 2003, Wang and Yong 2007). The release of heavy metal cations to water ("leaching") measures the susceptibility of the soil to transport processes and depends on the relative affinity of the metals to bind to reactive surfaces in the soil matrix (Tipping *et al*. 2003, Gustafson *et al*. 2003).

The Toxicity Characteristics Leaching Procedure (TCLP) has emerged as the most specific and result oriented method to evaluate metal mobilization from environmental samples (Hooper *et al*. 1998, Gonzalez and Barnes 2002, Sahuquillo *et al*. 2002, Udovic and Lestan 2007). The TCLP measures immediate leachability of toxic contaminants from various solid phases (Lagrega *et al*. 1994) and the gravitational downward seepage of contaminants through a solid phase due to a liquid percolating through it (Vijay and Sihorwala 2003). This is thus the prescribed method to determine the hazardous nature of a solid waste (Townsend and Brantley 1998). Leaching of contaminants can create conditions that favour high erosion and disturb normal ecosystem functioning (Sutherland 2000, Prez-de-Mora *et al*. 2007).

2. Study area

The area chosen for monitoring of urban soil with respect to trace metal composition and their leaching behavior was the city of Guwahati (91°33′E-91°52′E and 26°08′N-26°14′N), Assam, India. The city is surrounded by the river Brahmaputra, one of the largest rivers of the world, in the north and small and medium hills make up the southern boundary. Such hills appear in almost all areas of the city which has a total area of 231 km^2 for the current population of around 2 million. The total area consists of plain and marshy land interspersed with hills and is geologically made up of the Precambrian gneissic complex, directly overlain by Pleistocene-Holocene sediments. The hills are made up of gneisses and granite bodies with quartzite, amphibolites and biotite schists. The typical Brahmaputra sand, which makes up the land, has abundant biotite and silt (Masood 1982).

3. Materials and methods

3.1 Sample collection

31 sites were chosen for soil sample collection in this study. From each location, 8 different soil samples were collected from within a small radius and mixed thoroughly to obtain a composite, representative sample. The sites could be grouped into five different types of land use, viz., residential, commercial, industrial, public utilities (parks, place of worship, etc.), and roadside (Table 1) and they are shown in Fig. 1. Samples were carried aseptically to the laboratory in polythene bags, dried in a shade, lumps were broken and the fractions passing through a ~ 94 µm sieve (Pan *et al*. 2003) were preserved for analysis.

3.2 The leaching procedure

The toxicity characteristic leaching procedure (TCLP) developed by US EPA (Method 1311) and designed to determine the mobility of both organic and inorganic constituents present in liquid, solid, and multiphase wastes (Kaminski and Landsberger 2000, Wang and Yong 2007), was utilized to examine the leaching of the heavy metals from the soil. A rotary extraction apparatus (Fig. 2), capable of rotating the extraction vessel in an end-over-end fashion at 30 ± 2 rotations/min was used for the extraction keeping the axis of rotation horizontal and passing through the center

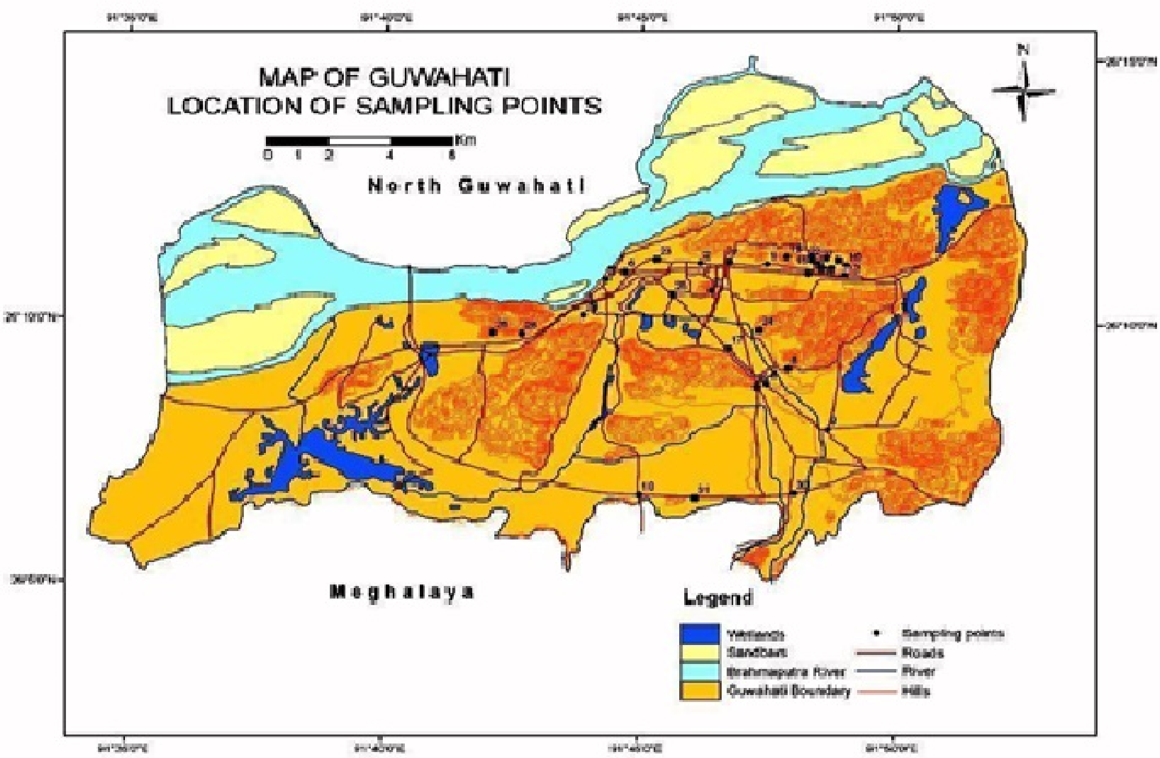

Fig. 1 Map of Guwahati showing the soil sampling locations

Table 1 Name and type of location of the soil collection sites at Guwahati, India

Sample No.	Location	Location type
1	Bamunimaidan	Residential
2	Silpukhuri	
3	Oil Refinery sector II	
4	Ganeshguri	
5	Panbazar	
6	Fancybazar	Commercial
7	Chandmari	
8	Hengerabari	
9	Sixmile	
10	Lakhra	
11	Oil Refinery	Industrial
12	Oil Refinery	
13	Oil Refinery	
14	Oil Refinery	
15	Oil Refinery	
16	Oil Refinery	
17	Christian Basti	Utilities
18	Noonmati	
19	Guwahati College	
20	Sarania	
21	Santipur	
22	Oil Refinery sector II	
23	Dighali Pukhuri	
24	Japorigog	
25	Ulubari	
26	Kamakhya	Roadside
27	Oil Refinery sector III	
28	Kalipur	
29	Ganeshguri	
30	Beltola chariali	
31	Garchuk	

of the vessel. Cylindrically shaped vessels of minimum 2 L size were used to hold the soil sample and the extraction fluid. In the present case, since only the metals were investigated, borosilicate glass bottles were used as the extraction vessels.

A suspension of 10 g of soil sample (in its state of natural pH) was taken in 250 ml of extraction fluid, which was a mixture of 5.7 ml glacial acetic acid, 500 ml of double distilled water, and 64.3 ml of 1N NaOH, the volume being made up to 1 L. The pH of this fluid was 4.93 ± 0.05. This suspension was shaken for 18 h, centrifuged and the supernatant liquid was separated and analyzed (Vijay and Sihorwala 2003, Wang and Yong 2007).

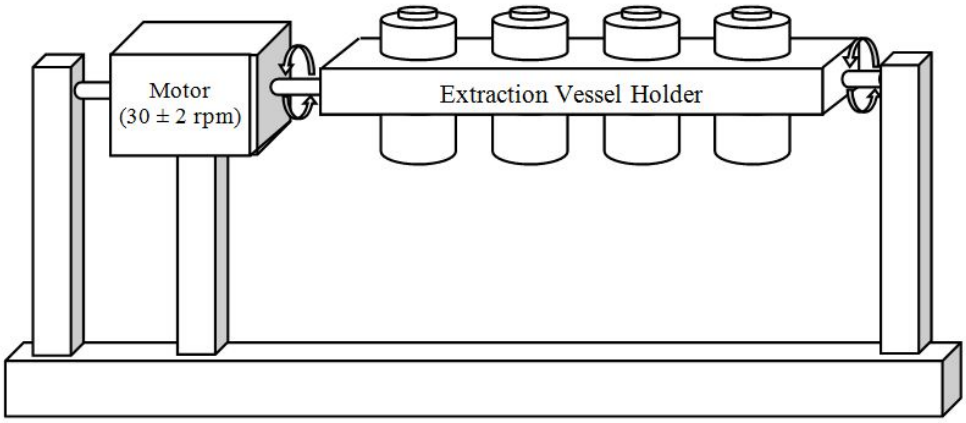

Fig. 2 Rotary extraction apparatus for the leachability experiments

3.3 Apparatus and reagents

Glassware used in the extraction procedure was initially cleaned with 1% HNO_3 (v/v) and detergents, washed thoroughly with tap water and distilled water. Extractions were done in 25-mL polypropylene centrifuge tubes, with a mechanical shaker to mix the solutions as necessary. Following each experiment, the mixture was centrifuged at 6000 rpm (Remi instruments, Mumbai, India) for 1 h and the supernatant liquid was separated by pipette (Huang *et al*. 2007), put into polythene bottles, and stored for analysis. The plasticware was pre-cleaned by soaking in 10% HNO_3. All the reagents were of analytical grade (Harrison *et al*. 1981).

The metals were estimated with atomic absorption spectrometry (Perkin-Elmer AAnalyst200, air-acetylene flame) using Merck calibration standards for each metal (Jaradat *et al*. 2006). Quantification of the results was done with calibration curves obtained with standard solutions of respective metals. The precision of the analysis was controlled by including triplicate samples in analytical batches and blanks (Krishna and Govil 2005).

4. Results and discussion

4.1 Accumulation of metals in the urban soil

Total concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in the soil samples of Guwahati are given in Table 2. Foreign materials such as small gravel; waste plastics, metal scraps and demolished construction debris were commonly observed in the soils, indicating that the soil was strongly affected by anthropogenic activities. These foreign materials could cause physical hindrance to plant root growth, and affect the characteristics of soil biology and chemistry. These were however removed manually as much as possible before sample preparation for metal analysis. Fig. 3 shows how the metals were distributed at each site in the soil.

The range of concentrations and the mean values for the metals with type of land use are presented in Table 3 and a comparison of the average concentrations of the eight metals in the different types of land use is shown in Fig. 4. Of all the metals, Cd had the least presence in the

Table 2 Total concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn (mg/kg) of the soil samples

Site	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
1	18.0	27.0	122.9	124.4	194.8	91.0	170.5	286.0
2	9.9	22.5	99.2	152.3	456.6	29.7	117.0	438.6
3	15.4	38.1	102.2	141.0	272.4	40.6	175.0	117.4
4	9.2	50.7	102.2	139.5	426.6	119.0	71.0	310.8
5	9.9	40.6	70.3	162.0	379.6	54.5	147.5	397.8
6	14.0	32.8	60.1	77.1	357.0	86.2	228.0	1606.2
7	9.9	31.0	92.3	102.6	353.2	95.7	139.5	280.8
8	13.1	51.2	132.0	151.6	223.2	83.6	160.0	165.8
9	12.0	37.8	65.9	108.2	379.6	78.8	154.5	212.2
10	8.0	47.7	109.1	99.8	466.3	112.1	162.4	341.2
11	11.9	29.3	101.8	134.6	350.4	84.5	160.5	177.4
12	12.0	52.5	134.9	173.5	551.8	81.8	185.0	355.8
13	9.8	55.0	177.0	247.6	636.0	36.7	208.0	461.0
14	7.4	35.9	162.6	170.4	379.4	65.1	272.5	138.0
15	6.5	42.1	730.7	130.3	300.8	24.1	192.0	166.4
16	12.3	42.0	201.3	148.4	383.2	60.9	163.7	204.4
17	11.8	42.2	111.3	99.9	294.8	144.2	156.0	132.6
18	11.9	49.6	117.8	238.1	377.8	23.9	144.5	284.6
19	14.0	36.8	105.5	108.2	256.8	73.4	137.5	264.2
20	7.3	39.4	106.2	93.7	246.8	91.4	142.7	385.0
21	11.4	41.8	119.0	194.2	282.2	94.1	123.8	135.0
22	11.2	41.7	157.6	99.4	503.8	74.0	126.5	162.8
23	9.2	36.6	123.6	133.4	320.0	61.7	185.5	183.8
24	6.9	39.4	125.9	162.8	273.2	96.4	65.0	134.8
25	7.8	47.4	96.4	133.0	466.2	58.2	26.0	1117.2
26	9.0	43.2	102.2	127.2	512.2	74.8	285.5	204.2
27	7.4	21.6	99.9	103.9	360.6	75.3	184.0	697.2
28	7.4	60.6	112.2	206.5	400.4	127.4	110.0	166.8
29	9.9	61.9	98.9	239.8	321.8	65.8	129.0	234.3
30	3.1	57.6	128.6	231.7	501.3	90.1	201.2	183.2
31	15.9	38.9	112.4	112.3	412.0	100.9	116.6	331.0
Std dev	3.2	10.1	114.5	46.9	102.3	28.8	53.5	308.6
mean	18.0	27.0	122.9	124.4	194.8	91.0	170.5	286.0

urban soil of Guwahati and the values did not differ much from one type of soil to another. In fact, Cd had a slightly lower presence in roadside soil compared to the other types of soil. The mean total concentrations of Cd for residential, commercial, industrial, utilities and roadside soil were 12.48, 11.40, 9.98, 10.17 and 8.78 mg/kg respectively. These results indicate that whatever Cd was present in the soil might be of lithogenic origin and was not contributed by anthropogenic activities.

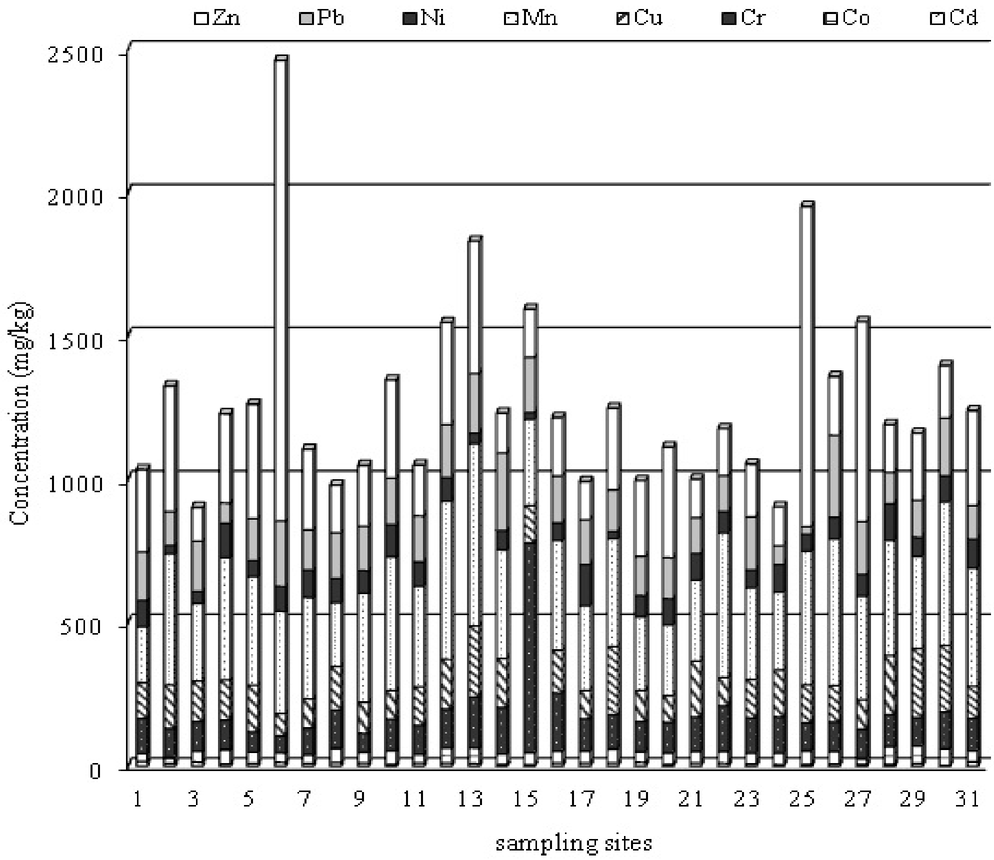

Fig. 3 Variation in the total concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn (in mg/kg) for all the sampling sites

Table 3 The ranges and the average concentrations of the metals in soil from the five types of land use

Metal	Concentration in mg/kg									
	Residential		Commercial		Industrial		Utilities		roadside	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Cd	9.2-18.0	12.5	8.0-14.0	11.0	6.5-12.3	10.0	6.9-11.9	10.2	3.1-15.9	8.8
Co	22.5-50.7	35.8	31.0-51.2	40.1	29.3-55.0	42.8	36.6-49.6	41.7	21.6-61.9	47.3
Cr	70.3-122.9	99.4	60.1-132.0	91.9	101.8-730.7	251.4	96.4-157.6	118.1	99.9-128.6	109.0
Cu	124.4-162.0	143.8	77.1-151.6	107.9	130.3-247.6	167.5	93.7-238.1	140.3	103.9-239.8	170.2
Mn	194.8-456.6	346.0	223.2-466.3	355.9	300.8-636.0	433.6	246.8-503.8	355.7	321.8-512.2	418.1
Ni	29.7-119.0	66.9	78.8-112.1	91.3	24.1-84.5	58.8	23.9-144.2	79.7	65.8-127.4	89.1
Pb	71.0-175.0	136.2	139.5-228.0	168.9	129.0-272.5	197.0	26.0-185.5	123.1	110.0-285.5	171.1
Zn	117.4-438.6	310.1	165.8-1606.2	521.2	138.0-461.0	250.5	132.6-1117.2	311.1	166.8-697.2	302.8

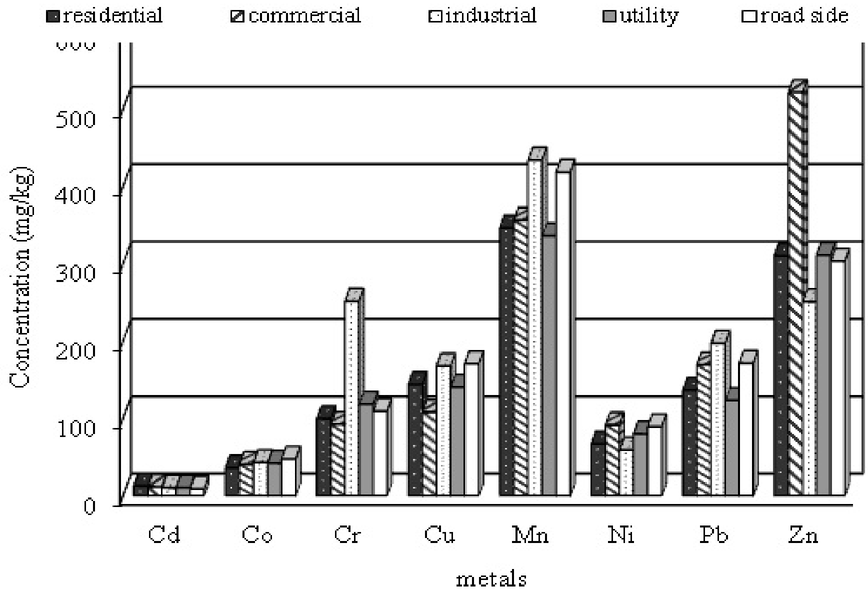

Fig. 4 The average concentration of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in the five types of land use

Co concentration was not significantly influenced by land use practices, but a slight tendency of enrichment is noticeable from residential to other types of land use.

Cr in the soil had strong anthropogenic influence and while Cr-content of residential, commercial, utilities and roadside soil had more or less stabilized near 100 mg/kg, the average Cr in industrial soil had gone up to > 250 mg/kg.

Cu content of the soil in the five types of land use fluctuated between 107 to 170 mg/kg and the commercial land use was found to contribute less Cu compared to residential land use. It is possible that wastes, particularly electronic garbage in residential areas, have led to accumulation of Cu in the soil.

Mn had predominance in all types of land and the average values were from 346 to 433 mg/kg. The industrial and the roadside soil had the highest enrichment of Mn compared to the other types of land use.

Ni contamination of the urban soil of Guwahati was much below the level of 100 mg/kg with the industrial area soil having the lowest content – lower than the residential area soil. While batteries and metallurgical goods are a common source of Ni (Charlesworth and Lees 1999), wastes might have contributed significantly to higher Ni-content in residential, commercial, utilities and roadside soil.

Pb showed large variation from one type of land use to another and the average values are in the order of industrial > roadside ≈ commercial > residential > utilities. The higher Pb-level at roadside might be due to use of leaded fuel in vehicles till a few years ago. The presence of a petroleum refinery in the industrial area might also have been responsible for higher Pb in soil. Sources of Pb such as medical wastes, printing and graphics wastes, etc., might have led to higher Pb accumulation in some areas (Charlesworth and Lees 1999), the utilities (public parks) being the least affected.

The average Zn-content of the soil was second only to Mn and the soil from commercial hubs

Table 4 The ranges and the average concentrations of the metals leaching out from the soil of five different types of land use

Metal	Concentration in mg/kg									
	Residential		Commercial		Industrial		Utilities		roadside	
	Range	mean	Range	mean	Range	mean	Range	mean	Range	mean
Cd	0.11-0.30	0.18	0.04-0.10	0.07	0.08-0.17	0.13	0.01-0.12	0.07	0.05-0.11	0.09
Co	0.23-0.49	0.34	0.29-0.51	0.40	0.25-0.47	0.38	0.26-0.42	0.32	0.24-0.39	0.33
Cr	0.06-0.24	0.14	0.07-0.56	0.21	0.04-0.29	0.11	0.03-0.29	0.14	0.07-0.16	0.11
Cu	0.04-0.33	0.11	0.13-1.50	0.64	0.18-1.61	0.49	0.16-0.75	0.39	0.13-1.00	0.37
Mn	1.05-24.62	8.72	1.29-18.03	9.99	0.72-15.24	3.59	0.70-13.04	4.52	0.12-9.02	2.47
Ni	0.42-0.98	0.66	0.30-0.45	0.38	0.21-0.57	0.41	0.15-0.54	0.31	0.17-0.62	0.36
Pb	0.35-0.62	0.46	0.35-0.56	0.49	0.29-0.56	0.46	0.32-0.50	0.37	0.29-0.53	0.43
Zn	0.04-2.75	1.50	0.04-0.42	0.18	0.02-7.02	1.30	0.02-1.69	0.28	0.02-0.66	0.21

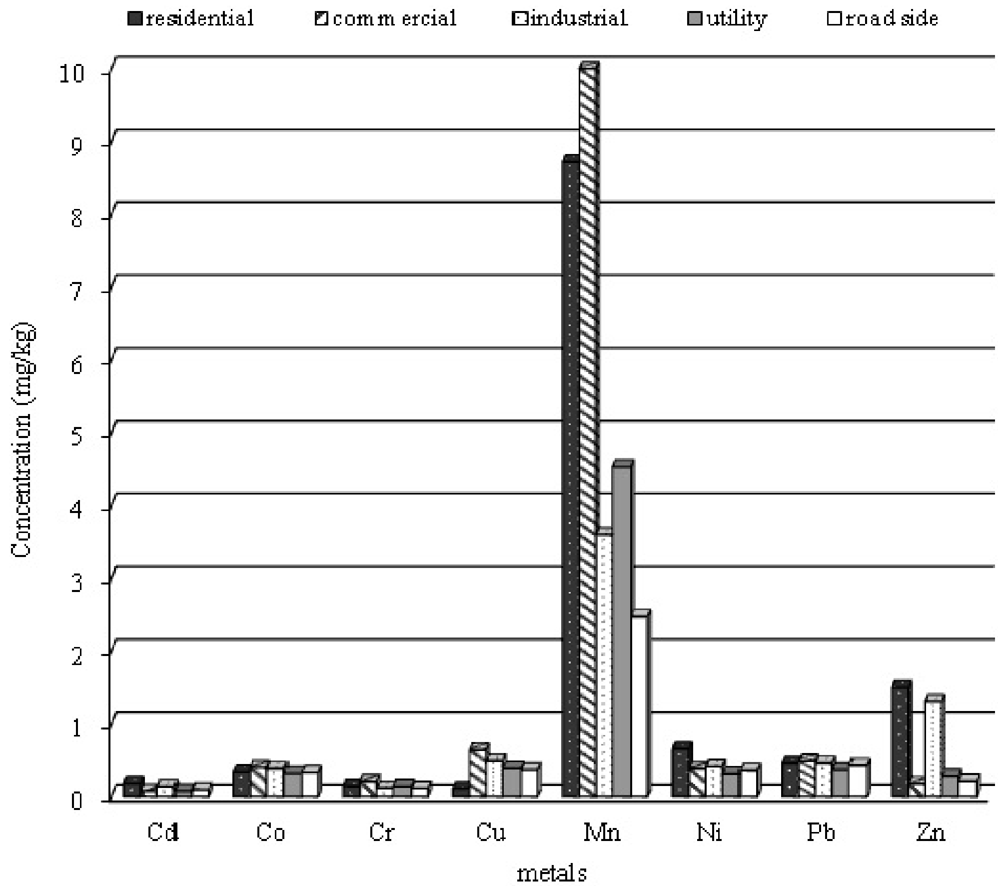

Fig. 5 The average concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn leaching out from the soil of five types of land use

was enriched with it (> 520 mg/kg) than in other types of land use. Soil from residential, utilities and roadside areas had Zn-content close to one another, but the industrial area had less accumulation of the metal.

4.2 TCLP to determine metal mobility

The range and the average concentrations of the metals extracted by TCLP from 31 urban soil samples are given in Table 4. The average leached amount depended on land use pattern (Fig. 5). The results of TCLP extractions could be summarized as follows:

Cd was the least leachable metal among all the metals analyzed in this present study. Amongst all the five types of land use, the residential land use showed maximum average Cd leaching of 0.18 mg/kg. The commercial, industrial, utilities and roadside soil released average Cd of 0.07, 0.13, 0.07 and 0.09 mg/kg respectively. With respect to the original content of Cd in the soil, the percentage leaching was in the order of 1.7, 1.5, 1.1, 0.8, and 0.6% (Table 5, Fig. 6) from soil samples of industrial, residential, roadside, utilities and commercial land use. Thus, most of Cd continues to be a part of the soil and is not extracted by the TCLP. As the major sources of Cd are sewage sludge from waste water treatment, fertilizers, textile, petroleum, Ni-Cd battery production, welding, etc. (Moustafa El Nemr *et al*. 2007), these materials keep Cd strongly bound to the matrix and very little is in the labile form, available to TCLP extraction. These results are in conformity with the speciation analysis that showed that as much as 52% of Cd is bound to the lattice or residual fraction (Bhattacharyya and Mahanta 2011).

The urban soil released slightly more Co under TCLP. The soil from commercial land use showed the maximum leaching with an average value of 0.40 mg/kg. The leaching from the industrial soil was also very close with an average value of 0.38 mg/kg followed by the residential, utilities and roadside soil with values of 0.34 mg/kg, 0.32 mg/kg and 0.33 mg/kg respectively. When leachability with respect to Co was calculated as percentage of the original content, the highest value of 1.2% was found with the residential soil. These values for industrial, commercial, utilities and roadside soils are respectively 1.1, 0.9, 0.7 and 0.7% (Table 5, Fig. 6). Co is principally attributed to input of soil parent mineral (Wang *et al*. 2005) and is a little loosely bound to the soil matrix because Co has bigger ionic radius than other metal cations (Abollino *et al*. 2002). The speciation studies had earlier shown that as much as 58% of Co was bound to the exchangeable and carbonate fractions (Bhattacharyya and Mahanta 2011), but the results here indicated that the extractants in the TCLP were not able to solubilize much of Co from urban soil.

Leachability with respect to Cr is similar to that of Cd. Soils collected from different land use types leach out Cr to the extent of 0.21 mg/kg (commercial), 0.14 mg/kg (residential), 0.11 mg/kg (industrial), 0.14 mg/kg (utilities) and 0.11 mg/kg (roadside). The residential and commercial soil releases 0.2% of Cr under TCLP. On the other hand, utility, roadside and industrial soils leach out very little Cr of 0.13, 0.10 and 0.09% respectively (Table 5, Fig. 6). Cr is toxic in its hexavalent form (Rowbotham *et al*. 2000) towards humans (Barceloux and Barceloux 1999) and animals (Stohs *et al*. 2001). The soil in the present work has retained most of Cr to itself and only a small fraction of the metal is likely to be carried by the runoff to the municipal water bodies. It is to be noted that Cr has a smaller ionic radius which makes it possible to bind the metal more strongly to the soil matrix (Abollino *et al*. 2002).

Cu leaching out from soils of different types of land use varies from 0.04 mg/kg in residential land use to 1.61 mg/kg in industrial land use. The lower value in residential soil might be due to the grass cover of the soils (Prez-de-Mora *et al*. 2007). The soil from commercial land use showed

Table 5 The average amount (in percentage) of the metals leaching out from the soil samples of five types of land use

Metal	Percentage leaching of heavy metals									
	Residential		Commercial		Industrial		Utilities		Roadside	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Cd	0.79-2.51	1.47	0.30-0.90	0.60	0.79-2.63	1.69	0.13-1.93	0.76	0.55-0.54	1.14
Co	0.74-1.80	1.20	0.70-1.20	0.90	0.46-1.72	1.09	0.51-1.02	0.71	0.38-0.92	0.72
Cr	0.06-0.40	0.17	0.06-0.48	0.18	0.01-0.27	0.09	0.03-0.41	0.13	0.07-0.20	0.10
Cu	0.03-0.26	0.09	0.12-0.82	0.39	0.07-1.72	0.46	0.09-0.76	0.28	0.06-0.93	0.31
Mn	0.37-6.90	2.40	0.25-6.62	3.18	0.20-5.93	1.27	0.17-5.84	1.48	0.03-2.38	0.64
Ni	0.67-1.43	0.93	0.31-1.95	0.79	0.47-1.22	0.74	0.18-0.97	0.39	0.23-0.95	0.44
Pb	0.22-0.36	0.28	0.19-0.39	0.27	0.14-0.39	0.26	0.17-1.22	0.44	0.15-0.34	0.28
Zn	0.02-0.96	0.37	0.02-0.31	0.10	0.00-1.82	0.33	0.00-0.22	0.16	0.01-0.36	0.10

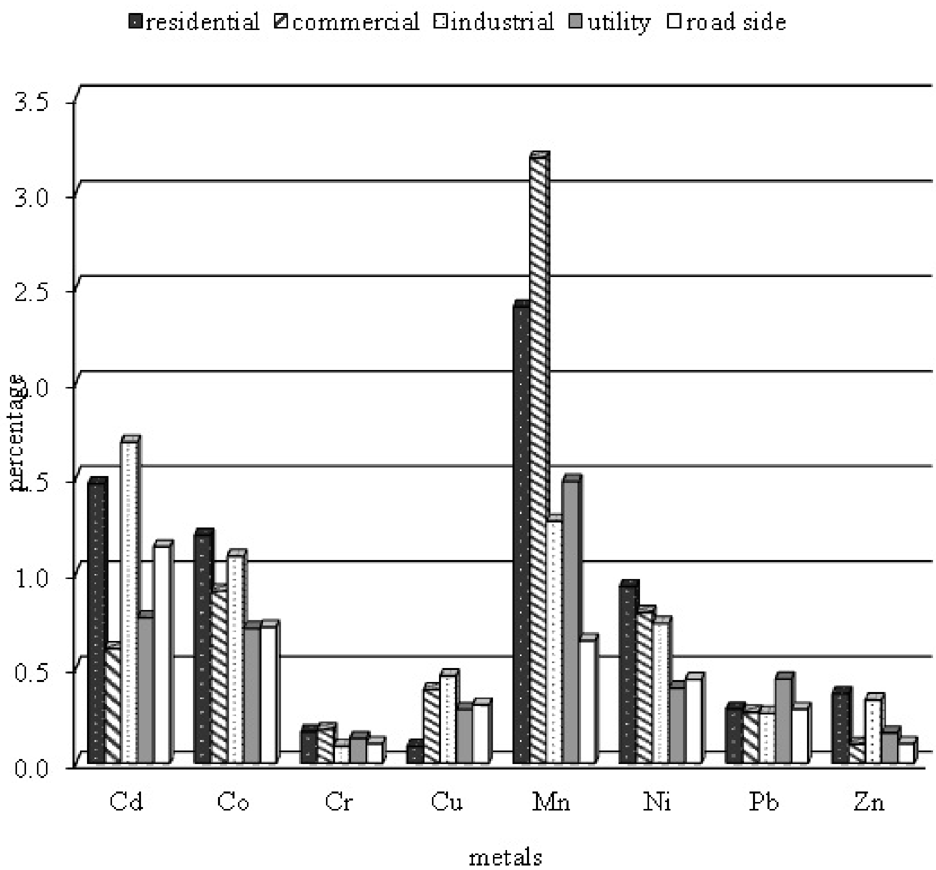

Fig. 6 The average amounts of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn (in percentage) leaching out from the soil of five types of land use

maximum leaching (mean 0.64 mg/kg) followed by industrial (0.49 mg/kg), utility (0.39 mg/kg) and roadside soil (0.37 mg/kg). When compared to the original content, the leaching was very low, 0.46% in industrial land use, 0.39% in commercial, 0.31% in roadside, 0.28% in utility land use, and 0.09% in residential land use (Table 5, Fig. 6). As the plant/grass cover reduces capability of the soil for Cu leaching to the environment, the roadside and utility soil samples have lower leaching capacity (Prez-de-Mora *et al*. 2007). Cu is also known to have a higher adsorption affinity such that it gets readsorbed to the soil matrix (Voegelin *et al*. 2003) reducing its leachability. These results are in conformity with the earlier observations of almost 90% of the metal being bound to the less labile, oxidizable fraction (~52%), iron-manganese dioxide fraction (~18%) and residual fraction (~19%) (Bhattacharyya and Mahanta 2011).

Large amount of Mn in the soils was found extractable with TCLP; the maximum was 9.99 mg/kg (average) the soil of commercial land use type – which was equivalent to 3.18% of Mn present. The soil of residential, utilities, industrial and roadside land released Mn to the extent of 8.72, 4.52, 3.59 and 2.47 mg/kg respectively and these are equivalent to 2.40, 1.48, 1.27 and 0.64% of Mn originally present (Table 5, Fig. 6). Mn-leachability is thus in the order of commercial > residential > utilities > industrial > roadside soil. The speciation studies have shown that much of Mn was associated with the comparatively labile exchangeable fraction (6%), carbonate fraction (27%), reducible fraction (45%), and organic fraction (4%), while the least labile residual fraction contains only a small portion (18%) (Bhattacharyya and Mahanta 2011). Thus, it is not surprising that the urban soil gives off Mn much more than the other metals in the TCLP extraction.

The highest TCLP extraction of 0.66 mg/kg was from the soil of residential land use. The soil in residential areas are exposed to various wastes including batteries, electronic wastes, etc., which might have increased Ni-level of the soil (Abollino *et al*. 2002). However, most of Ni seems to have found a permanent host in the soil and does not come out during leaching. The other soil types released very similar amount of Ni in TCLP extraction, i.e., 0.41 mg/kg (industrial), 0.38 mg/kg (commercial), 0.36 mg/kg (roadside) and 0.31 mg/kg (utility). The leached fraction constituted 0.39% in utility land use to a high of 0.93% in residential land use (Table 5, Fig. 6), which can be considered as low. In chemical speciation study, it was found that the exchangeable, carbonate and Fe/Mn oxide fractions together held 67% of Ni and the oxidizable and residual fractions 33% (Bhattacharyya and Mahanta 2011). Thus, a large amount of Ni might be held in comparatively labile fractions, but the TCLP brings out very little Ni indicating that Ni in the urban soil may not be an ecological hazard.

Pb leaching was also not much. The average extractions were only 0.49 mg/kg (commercial land use), 0.46 mg/kg (residential and industrial land use), 0.43 mg/kg (roadside land use) and 0.37 mg/kg (utility land use), which constituted 0.44, 0.28, 0.28, 0.27, and 0.26% of the original Pb present in utilities, residential, roadside, commercial and industrial land use (Table 5, Fig. 6). Pb extractions have not exceeded TCLP limits. The speciation studies have earlier shown that as much as 42% o Pb was bound to the residual or lattice fraction of the soil matrix followed by 20% and 6% bound to the less labile reducible and oxidizable fractions. The exchangeable and carbonate fractions held 27 and 5% of Pb (Bhattacharyya and Mahanta 2011). Thus, TCLP is not likely to bring out a large amount of Pb from the soil. Similar results have been earlier reported by other researchers (e.g., Kaminski and Landsberger 2000) for the urban soil of East St. Louis, IL.

TCLP extractable Zn was 1.50 mg/kg in the soil of residential land use and 1.30 mg/kg in industrial land use that represented the maximum leachable Zn. Leaching from other soil types was much less, i.e. utility (0.28 mg/kg), roadside (0.21 mg/kg) and commercial land use (0.18 mg/kg). In percentage of the original amount of Zn present in the soils, the leaching was 0.37% for the residential soil type, 0.33% for industrial land use, 0.16% for utilities, and 0.10% for both commercial and roadside soils (Table 5, Fig. 6). The higher leaching from the soil of residential and industrial land use points to higher anthropogenic contribution (Abollino *et al*. 2002, Saeedi *et al*. 2008). The TCLP extractions, however, do not conform to the distribution of Zn in the different chemical fractions; the speciation study showed 67% of Zn as bound to the exchangeable, carbonate and Fe/Mn fractions (Bhattacharyya and Mahanta 2011) and consequently, a higher amount of Zn was expected to be leached out. It is possible that Zn is present in some salts that are not extractable by the TCLP solvent system.

The overall leachability trend of the heavy metals was Cd < Cr < Co < Cu < Ni < Pb < Zn << Mn, a trend also reported by other researchers (e.g., Saeedi *et al*. 2009). Taking the mean values for all the five types of urban soil, the percentage of the total content of each metal leached out from the soil follows the trend Cr < Zn < Cu < Pb < Ni < Co < Cd << Mn. It is found that Mn is the most leachable metal.

5. Conclusions

The present study assessed the total as well as leachable concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in urban soil belonging to five different types of land use. The different soils have very similar concentrations of Cd and Co while Cr, Mn and Pb are present in higher concentrations in soils of industrial land use. Ni and Zn are found in higher amounts in soils from commercial areas.

With respect to TCLP extractions, Mn was found to be the most leachable metal with the soil from commercial land use giving off the maximum. Leachability of Cd, Co, Cr, Cu, Ni and Pb from different types of soil was small and are not expected to be a major ecological hazard.

References

Abollino, O., Aceto, M., Malandrino, M., Mentasti, E., Sarzanini, C. and Barberis, R. (2002), "Distribution and mobility of metals in contaminated sites: Chemo metric investigation of pollutant profiles", *Environ. Pollut*., **119**(2), 177-193.

Adriano, D.C. (2001), "Biogeochemistry, bioavailability and risks of metals", *Trace Elements in the Terrestrial Environment*: (2nd Edition), Springer-Verlag, New York, NY, USA.

Barceloux, D.G. and Barceloux, D. (1999), "Chromium", *Clin. Toxicol*., **37**(2), 173-194.

Bhattacharyya, K.G. and Mahanta, M.J. (2011), "Total concentrations, fractionation and mobility of heavy metals in soils of urban area of Guwahati, India", *Environ. Monit. Assess*., **173**(1-4), 221-240.

Bullock, P. and Gregory, P.J. (Eds.) (1991), *Soil in the Urban Environment*, Oxford, Blackwell Scientific Publications, Boston.

Charlesworth, S.M. and Lees, J.A. (1999), "The distribution of heavy metals in deposited urban dusts and sediments, Coventry, England", *Environ. Geochem. Health*, **21**(2), 97-115.

Chlopecka, A., Bacon, J.R., Wilson, M.J. and Kay, J. (1996), "Forms of cadmium, lead and zinc in contaminated soils from southwest Poland", *J. Environ. Quality*, **25**(1), 69-79.

Glennon, M., Harris, P., Ottesen, R.T., Scanlon, R.P. and O'Connor, P. (2014), "The Dublin SURGE Project: Geochemical baseline for heavy metals in topsoils and spatial correlation with historic industry in Dublin, Ireland", *J. Environ. Geochem. Health*, **36**(2), 235-254.

Gonzalez, A.M. and Barnes, R.M. (2002), "Comparison of microwave-assisted extraction and waste extraction test (WET) preparation for inductively coupled plasma spectroscopic analyses of waste samples", *Anal. Bioanal. Chem.*, **374**(2), 255-261.

Govil, P.K., Sorlie, J.E., Murthy, N.N., Sujatha, D., Reddy, G.L.N., Rudolph-Lund, K., Krishna, A.K. and Rama Mohan, K. (2008), "Soil contamination of heavy metals in the Katedan Industrial Development Area, Hyderabad, India", *Environ. Monit. Assess.*, **140**(1-3), 313-323.

Gustafson, J.P., Pechova, P. and Berggren, D. (2003), "Modeling metal binding to soils: the role of natural organic matter", *Environ. Sci. Tech.*, **37**(12), 2767-2774.

Harrison, R.M., Laxen, D.P.H. and Wilson, S.J. (1981), "Chemical associations of lead, cadmium, copper, and zinc in street dusts and roadside soils", *Environ. Sci. Tech.*, **15**(11), 1378-1383.

Heasman, L., van der Sloot, H.A. and Quevauviller, Ph. (1997), "Chapter 4: Contaminated Soil", *Harmonization of Leaching/Extraction Tests*, Elsviere, pp. 57-74.

Herreweghe, S.V., Swennen, R., Vandecasteele, C. and Cappuyns, V. (2003), "Solid phase speciation of arsenic by sequential extraction in standard reference materials and industrially contaminated soil samples", *Environ. Pollut.*, **122**(3), 323-342.

Hooper, K., Iskander, M., Sivia, G., Hussein, F., Hsu, J., Deguzman, M., Odion, Z., Ilejay, Z., Sy, F., Petreas, M. and Simmons, B. (1998), "Toxicity characteristic leaching procedure fails to extract oxoanion-forming elements that are extracted by municipal solid waste leachates", *Environ. Sci. Tech.*, **32**(23), 3825-3830.

Hu, Y., Liu, X., Bai, J., Shih, K., Zeng, E.Y. and Cheng, H. (2013), "Assessing heavy metal pollution in the surface soils of a region that had undergone three decades of intense industrialization and urbanization", *Environ. Sci. Pollut. Res.*, **20**(9), 6150-6159.

Huang, J., Huang, R., Jiao, J.J. and Chen, K. (2007), "Speciation and mobility of heavy metals in mud in coastal reclamation areas in Shenzhen, China", *Environ. Geol.*, **53**(1), 221-228.

Jaradat, Q.M., Massadeh, A.M., Zaitoun, M.A. and Maitah, B. (2006), "Fractionation and sequential extraction of heavy metals in the soil of scrap yard of discarded vehicles", *Environ. Monit. Assess.*, **112**(1-3), 197-210.

Kaminski, M.D. and Landsberger, S. (2000), "Heavy metals in urban soils of East St. Louis, IL Part 2: Leaching characteristics and modeling", *J. Air Waste Manag. Assoc.*, **50**(9), 1680-1687.

Krishna, A.K. and Govil, P.K. (2005), "Heavy metal distribution and contamination in soils of Thane-Belapur industrial development area, western India", *Environ. Geol.*, **47**(8), 1054-1061.

Lagrega, M.D., Buckingham, P.L. and Evans, J.C. (1994), *Hazardous Waste Management*, McGraw-Hill Inc., Singapore, pp. 50-51.

Linde, M., Bengtsson, H. and Öborn, I. (2001), "Concentrations and pools of heavy metals in urban soils in Stockholm, Sweden", *Water, Air and Soil Pollution: Focus*, **1**(3-4), 83-101.

Lu, Y., Zhu, F., Chen, J., Gan, H. and Guo, Y. (2007), "Chemical fractionation of heavy metals in urban soils of Guangzhou, China", *Environ. Monit. Assess.*, **134**(1-3), 429-439.

Masood, Md. (1982), "Structural history of the Precambrian rocks around Guwahati, Assam", *Quart. J. Geol. Min. Meteorol. Soc. India*, **54**(1-2), 33-38.

Moustafa El Nemr, A., El Sikaily, A. and Khaled, A. (2007), "Total and leachable heavy metals in muddy and sandy sediments of Egyptian Coast along Mediterranean Sea", *Environ. Monit. Assess.*, **129**(1-3), 151-168.

Moller, A., Muller, H.W., Abdullah, A., Abdelgawad, G. and Utermann, J. (2005), "Urban soil pollution in Damascus, Syria: Contamination and patterns of heavy metals in this soils of the Damacus Ghouta", *Geoderma*, **124**, 63-71.

Pan, Shih-C., Lin, Chin-C. and Tseng, Dyi-H. (2003), "Reusing sewage sludge ash as adsorbent for copper removal from wastewater", *Resour. Conserv. Recy.*, **39**(1), 79-90.

Prez-de-Mora, A., Burgos, P., Cabrera, F. and Madejon, E. (2007), ""In situ" amendments and revegetation reduce trace element leaching in a contaminated soil", *Water Air Soil Pollut.*, **185**(1-4), 209-222

Rakib, M.A., Ali, M., Akter, M.S. and Bhuiyan, M.A.H. (2014), "Assessment of heavy metal (Pb, Zn, Cr and Cu) content in roadside dust of Dhaka metropolitan city, Bangladesh", *Int. Res. J. Environ. Sci.*, **3**(1), 1-5.

Rauret, G. (1998), "Extraction procedure for the determination of heavy metals in contaminated soil and sediment", *Talanta*, **46**(3), 449-455.
Ross, S.M. (1994), "Sources and forms of potentially toxic metal in soil-plant system", *Toxic Metals in Soil-Plant Systems*, **(**S.M. Ross Eds.), John Wiley & Sons, New York, NY, USA, pp. 3-25.
Rowbotham, A.L., Levy, L.S. and Shuker, L.K. (2000), "Chromium in the environment: An evaluation of exposure of the UK general population and possible adverse health effects", *J. Toxicol. Environ. Health B*, **3**(3), 145-178.
Ruiz-Cortés, E., Reinoso, R., Diaz-barrientos, E. and Madrid, L. (2005), "Concentrations of potentially toxic metals in urban soils of Seville: Relationship with different land uses", *Environ. Geochem. Health*, **27**(5-6), 465-474.
Saeedi, M., Hosseinzadeh, M., Jamshidi, A. and Pajooheshfar, S.P. (2009), "Assessment of heavy metals contamination and leaching characteristics in highway side soils, Iran", *Environ. Monit. Assess.*, **151**(1-4), 231-241.
Sahuquillo, A., Rigol, A. and Rauret, G. (2002), "Comparison of leaching tests for the study of trace metals remobilization in soils and sediments", *J. Environ. Monit.*, **4**(3), 1003-1009.
Stephen, L., David, S., Claus, S. and Edward, T. (2004), "Deriving soil critical limits for Cu, Zn, Cd, and Pb: A method based on free ion concentrations", *Environ. Sci. Tech.*, **38**(13), 3623-3631.
Stohs, S.J., Bagchi, D., Hassoun, E. and Bagchi, M. (2001), "Oxidative mechanisms in the toxicity of chromium and cadmium ions", *J. Environ. Pathol. Tox. Oncol.*, **20**(2), 77-88.
Sutherland, R.A. (2000), "Comparison between non-residual Al, Co, Cu, Fe, Mn, Ni, Pb and Zn released by a three-step sequential extraction procedure and a dilute hydrochloric acid leach for soil and road deposited sediment", *Appl. Geochem.*, **17**(4), 353-365.
Temminghoff, E.J.M., Van der Zee, S.E.A.T.M. and de Haan, F.A.M. (1997), "Copper mobility in a copper-contaminated sandy soil as affected by pH and solid and dissolved organic matter", *Environ. Sci. Tech.*, **31**(4), 1109-1115.
Thornton, I. (1991), "Metal contamination of soils in urban areas", *Soils in the Urban Environment*, (P. Bullock and P.J. Gregory Eds.), Blackwell Scientific Publications, Oxford, UK, pp. 47-75.
Tiller, K.G. (1992), "Urban soil contamination in Australia", *Australian J. Soil Res.*, **30**(6), 937-957.
Tipping, E., Rieuwerts, J., Pan, G., Ashmore, M.R., Lofts, S., Hill, M.T.R., Farago, M.E. and Thornton, I. (2003), "The solid–solution partitioning of heavy metals (Cu, Zn, Cd, Pb) in upland soils of England and Wales", *Environ. Pollut.*, **125**(2), 213-225.
Townsend, T.G. and Brantley, A. (1998), "Leaching characteristics of asphalt road waste", Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL, USA.
Udovic, M. and Lestan, D. (2007), "EDTA leaching of Cu contaminated soils using Ozone/UV for treatment and reuse of washing solution in a closed loop", *Water Air Soil Pollut.*, **181**(1-4), 319-327.
Vijay, R. and Sihorwala, T.A. (2003), "Identification and leaching characteristics of sludge generated from metal pickling and electroplating industries by toxicity characteristics leaching procedure (TCLP)", *Environ. Monit. Assess.*, **84**(3), 193-202.
Voegelin, A., Barmettler, K. and Kretzschmar, R. (2003), "Heavy metal release from contaminated soils: Comparison of column leaching and batch extraction results", *J. Environ. Quality*, **32**(3), 865-875.
Wang, X.S. and Yong, Q. (2007), "Leaching characteristics of heavy metals and as from two urban roadside soils", *Environ. Monit. Assess.*, **132**(1-3), 83-92.
Wang, X.S., Qin, Y. and Sun, S.X. (2005), "Accumulation and sources of heavy metals in urban top soils: A case study from the city of Xuzhou, China", *Environ. Geol.*, **48**(1), 101-107.

WL