Journal of Geochemical Exploration 158 (2015) 212–222

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/jgeoexp

Distribution of trace elements in different soils and risk assessment: A case study for the urbanized area in Bangladesh

Saiful Islam [a,*], Kawser Ahmed [b], Habibullah Al-Mamun [c,d]

[a] Department of Soil Science, Patuakhali Science and Technology University, Dumki, Patuakhali 8602, Bangladesh
[b] Department of Oceanography, University of Dhaka, Dhaka 1000, Bangladesh
[c] Graduate School of Environment and Information Sciences, Yokohama National University, Yokohama, Kanagawa 240-8501, Japan
[d] Department of Fisheries, University of Dhaka, Dhaka 1000, Bangladesh

ARTICLE INFO

Article history:
Received 21 July 2014
Revised 14 July 2015
Accepted 31 July 2015
Available online 8 August 2015

Keywords:
Trace elements
Soil
Risk assessment
Element partitioning
Bangladesh

ABSTRACT

The objective of this study was to assess the potential ecological and health risks of trace elements in soil of different land use types that are presently being used in the urbanized area in Bangladesh. In this regard, the concentrations of the following priority trace elements (Cr, Ni, Cu, As, Cd, and Pb) were measured using inductively coupled plasma mass spectrometer (ICP-MS) after microwave digestion. Fifty locations were selected representing eight different types of land uses; namely, agricultural farm (AF), metal workshop (MW), play ground (PG), railway station (RS), waste disposal site (WD), construction site (CS), car workshop (CW) and petrol station (PS). The element concentrations were subsequently used to establish Hazard Indices (for adults and children). Soils of the study sites were severely polluted with trace elements which can lead to potential ecological risk and adverse impact on human health.

1. Introduction

Soil contamination by trace elements is of great concern because of their long persistence in the environment, and of their toxicity for human and other organisms (Radha et al., 1997). Soil, one of the most important component of the environment, is being contaminated by toxic metals released from solid waste disposal, wastewater irrigation, application of sewage sludge and chemical fertilizers, vehicular exhaust, etc. (Islam et al., 2015a; Khan et al., 2008; Singh et al., 2005). In Bangladesh, the scenario is worse in urban soils due to the recent dramatic industrialization and urbanization activities to meet up the demands of increasing population. Elevated concentrations of potentially toxic elements in the urban soils (Luo et al., 2012; Thornton et al., 2008; Wong et al., 2006) indicate that the urban residents are exposed to contaminated soils. Infants and toddlers are particularly vulnerable to trace metal exposure and poisoning due to the maximal brain growth and differentiation of children at early ages (Ljung et al., 2007). Moreover, trace element adsorptions from the digestion system and hemoglobin sensitivity to trace elements are much higher in children compared to adults (Bellinger, 1995). This problem is particularly relevant in Bangladesh, due to large population in close proximity to industrial and other urbanized activities. Recently, many farmers or owners of agricultural land switched their activity to more profitable uses, such as open storage sites, making station, metal workshop and car workshops. These new activities are the non-conforming land uses are potentially dangerous to the surrounding environment and may jeopardize human health (Bryant and Johnston, 1992; Man et al., 2010).

Over the last few decades, a significant number of studies have already been addressed to the contamination of soils with trace elements (Gimeno-García et al., 1996; Gomez-Parra et al., 2000; Islam et al., 2014a; Liu et al., 2005; Wong et al., 2002), to the author's best knowledge; no such study has yet been conducted in Bangladesh. Therefore, this is the first study reporting the scenario of trace element contamination in soils of residential urbanized area in Bangladesh. Knowledge of trace element concentrations in soils from different land use types has scarcely been investigated and is of critical importance in assessing trace element contamination in soils and their impact on the environment (Chen et al., 2005; Islam et al., 2015a,b; Luo et al., 2007). Therefore, the objectives of this study are to determine the concentrations of trace elements in soils of different land use types, to evaluate possible ecological risks by using risk indices and to assess non-carcinogenic health impacts on adults and children due to the ingestion of these soils.

2. Materials and methods

2.1. Study area and sampling

For the present study, soil samples were collected during August–September, 2013 from eight areas with different land uses (AF =

* Corresponding author.
E-mail addresses: msaifulpstu@yahoo.com, islam-md.saiful-nj@ynu.jp (S. Islam).

http://dx.doi.org/10.1016/j.gexplo.2015.07.017
0375-6742/

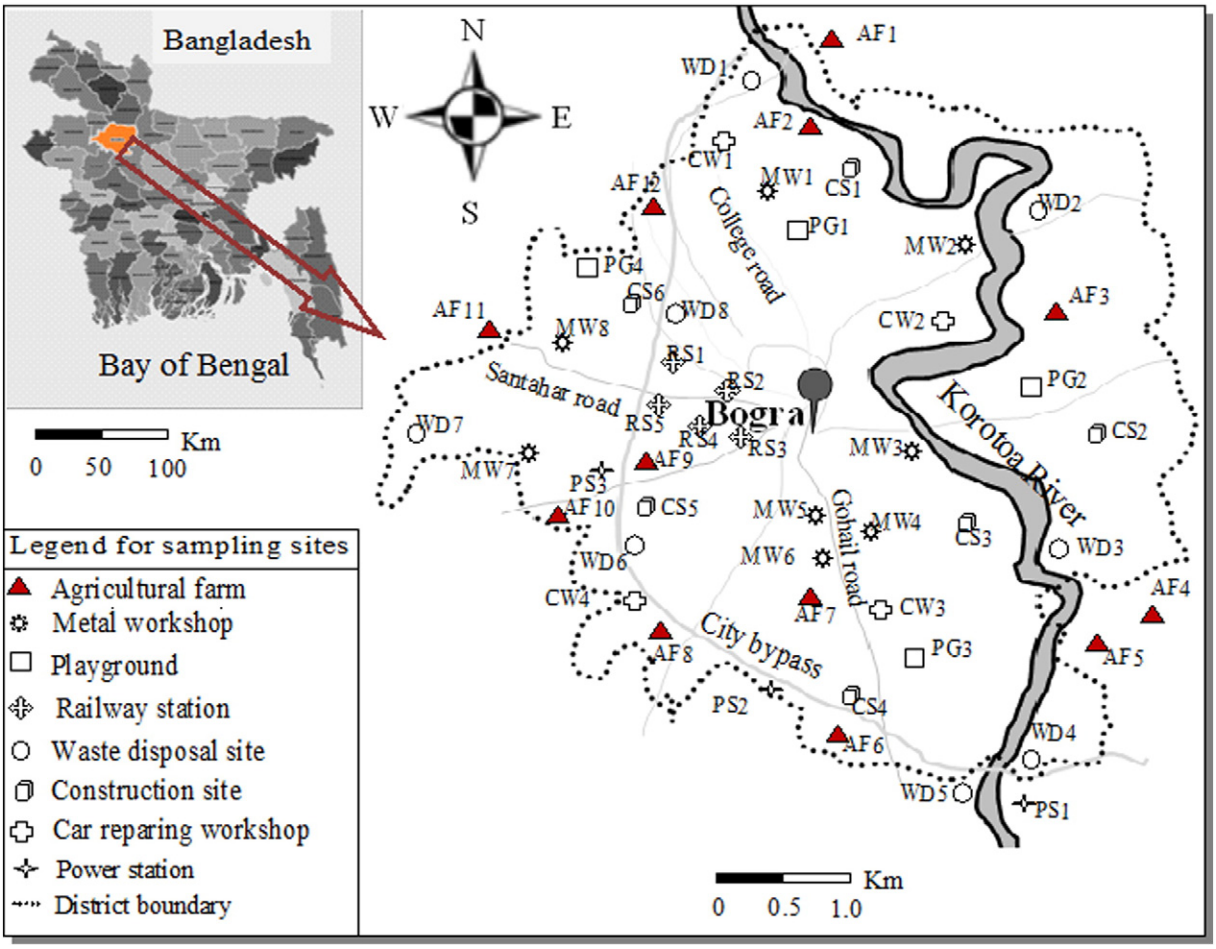

Fig. 1. Map of the study area of Bogra District in Bangladesh.

agriculture farm, MW = metal workshop, PG = play ground, RS = railway station, WD = waste dispose, CS = construction site, CW = car repairing workshop and PS = petrol station) of Bogra District in Bangladesh (Fig. 1). Sampling sites were evenly distributed throughout the city. The area of Bogra District is about 71.56 km^2, total population is about 350,397. The study area is located at the northern part of Bangladesh and the coordinates of Bogra District is 24°84′91.82″ N and 89°37′29.57″ E. Fifty sampling sites were chosen in order to include different land uses. Detailed information about the sampling sites is presented in Table 1. At each sampling station, soil sample (up to 10 cm depth) was collected in the form of sub-samples. From each site five sub-samples were thoroughly mixed to form a composite sample. Soil samples were air-dried at room temperature for two weeks (ISO-11464, 2006), then grounded and homogenized. The dried soil samples were crumbled and pulverized with a porcelain mortar and pestle and sieved through 2 mm nylon sieve and stored in airtight clean zip lock bag in a refrigerator at 4 °C until chemical analysis was carried out. The processed samples were brought to Yokohama National University, Japan for chemical analysis.

2.2. Measurement of soil physicochemical properties

The pH of soil was measured in 1:2.5 soils to water ratio. The suspension was allowed to stand overnight prior to pH determination. The pH was measured using a pH meter with the calibration of pH 4, pH 7 and pH 9 standards. For EC determination, 5.0 g of soil was taken in 50 mL polypropylene tubes and 30 mL of Milli-Q water was added to the tube. The lid was closed properly and was shaken for 5 min. After that, EC was measured using an EC meter (Horiba D-52). Organic carbon of soil was measured using elemental analyzer (model type: Vario EL III, Elementar, Germany). The catalytic combustion was carried out at a permanent temperature of up to 1200 °C. The carbon concentration

Table 1
Description of different types of land uses and their respective number of sites under investigation.

Types of land use	Number of sites	Site description
Agriculture farm (AF)	12	Traditional farming systems, grown different types of vegetables and cereal crops with chemical fertilizers and pesticides.
Metal workshop (MW)	8	Recycling of trace elements with some machinery activities, metal smelting and preparing new products.
Play ground (PG)	4	The field for play to the children, adults and other residents as a regular basis.
Railway station (RS)	5	The area around the railway station, huge number of people movement to this site.
Waste dispose (WD)	8	Disposal of town household waste, small scale breaking down of electric waste and burning of waste to the open field.
Construction site (CS)	6	Open field for construction, demolishing building materials, wood, scrap metal, concrete and bamboo etc.
Car repairing workshop (CW)	4	Repairing, washing and breaking down cars or vehicles on the existing lands.
Petrol station (PS)	3	Petrol filling station, dispose of some waste from the car around the station.

from the detector signal, and the sample weight on the basis of stored calibration curves were measured. Particle size distribution was determined using the hydrometer method (Zhao et al., 2014). The soil particles were classified for their size using the United States Department of Agriculture (USDA) classification system (gravel [>2 mm], sand [2–0.05 mm], silt [0.05–0.002 mm] and clay [<0.002 mm]).

2.3. Sample analysis for trace elements

All chemicals were analytical grade reagents and Milli-Q (Elix UV5 and Milli-Q, Millipore, USA) water was used for solution preparation. The Teflon vessel and polypropylene containers were cleaned, soaked in 5% HNO_3 for more than 24 h, then rinsed with Milli-Q water and dried. For trace element analysis, 0.2–0.3 g of the soil sample was treated with 1.5 mL 69% HNO_3 (Kanto Chemical Co., Japan) and 4.5 mL 35% HCl (Kanto Chemical Co., Japan) in a closed Teflon vessel and was digested in a Microwave Digestion System (Berghof speedwave®, Germany). The digested soil samples were then transferred into a Teflon beaker and total volume was made up to 50 mL with Milli-Q water. The digested solution was then filtered by using syringe filter (DISMIC® — 25 HP PTFE, pore size = 0.45 μm) Toyo Roshi Kaisha, Ltd., Japan and stored in 50 mL polypropylene tubes (Nalgene, New York). Afterwards, the vessels were cleaned by Milli-Q water and dried in air. Finally, blank digestion with 5 mL HNO_3 was carried out to clean the digestion vessels.

For chemical partitioning of trace elements, soil samples were analyzed using Tessier sequential chemical extraction procedure (Tessier et al., 1979). The sequential extraction procedure was divided into five operationally defined chemical fractions: (F1) the exchangeable fraction: readily soluble and exchangeable; (F2) the carbonate bound and specifically adsorbed fraction: carbonate-bound, specifically adsorbed and weak organic and inorganic complexes; (F3) the Fe–Mn oxides fraction: bound to iron and manganese oxides (Fe–Mn oxides); (F4) the organic/sulfide fraction: bound to stable organic and/or sulfide (organic) complexes; and (F5) the residual fraction: held in primary and secondary minerals within their crystal structure. The detailed geochemical fractionation procedure of soil is presented in Table S1.

2.4. Instrumentation and quality assurance

For trace elements, samples were analyzed using inductively coupled plasma mass spectrometer (ICP-MS). Multi-element Standard XSTC-13 (SPEX CertiPrep® USA) solutions was used to prepare calibration curve. The calibration curves with $R^2 > 0.999$ were accepted for concentration calculation. Internal calibration standard solutions containing 1.0 mg/L of indium, yttrium, beryllium, tellurium, cobalt and thallium were purchased from SPEX CertiPrep® USA. Working standards were prepared daily in 5% (V/V) HNO_3 at 69% ultrapure grade and were used. A blank also carried out in the sequential extraction experiment. All test batches were evaluated using an internal quality approach and validated if they satisfied the defined Internal Quality Controls (IQCs). Before starting the analysis sequence, relative standard deviation (RSD, < 5%) was checked by using tuning solution purchased from Agilent Technologies.

2.5. Data calculation

2.5.1. Ecological risk assessment

To assess the quality of soil, an integrated approach of pollution load index (PLI) of six trace elements is calculated according to Suresh et al. (2011). The PLI is defined as the n^{th} root of the multiplications of the contamination factor (CF) of trace elements.

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots\ldots \times CF_n)^{1/n} \quad (1)$$

where, $CF_{\text{trace elements}}$ is the ratio between the content of each element to the background values in soil, $CF_{\text{trace elements}} = CH_{\text{trace elements}} / CH_{\text{back}}$. The PLI gave an assessment of the overall toxicity status of the sample and also it is a result of the contribution of six trace elements.

Ecological risk index (*RI*) is also introduced to assess the contamination degree of trace elements in soils. The equations for calculating the *RI* were proposed by Guo et al. (2010); Luo et al. (2007) and are as follows.

$$C_f^i = \frac{C^i}{C_n^i}, \qquad C_d = \sum_{i=1}^{n} C_f^i \quad (2)$$

$$E_r^i = T_r^i \times C_f^i, \qquad RI = \sum_{i=1}^{m} E_r^i \quad (3)$$

where, C_f^i is the single element contamination factor, C^i is the content of the trace elements in samples and C_n^i is the reference value of the trace elements. The reference values of Cr, Ni, Cu, As, Cd and Pb in soils were 90, 68, 45, 13, 0.3 and 20 mg/kg, respectively (Turekian and Wedepohl, 1961). The sum of C_f^i for all trace elements examined represents the integrated pollution degree (C_d) of the environment, E_r^i is the potential ecological risk index of an individual element and T_r^i is the biological toxic factor of an individual element. The toxic-response factors for Cr, Ni, Cu, As, Cd and Pb were 2, 6, 5, 10, 30 and 5, respectively (Amuno, 2013; Gong et al., 2008; Guo et al., 2010; Hakanson, 1980; Islam et al., 2015b; Jintao et al., 2011; Luo et al., 2007; Wu et al., 2010). Ecological risk index is the comprehensive potential ecological index, which is the sum of E_r^i. It represents the sensitivity of the biological community to the toxic substance and illustrates the ecological risk caused by the overall contamination.

2.5.2. Health risk assessment

Numerical expressions for performing non-cancer risk assessments for the local residents were taken from the US Environmental Protection Agency "Exposure Factors Handbook" (USEPA, 1997). For

Table 2
Physicochemical properties (mean ± SD) of soils, at different types of land uses, of Bogra District urban area, Bangladesh.

Land types	pH (1:2.5 H_2O)	EC (μS/cm)	Organic carbon (g/kg)	Sand (g/kg in < 2 mm)	Silt	Clay	Soil texture[a]
AF	6.7 ± 1.1	170 ± 76	24 ± 12	530	250	220	Sandy clayey loam
MW	6.4 ± 1.9	34 ± 19	6.1 ± 4.2	680	200	120	Sandy loam
PG	5.7 ± 0.55	17 ± 6.0	5.8 ± 7.6	890	60	50	Sand
RS	7.2 ± 0.69	16 ± 5.9	8.8 ± 4.1	670	240	90	Sandy loam
WD	6.3 ± 1.1	41 ± 39	13 ± 6.5	750	150	100	Sandy loam
CS	5.8 ± 1.4	35 ± 25	4.3 ± 3.7	810	150	40	Loamy sand
CW	8.0 ± 1.2	36 ± 28	11 ± 4.1	570	240	190	Sandy clayey loam
PS	6.1 ± 1.1	12 ± 3.8	8.4 ± 0.65	580	180	240	Sandy clayey loam

[a] According to the United States Department of Agriculture soil classification system.

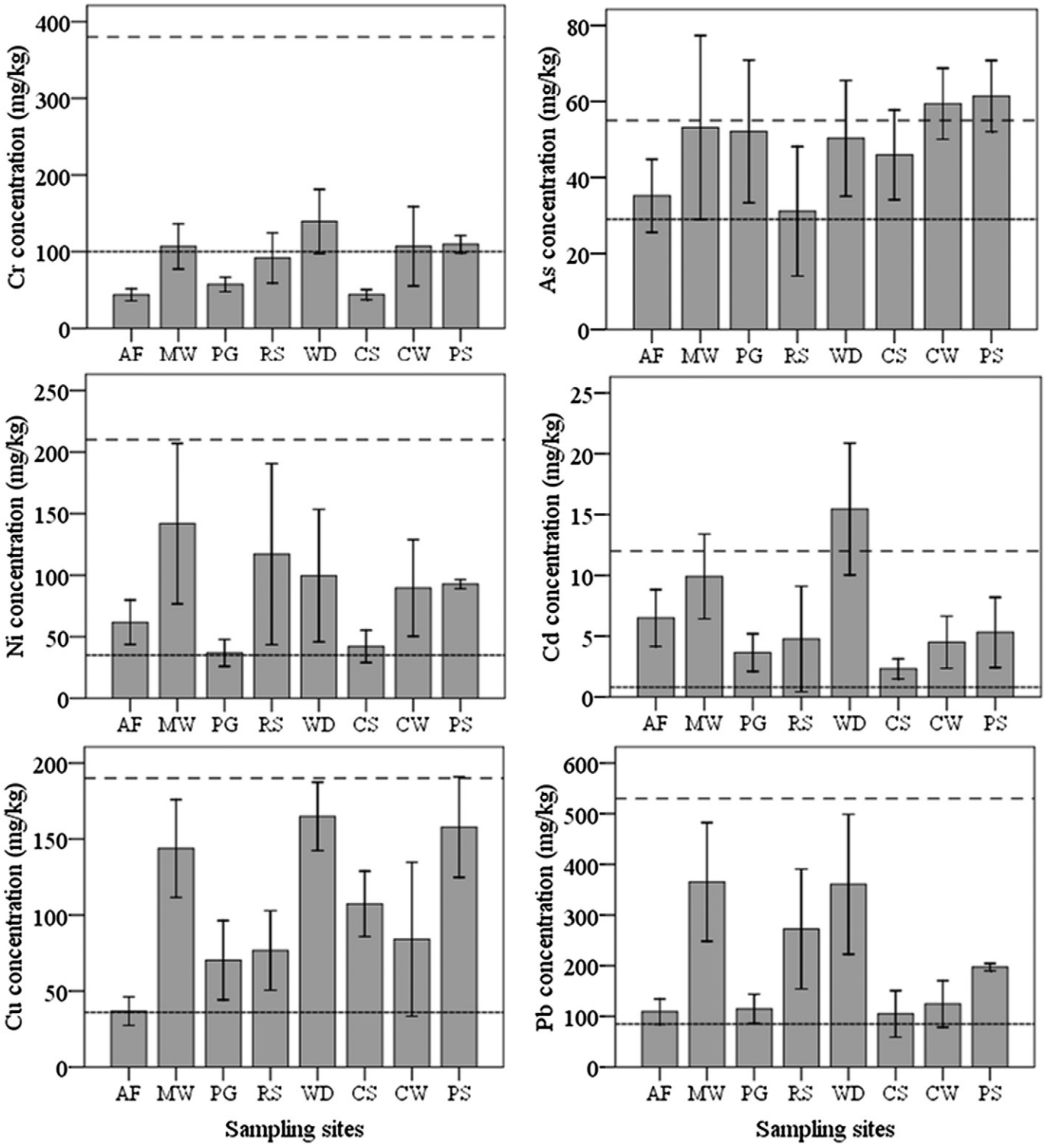

Fig. 2. Bar chart of metalloid (As) and trace elements (Cr, Ni, Cu, Cd and Pb) of eight different types of land uses. AF = agriculture farm, MW = metal workshop, PG = play ground, RS = railway station, WD = waste dispose, CS = construction site, CW = car repairing workshop and PS = petrol station. Bar represents ±standard deviation. Solid and dotted lines indicate the Dutch Soil Quality Target and the Intervention Values, respectively.

trace elements in the contaminated soils, ingestion and dermal absorption play the most important roles among the potential exposure pathways (Fryer et al., 2006; Qu et al., 2012). For instance, Ordóñez et al. (2011) found that ingestion of soil is the most common exposure pathway for As, Cd, Cr, Cu, Ni, and Pb in the mercury mining areas of Northern Spain. Considering the ingestion pathway, the average daily intakes (ADIs) (mg/kg/day) through ingestion (ADI_{ingest}) for adults and children were estimated using the Eq. (4).

$$ADI_{ingest} = \frac{C_{soil} \times IngR \times EF \times ED}{BW \times AT} \times CF \quad (4)$$

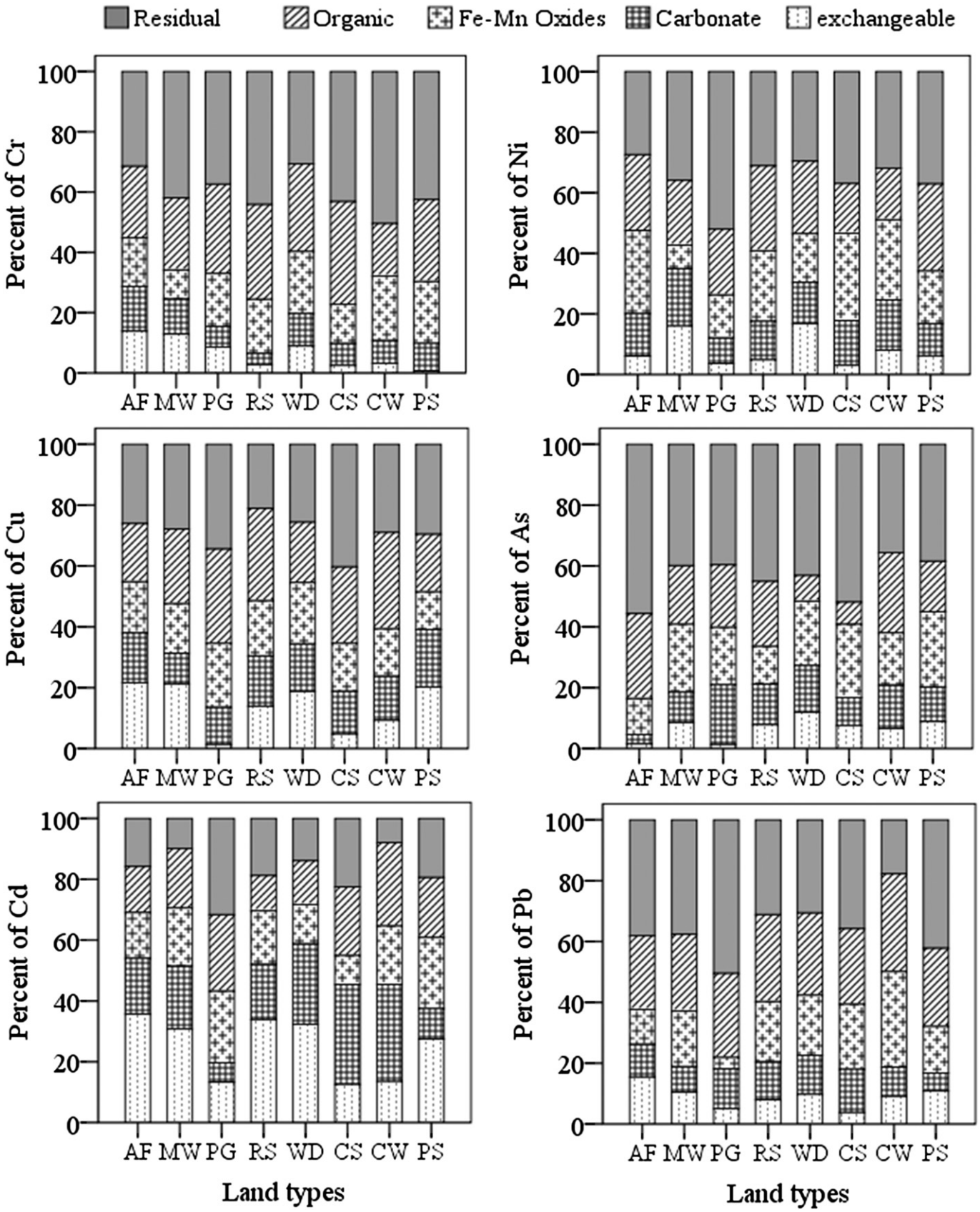

Fig. 3. Geochemical distribution of trace elements in different land type uses of soil in Bogra District, Bangladesh.

where, C_{soil} is the trace element concentration in soil (mg/kg), IngR is the ingestion rate of soil (mg/day), EF is the exposure frequency (days/year), ED is the exposure duration (years), BW is the average body weight (kg), AT is the average time (days) and CF is the conversion factor (1×10^{-6} mg/kg).

Conservative soil ingestion rate (IngR) of 100 mg/day was chosen for adults and 200 mg/day for children (Calabrese et al., 1987; USEPA, 1997). The exposure duration (ED) was chosen for six years and exposure frequency (EF) was assumed to be 350 days/year whereby workers, farmers or children are working or playing on the farms all year round (except 15 days for holiday and the average time (AT) was 2190 days for workers and farmers). In this study, the body weight was 60 kg for an adult and 15 kg for child (FAO, 2006; Islam et al., 2014b; Islam et al., 2015a; Lee et al., 1994).

After the ADI for the exposure pathways (ADI_{ingest}) was calculated, a hazard quotient (HQ) based on non-cancer risk can be calculated by dividing the average daily dose to a specific reference dose (RfD): Eq. (5) (USEPA, 1989).

$$HQ = \frac{ADI}{RfD}. \quad (5)$$

The reference dose (RfD) (mg/kg/day) is an estimation of maximum permissible risk on human population through daily exposure taking into consideration of sensitive group (children) during a lifetime. In general, the RfD for ingestion exposure pathway; where the RfD for Cr, Ni, Cu, As, Cd and Pb were 0.003, 0.02, 0.04, 0.0003, 0.0005 and 0.0035 mg/kg/day, respectively (USDOE, 2011; USEPA, 2002). If the ADI is less than the RfD, HQ ≤ 1, it is considered that there will be no adverse health effects, whereas if the ADI exceeds the RfD, HQ > 1, it is likely that there will be adverse health effects (USEPA, 1989, 2001). Furthermore, the guidelines for health risk assessment of chemical mixtures assumed that "simultaneous sub-threshold exposures to several chemicals could result in an adverse health effect" and "the magnitude of the adverse effect will be proportional to the sum of the ratios of the sub-threshold exposures to acceptable exposures" (USEPA, 1986). Hence, HQs can be added and generate a hazard index (HI) to estimate the risk of mix contaminates Eq. (6) (USEPA, 1989). The guidelines also state that "any single chemical with an exposure level greater than the toxicity value will cause the hazard index to exceed unity, for multiple chemical exposures the Hazard Index can also exceed unity even if no single chemical exposure exceeds its RfD".

$$HI = \sum HQ_i. \quad (6)$$

The hazard index (HI) is used to assess the total non-cancer risk for mixed trace metals and/or multiple exposure pathways. The total non-cancer risk for mixed metals can be calculated by adding the HQs of the different contaminants for a specific exposure pathway, as shown in Eq. (7) (USEPA, 1989).

$$HI = HQ(\text{elements } 1) + HQ(\text{elements } 2) + \ldots\ldots\ldots + HQ(\text{elements } n). \quad (7)$$

Table 3
Contamination factors, degree of contamination, contamination level and pollution load index of trace elements in soils.

Sites	Contamination factors (C_f^i)						Degree of contamination (C_d)	Contamination level	PLI
	Cr	Ni	Cu	As	Cd	Pb			
AF	0.49	0.91	0.82	2.7	**22**	5.5	**32**	Very high	**2.2**
MW	1.2	2.1	3.2	4.1	**33**	18	**62**	Very high	**5.2**
PG	0.64	0.54	1.6	4.0	**12**	5.7	**25**	Very high	**2.3**
RS	1.0	1.7	1.7	2.4	**16**	14	**36**	Very high	**3.4**
WD	1.6	1.5	3.7	3.9	**51**	**18**	**80**	Very high	**5.6**
CS	0.49	0.62	2.4	3.5	**7.7**	5.2	20	Considerable	**2.2**
CW	1.2	1.3	1.9	4.6	**15**	**6.2**	**30**	Very high	**3.3**
PS	1.2	1.4	3.5	4.7	**18**	**9.9**	**38**	Very high	**4.1**

Note: Bold indicates very high contamination.

Table 4
Ecological risk factors E_r^i and potential ecological risk indexes (PER) of trace elements in soils.

Sites	Ecological risk factor (E_r^i)						Risk index	Pollution degree
	Cr	Ni	Cu	As	Cd	Pb		
AF	1.0	5.4	4.1	27	**650**[a]	27	**715**	Very high
MW	2.4	13	16	41	**991**	91	**1154**	Very high
PG	1.3	3.2	7.8	40	**364**	29	**446**	Very high
RS	2.0	10	8.5	24	**477**	68	**589**	Very high
WD	3.1	8.8	18	39	**1545**	90	**1704**	Very high
CS	1.0	3.7	12	35	231	26	**309**	Very high
CW	2.4	7.9	9.3	46	**449**	31	**546**	Very high
PS	2.4	8.2	18	47	**531**	49	**656**	Very high

[a] Bold numbers indicate very high potential ecological risk factors.

2.5.3. Statistical analysis

The data were statistically analyzed using the statistical package, SPSS 16.0 (SPSS, USA). The means and standard deviations of the trace element concentrations in soils were calculated. For health risk, the median, 5th and 95th percentile values were calculated.

3. Results and discussion

3.1. Physicochemical properties and metal concentration in soil

The physicochemical properties of soil are presented in Table 2. The studied soils were slightly acidic to neutral except CW site (pH 8.0). The range of organic carbon (g/kg) was 4.3 to 24 and the highest value was observed in soil collected from AF site. The concentrations of trace elements (Cr, Ni, Cu, As, Cd and Pb) in soils of different land type uses are presented in Fig. 2 and Table S2. The mean concentrations of trace elements in soil were in the decreasing order of Pb > Cu > Ni > Cr > As > Cd. The levels of trace elements varied among the sampling sites of different types of land uses. The highest mean concentration of Cr was obtained at WD site (140 mg/kg), whereas the lowest was obtained at CS site (37 mg/kg) (Table S2). WD and MW sites showed comparatively higher levels of metals than the other sites (Fig. 2). The highest mean concentration of Cd was obtained in soil collected from the WD site (15 mg/kg), which was due to release of Cd from household waste and other sources. The highest mean concentration of Pb was obtained in soil at the MW site (365 mg/kg). During our sampling campaign, we found metal processing factories that are releasing their waste to this site. The studied elements might be derived from the anthropogenic factors such as the agrochemical materials (including fertilizers and pesticides) according to the previous reports (Karim et al., 2008; Nziguheba and Smolders, 2008). From the data, it was observed that some trace metals showed higher standard deviation, and such high deviation may be indicative of the lack of uniformity of the elemental distribution across the sites. Possible causes for this may have been due to the intensification of land use activities, such as digging, excavation, and construction, as well as other natural processes, such as weathering and erosion, which could alter stabilization of the soil environment (Amuno, 2013).

The mean concentrations of the studied trace elements were compared with the Dutch Soil Quality Standard (VROM, 2000), Canadian Environmental Quality Guidelines (CCME, 2003) and Australian Guideline for Soil Quality (DEP, 2003) (Fig. 2 and Table S2). Trace elements in soil of the most sites were higher than Dutch Soil Quality Target Value

Table 5
Indices and grades of potential ecological risk of trace element pollution (Amuno, 2013; Hakanson, 1980; Luo et al., 2007).

C_f^i	Degree of contamination for individual element	C_d	Contamination degree of the environment	E_r^i	Grades of ecological risk of individual element	RI	Grades of potential ecological risk of the environment
$C_f^i < 1$	Low	$C_d < 5$	Low	$E_r^i < 40$	Low risk	$RI < 65$	Low risk
$1 \le C_f^i < 3$	Moderate	$5 \le C_d < 10$	Moderate	$40 \le E_r^i < 80$	Moderate risk	$65 \le RI < 130$	Moderate risk
$3 \le C_f^i < 6$	Considerable	$10 \le C_d < 20$	Considerable	$80 \le E_r^i < 160$	Considerable risk	$130 \le RI < 260$	Considerable risk
$C_f^i \ge 6$	Very high	$C_d \ge 20$	Very high	$160 \le E_r^i < 320$	High risk	$RI \ge 260$	Very high risk
				$E_r^i \ge 320$	Very high risk		

(Fig. 2). The functional properties of these soils such as nutrients and contaminant storage, transformation and biomass production may be seriously affected due to continuous crop production, which could potentially cause adverse effect on humans, plants and animals (VROM, 2000). The present study mainly used the Dutch Soil Quality Standard (VROM, 2000) which is regarded as the most comprehensive guideline considering all possible exposure pathways for protecting humans, plants and animals. Trace element concentration in soil below its respective Dutch Target Value is considered being clean and safe. If the concentration level lies between the target values and intervention values, the soil is regarded as slightly to moderately contaminated. In contrast, if the value is above the Dutch Intervention Value, the soil is considered to be detrimental to humans, plants and animals. The mean concentration of Cd and Pb was much higher than Dutch Target Value, Canadian Environmental Quality Guidelines and Australian Guidelines (Table S2) which elucidated that the level of Cd and Pb in soil was the most caution to the ecosystems of the study area.

3.2. Geochemical distribution of trace elements in soil

The mobility and toxicity of trace elements are mainly dependent on metal speciation in soil. The relative distributions of trace elements in different fractions of soils are shown in (Fig. 3). In general, results indicated that Cr, Ni, Cu, As and Pb were predominantly associated with the residual fraction for Cr (31–50%), Ni (27–52%), Cu (21–40%), As (36–56%) and Pb (18–51%) (Fig. 3). In this study, the residual phase is believed to consist mainly of primary and secondary minerals, which hold metals within their crystalline structure (Islam et al., 2014a,b; Murray et al., 1999; Szolnoki and Farsang, 2013). In the case of Cu, the organic bound fraction (coinciding with organic matter and sulfides) was also noticeable (19–32%). These findings are in agreement with the results obtained by Wang et al. (1998), where it was stated that high proportions of Cu in the organic bound fraction was due to the high stability of the organic Cu complexes. Like for Cu, also a considerable fraction of Cr, Ni and Pb in the studied soils are bound to the organic phases. In comparison with other metals, Cd displayed a distinct character in soil. According to the partitioning pattern, a considerable proportion of Cd was associated with the exchangeable fraction (13–36%), which indicated that the surface soil was contaminated with Cd originating from anthropogenic activities. Chlopecka et al. (1996) reported that metals from anthropogenic sources are more mobile than those derived from parent materials. Higher proportion of Cd in the exchangeable fraction indicated that Cd from AF, MW, RS, WD and PS sites can easily entered into the agricultural crops and other soil living organisms as well.

3.3. Assessment of ecological risk

Ecological risk assessment for trace element pollution in the environment was performed following the methodology developed by Hakanson (1980). In the present study, values of contamination factor (C_f^i) existed in the order of Cd > Pb > As > Cu > Ni > Cr in soils of different types of land uses (Table 3). The assessment of integrated trace element pollution in soil was based on the degree of contamination (C_d). The degree of contamination of most sites showed very high to considerable degree of contamination, and followed the descending order of WD > MW > PS > RS > AF > CW > PG > CS. The element specific degree of contamination (C_d) in the studied soils was considerable to very high class, where the range of degree of contamination was 20–80 (Table 3). Among the studied metals, Cd showed very high contamination for all sites, whereas Pb posed very high contamination factor at WD, CW and PS sites (Table 3). According to Suresh et al. (2011), pollution load index (PLI) value equal to zero indicates non-polluted; value of unity indicates the presence of only baseline level of pollutants and values above unity indicates progressive deterioration due to trace element pollution. Extent of pollution increases with the increased PLI value. As per above grade, present study depicted that soils were considerably polluted, since PLI of all sites were higher than unity (Table 3).

The ecological risk factor for individual element (E_r^i) and the potential ecological risk index (RI) are summarized in Table 4. The potential ecological risk factor of trace elements in soils were in the descending order of Cd > Pb > As > Cu > Ni > Cr. Considering the potential ecological risk factor (E_r^i) for the individual element, Cd showed very high potential ecological risk with the E_r^i factor ranging between 231–1545 (Table 4). Potential ecological risk factor of individual elements was low. The sites AF, MW and WD showed a considerable ecological risk for Cd which might be due to the application of phosphate fertilizers to the agricultural fields and waste disposal from the town (ATSDR, 2008). The potential ecological risk indexes (RIs) in the sampling sites ranged from 309 to 1704, indicating very high risk (Table 4). The contamination factor (C_f^i), degree of contamination (C_d), ecological risk (E_r^i) and risk index (RI) classes are shown in Table 5. Ecological risk assessment showed that Cd posed potential ecological risk for all sites, whereas, WD, MW, PS and RS sites were prevalently contaminated by the other elements.

3.4. Health risk assessment

In this study, total trace element concentrations were used to estimate the non-carcinogenic risk on human through ingestion of soil. In order to evaluate the risk, the average daily intakes (ADIs), hazard quotients (HQs) and hazard index (HI) of the studied metals were estimated for adults and children and the results are presented in Figs. 4 and 5 and Tables 6 and S3. Among the investigated trace elements; people are mostly exposed to As, Cd and Pb for most of the sites. The hazard quotients (HQs) values were found in the descending order of As > Pb > Cd > Cr > Cu > Ni for both adults and children. The non-cancer health risks related to individual element exposure through soil ingestion was low for all investigated elements except As, which resulted in a HQ > 1, indicating a potential risk for both adults and children (Figs. 4 and 5 and Table S3). The combined effects of exposed metals and metalloids were calculated as hazard index (HI) and the data indicated that the HI values were > 1. Therefore, most of the sites posed high risk to the exposed adults and children (Table 6). The risk index values for children were higher than that of adult inhabitants indicating children were more susceptible to the trace elements. The elevated non-cancer risk noted in soil from AF was mainly attributed to the level of As. Arsenic in agricultural soils can be derived from the uncontrolled application of As contaminated herbicides, pesticides, wood preservatives (Nriagu and Pacyna, 1988), and low quality As-enriched fertilizers (Renner, 2004). In general, the selected types of

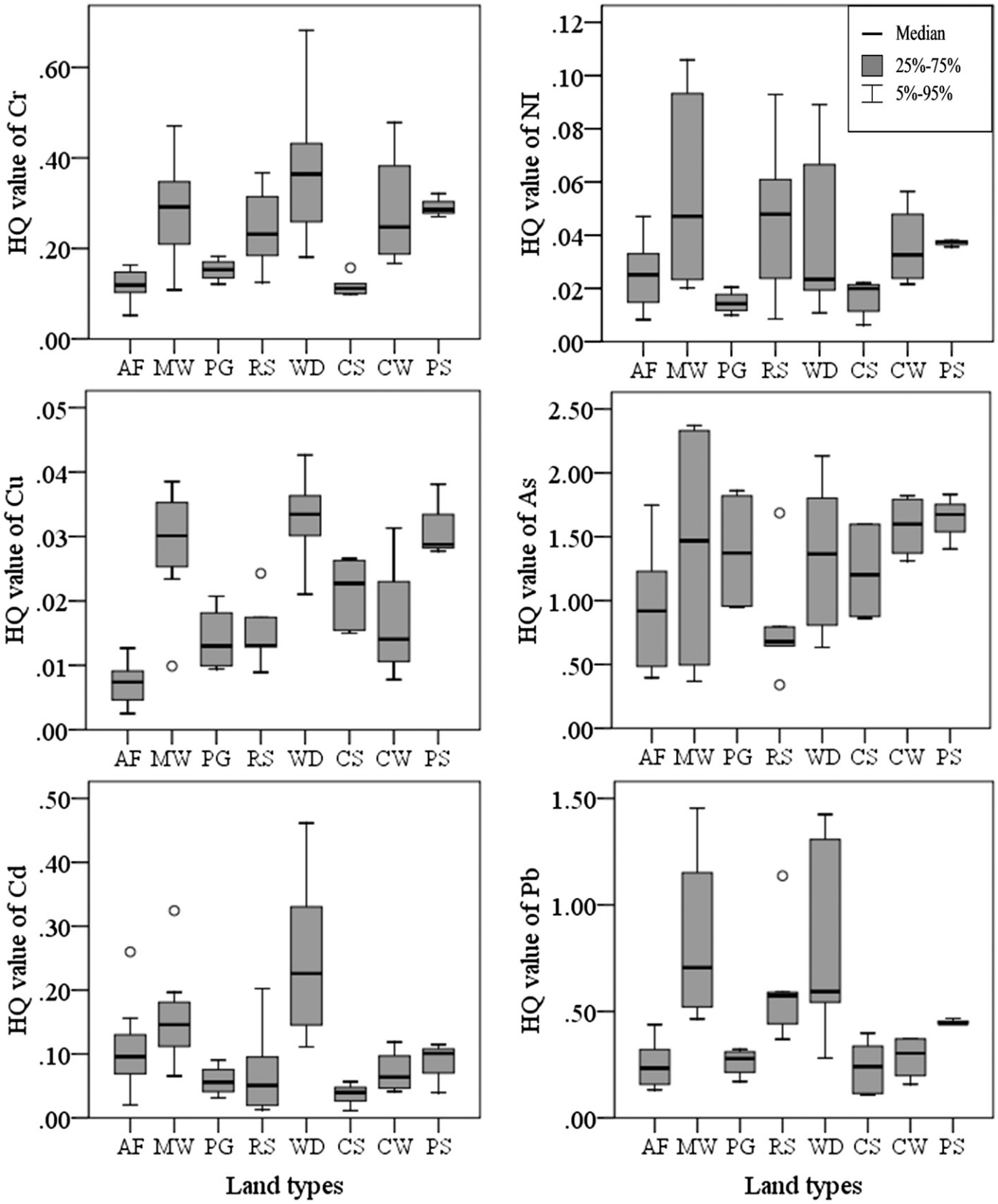

Fig. 4. Hazard quotients (HQ) of adult residents due to trace element exposure to soil from land type uses.

land use in the study areas were more detrimental to children than adults through ingestion of soil. Children might be exposed to soil bounded contaminants, including trace metals, at elevated levels due to their behaviors increasing indirect ingestion by way of hand-to-mouth activities, touching and mouthing of various dust-contaminated objects (Mielke et al., 1999). Through ingestion, children tend to be exposed to greater amounts of soil than adults due to pica and play behavior (Beamer et al., 2008; CDC, 2005; Murgueytio et al., 1998).

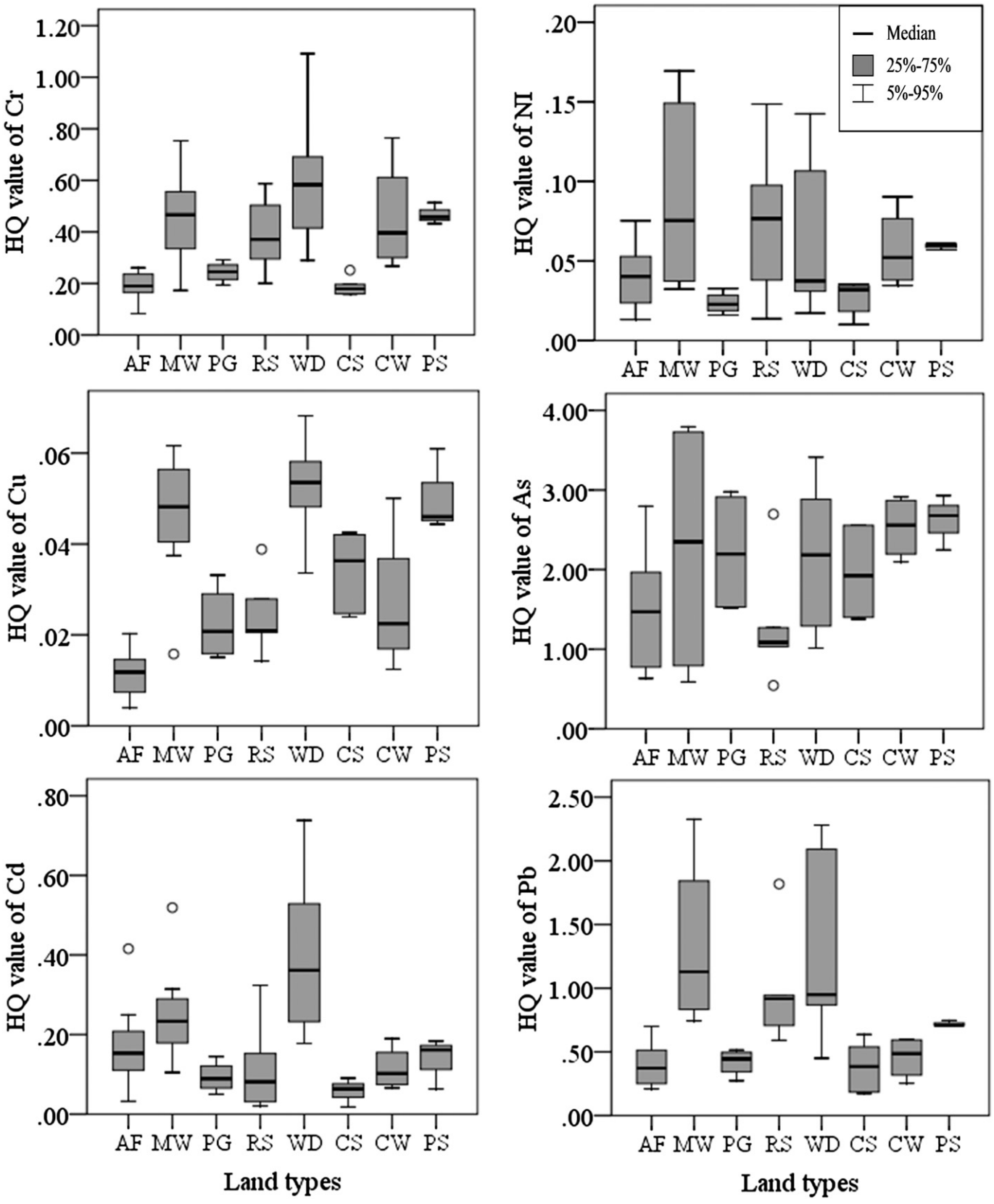

Fig. 5. Hazard quotients (HQ) of children due to trace element exposure to soil from land type uses.

4. Conclusions

In this paper, an attempt has been made to describe the problem of soil potentially toxic element contamination in different land use types and the resulting of ecological risks and health risks. In the case of the study area, there is an understanding that the associated soils (especially MW, RS, WD and PS) are enriched with some potentially toxic elements, particularly As, Cd and Pb. The accidental soil ingestion for

Table 6
Hazard index (HI) of ingestion of soil in adult and child in eight different types of land uses based on trace metal exposure.

Sampling sites	Hazard index (HI) due to ingestion of metals from soil							
	Adult				Child			
	Min	Median	Max	Mean ± SD	Min	Median	Max	Mean ± SD
AF	0.72	1.4	2.4	1.4 ± 0.58	1.2	2.2	3.9	2.3 ± 0.93
MW	1.6	2.9	4.2	2.8 ± 0.94	2.6	4.6	6.6	4.4 ± 1.5
PG	1.3	1.9	2.5	1.9 ± 0.56	2.2	3	3.9	3.0 ± 0.89
RS	1.1	1.5	3.5	1.8 ± 1.0	1.8	2.3	5.6	2.9 ± 1.5
WD	2.1	2.9	3.4	2.9 ± 0.48	3.4	4.6	5.5	4.6 ± 0.78
CS	1.1	1.6	2.2	1.7 ± 0.52	1.8	2.6	3.5	2.6 ± 0.83
CW	1.7	2.3	2.8	2.3 ± 0.52	2.7	3.6	4.5	3.6 ± 0.83
PS	2.3	2.6	2.7	2.5 ± 0.21	3.7	4.1	4.3	4.1 ± 0.33

children is the major pathway of the potential hazardous element exposure with high substantial values based on high HI (HI > 1). Children are the most vulnerable to the soil contamination and adults are also susceptible to the potential risks as well. Further detailed study is recommended on soil and inhabitants of the study area in order to assess a comprehensive risk due to trace element contamination.

Acknowledgments

The authors thank the authority of Patuakhali Science and Technology University, Bangladesh, Soil Resources Development Institute (SRDI), Bangladesh and Yokohama National University, Japan for providing laboratory facilities. The authors are also delighted to express their gratefulness and sincerest thanks to Professor Dr. Md Shams-Ud-Din (Vice Chancellor, PSTU), for his valuable suggestions and cooperation to carry out this research. Furthermore, we are thankful for the kind help from the members of the Department of Soil Science, Patuakhali Science and Technology University, Bangladesh during the field sampling.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.gexplo.2015.07.017.

References

Amuno, S.A., 2013. Potential ecological risk of heavy metal distribution in cemetery soils. Water Air Soil Pollut. 224, 1435–1446.
ATSDR, 2008. Agency for Toxic Substances and Disease Registry. Division of Toxicology and Environmental Medicine/Applied Toxicology Branch, MN (Retrieved March 10 2012, from http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=102&tid=23S).
Beamer, P., Key, M.E., Ferguson, A.C., Canales, R.A., Auyeung, W., Leckie, J.O., 2008. Quantified activity pattern data from 6 to 27 month-old farmworker children for use in exposure assessment. Environ. Res. 108, 239–246.
Bellinger, D., 1995. Neuropsychologic functions in children exposed to environmental lead. Epidemiology 6, 101–103.
Bryant, C.R., Johnston, T.R.R., 1992. Agriculture in the City's Countryside. Belhaven, London.
Calabrese, E.J., Kostecki, P.T., Gilbert, C.E., 1987. How much dirt do children eat? An emerging environmental health question. Comments Toxicol. 1, 229–241.
CCME (Canadian Council of Ministers of the Environment), 2003. Canadian Environmental Quality Guidelines.
CDC (Centers for Disease Control and Prevention), 2005. Preventing Lead Poisoning in Young Children. CDC (Centers for Disease Control and Prevention), Atlanta.
Chen, T.B., Zheng, Y.M., Chen, H., et al., 2005. Arsenic accumulation in soils for different land use types in Beijing (in Chinese). Geogr. Res. 24 (2), 229–235.
Chlopecka, A., Bacon, J.R., Wilson, M.J., Kay, J., 1996. Forms of cadmium, lead and zinc in contaminated soils from southwest Poland. J. Environ. Qual. 25, 69–79.
DEP (Department of Environmental Protection), 2003. Assessment Levels for Soil, Sediment and Water Contaminated Sites Management Series Perth's, Australia, www.environ.wa.gov.au/.
FAO (Food and Agriculture Organization), 2006. Arsenic Contamination of Irrigation Water, Soil and Crops in Bangladesh: Risk Implications for Sustainable Agriculture and Food Safety in Asia. Food and Agriculture Organization of the United Nations Regional Office for Asia and the Pacific, Bangkok.
Fryer, M., Collins, C.D., Ferrier, H., Colvile, R.N., Nieuwenhuijsen, M.J., 2006. Human exposure modeling for chemical risk assessment: a review of current approaches and research and policy implications. Environ. Sci. Pol. 9, 261–274.
Gimeno-García, E., Andreu, V., Boluda, R., 1996. Heavy metals incidence in the application of inorganic fertilizers and pesticides to rice farming soils. Environ. Pollut. 92 (1), 19–25.
Gomez-Parra, A., Forja, J.M., DelValls, T.A., Saenz, I., Riba, I., 2000. Early contamination by heavy metals of the Guadalquivir estuary after the Aznalcóllar mining spill (SW Spain). Mar. Pollut. Bull. 40 (12), 1115–1123.
Gong, Q., Deng, J., Xiang, Y., Wang, Q., Yang, L., 2008. Calculating pollution indices by heavy metals in ecological geochemistry assessment and a case study in parks of Beijing. J. China Univ. Geosci. 19 (3), 230–241.
Guo, W., Liu, X., Liu, Z., Li, G., 2010. Pollution and potential ecological risk evaluation of heavy metals in the sediments around Dongjiang Harbor, Tianjin. Procedia Environ. Sci. 2, 729–736.
Ha°kanson, L., 1980. An ecological risk index for aquatic pollution control: a sedimentological approach. Water Res. 14, 975–1001.
Islam, M.S., Ahmed, M.K., Al-Mamun, M.H., 2014a. Heavy metals in cereals and pulses: health implications in Bangladesh. J. Agric. Food Chem. 62, 10828–10835.
Islam, M.S., Ahmed, M.K., Al-Mamun, M.H., Masunaga, S., 2014b. Trace metals in soil and vegetables and associated health risk assessment. Environ. Monit. Assess. 186, 8727–8739.
Islam, M.S., Ahmed, M.K., Al-Mamun, M.H., 2015a. Metal speciation in soil and health risk due to vegetables consumption in Bangladesh. Environ. Monit. Assess. 187, 288–303.
Islam, M.S., Ahmed, M.K., Al-Mamun, M.H., Masunaga, S., 2015b. Potential ecological risk of hazardous elements in different land-use urban soils of Bangladesh. Sci. Total Environ. 512–513, 94–102.
ISO-11464, 2006. Soil Quality — Pretreatment of Samples for Physico-chemical Analysis. International Standard Organization, Geneva, Switzerland.
Jintao, L., Chen, C., Song, X., Han, Y., Liang, Z., 2011. Assessment of heavy metal pollution in soil and plants from Dunhua sewage irrigation area. Int. J. Electrochem. Sci. 6, 5314–5324.
Karim, R.A., Hossain, S.M., Miah, M.M.H., Nehar, K., Mubin, M.S.H., 2008. Arsenic and heavy metal concentrations in surface soils and vegetables of Feni District in Bangladesh. Environ. Monit. Assess. 145, 417–425.
Khan, S., Cao, Q., Zheng, Y.M., Huang, Y.Z., Zhu, Y.G., 2008. Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. Environ. Pollut. 152, 686–692.
Lee, M.M., Wuwilliams, A., Whittemore, A.S., Zheng, S., Gallagher, R., Teh, C.Z., Zhou, L., Wang, X., Chen, K., Ling, C., et al., 1994. Comparison of dietary habits, physical-activity and body-size among Chinese in North-America and China. Int. J. Epidemiol. 23 (5), 984–990.
Liu, W., Zhao, J., Ouyang, Z., Soderlund, L., Liu, G., 2005. Impacts of sewage irrigation on heavy metal distribution and contamination in Beijing, China. Environ. Int. 31 (6), 805–812.
Ljung, K., Oomen, A., Duits, M., Selinus, O., Berglund, M., 2007. Bioaccessibility of metals in urban playground soils. J. Environ. Sci. Health, Part A: Tox. Hazard. Subst. Environ. Eng. 42, 1241–1250.
Luo, W., Lu, Y., Gisey, J.P., Wang, T., Shi, Y., Wang, G., Xing, Y., 2007. Effects of land use on concentrations of metals in surface soils and ecological risk around Guanting Reservoir, China. Environ. Geochem. Health 29, 459–471.
Luo, X.S., Yu, S., Zhu, Y.G., Li, X.D., 2012. Trace metal contamination in urban soils of China. Sci. Total Environ. 421–422, 17–30.
Man, Y.B., Sun, X.L., Zhao, Y.G., Lopez, B.N., Chung, S.S., Wu, S.C., Cheung, K.C., Wong, M.H., 2010. Health risk assessment of abandoned agricultural soils based on heavy metal contents in Hong Kong, the world's most populated city. Environ. Int. 36, 570–576.
Mielke, H.W., Gonzales, C.R., Smith, M.K., Mielke, P.W., 1999. The urban environment and children's health: soils as an integrator of lead, zinc, and cadmium in New Orleans, Louisiana, USA. Environ. Res. 81, 117–129.
Murgueytio, A.M., Evans, R.G., Sterling, D., Serrano, F., Roberts, D., 1998. Behaviors and blood lead levels of children in a lead-mining area and a comparison community. J. Environ. Health 60, 14–20.
Murray, K.S., Cauvet, D., Lybeer, M., Thomas, J.C., 1999. Particle size and chemical control of heavy metals in bed sediment from the Rouge River, Southeast Michigan. Environ. Sci. Technol. 33, 987–992.
Nriagu, J., Pacyna, J., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 333, 134–139.
Nziguheba, G., Smolders, E., 2008. Inputs of trace elements in agricultural soils via phosphate fertilizers in European countries. Sci. Total Environ. 390, 53–57.
Ordóñez, A., Álvarez, R., Charlesworth, S.De., Miguel, E., Loredo, J., 2011. Risk assessment of soils contaminated by mercury mining, Northern Spain. J. Environ. Monit. 13, 128–136.
Qu, C.S., Sun, K., Wang, S.R., Huang, L., Bi, J., 2012. Monte Carlo simulation based health risk assessment of heavy metal pollution: a case study in Qixia mining area, China. Hum. Ecol. Risk. Assess. 18 (4), 733–750.
Radha, R., Tripathi, R.M., Vinod, K.A., Sathe, A.P., Khandekar, R.N., Nambi, K.S.V., 1997. Assessment of Pb, Cd, Cu and Zn exposures of 10 year old children in Mumbai. Environ. Res. 80, 215–221.
Renner, R., 2004. Arsenic and lead leach out of popular fertilizer. Environ. Sci. Technol. 38, 382A.
Singh, A.N., Zeng, D.H., Chen, F.S., 2005. Heavy metal concentrations in redeveloping soil of mine spoil under plantations of certain native woody species in dry tropical environment, India. J. Environ. Sci. 1, 168–174.
Suresh, G., Ramasamy, V., Meenakshisundaram, V., Venkatachalapathy, R., Ponnusamy, V., 2011. Influence of mineralogical and heavy metal composition on natural radionuclide contents in the river sediments. Appl. Radiat. Isot. 69, 1466–1474.

Szolnoki, Z., Farsang, A., 2013. Evaluation of metal mobility and bioaccessibility in soils of urban vegetable gardens using sequential extraction. Water Air Soil Pollut. 224, 1737–1752.
Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51, 844–851.
Thornton, I., Farago, M.E., Thums, C.R., Parrish, R.R., McGill, R.A.R., Breward, N., Fortey, N.J., Simpson, P., Young, S.D., Tye, A.M., Crout, N.M.J., Hough, R.L., Watt, J., 2008. Urban geochemistry: research strategies to assist risk assessment and remediation of brownfield sites in urban areas. Environ. Geochem. Health 30, 565–576.
Turekian, K.K., Wedepohl, K.H., 1961. Distribution of the elements in some major units of the earth's crust. Geol. Soc. Am. Bull. 72, 175–192.
US EPA, 1997. Exposure Factors Handbook. EPA/600/P-95/002F. Environmental Protection Agency, Office of Research and Development, Washington, D.C.
USDOE, 2011. The Risk Assessment Information System (RAIS). U.S. Department of Energy's Oak Ridge Operations Office (ORO).
USEPA, 1986. Guidelines for the Health Risk Assessment of Chemical Mixtures. 51 Federal Register 34014, Washington, D.C.
USEPA, 1989. Risk Assessment Guidance for Superfund, Vol. I: Human Health Evaluation Manual. EPA/540/1–89/002. Office of Solid Waste and Emergency Response, Washington, D.C.
USEPA, 2001. Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites. OSWER 9355.4–24. Office of Solid Waste and Emergency Response, Washington, D.C.
USEPA, 2002. Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites. U.S. Environmental Protection Agency, pp. 4–24 (OSWER 9355).
VROM (Volkshuisvesting, RuimtelijkeOrdening en Milieubeheer), 2000. Ministry of Housing, Spatial Planning and Environment. Circular on Target Values and Intervention Values for Soil Remediation. Ministry of Housing, Netherlands.
Wang, W.H., Wong, M.H., Leharne, S., Fisher, B., 1998. Fractionation and biotoxicity of heavy metals in urban dusts collected from Hong Kong and London. Environ. Geochem. Health 20, 185–198.
Wong, S.C., Li, X.D., Zhang, G., Qi, S.H., Min, Y.S., 2002. Heavy metals in agricultural soils of the Pearl River Delta, South China. Environ. Pollut. 119 (1), 33–44.
Wong, C.S.C., Li, X.D., Thornton, I., 2006. Urban environmental geochemistry of trace metals. Environ. Pollut. 142, 1–16.
Wu, Y., Xu, Y., Zhang, J., Hu, S., 2010. Evaluation of ecological risk and primary empirical research on heavy metals in polluted soil over Xiaoqinling gold mining region, Shaanxi, China. Trans. Nonferrous Metals Soc. China 20 (4), 688–694.
Zhao, L., Xu, Y., Hou, H., Shangguan, Y., Li, F., 2014. Source identification and health risk assessment of metals in urban soils around the Tanggu chemical industrial district, Tianjin, China. Sci. Total Environ. 468–469, 654–662.