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Distribution, bioaccessibility and human health risks of toxic metals in peri-urban topsoils of the Kumasi Metropolis

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ABSTRACT

The occurrence of heavy metals in urban soils is of great environmental concern due to the unwanted health effect associated with their excessive exposure. The study assessed levels of heavy metals (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sn, V, and Zn) in peri-urban communities of the Kumasi metropolis and evaluated sources and potential health risk associated with exposure to these metals. Soil samples collected from topsoils at a depth of 0–10 cm were subjected to x-ray fluorescence (XRF) spectroscopy analysis for total metal quantification. The XRF results were then confirmed by inductively coupled plasma mass spectrometry. Soil pH, conductivity, and total organic carbon were determined using standard procedures. The mean concentrations (mg/kg) of metals were As (10.11), Cd (12.91), Cr (77.97), Cu (20.20), Fe (23031), Pb (18.60), Mn (158.68), Ni (29.33), Sn (8.83), V (78.21) and Zn (49.27). The pH and electrical conductivity were in a range of 6.5 - 8.5 and 153 - 8990 µS/cm respectively. The mean total organic carbon was 8.85%. Pollution indicators such as enrichment factor, contamination factor, and pollution load index all showed that soil in the study area is of low degree of contamination. The potential ecological risk index projected a low-risk effect. In contrast, the hazard index and carcinogenic risk index indicated no significant human health risk associated with exposure to the metals presently. However, to regulate bioaccumulation effects, constant monitoring is essential.

Introduction

Peri-urban lands are routinely used worldwide for intensive farming activities, especially for vegetable farming. Many farmers normally apply fertilizers and pesticides to help improve crop yield and quality. These agricultural inputs are likely sources of heavy metals and their continuous application to soils could lead to increased heavy metal loads in soils. Additionally, soils in peri-urban communities could potentially be impacted by heavy metal pollution through the discharge

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of industrial effluents, municipal waste disposal, sewage, and sludge as well as vehicular emissions. The presence of these heavy metals in soils often leads to degradation of soil health and subsequent contamination of the food chain, primarily through the cultivation of vegetables on such soils. Vegetables grown on heavy metal contaminated soils usually suffer low yields due to a reduction in the plant's metabolic processes. Additionally, humans can be exposed to contaminants in polluted soils, especially the topsoils, via inhalation and dermal contact.

Soil serves as not only a sink for heavy metals but also a transmitter of accumulated heavy metals [1,2]. Soil can transmit heavy metal pollutants to groundwater, the atmosphere, and plants and animals. Thus, when soil is contaminated, there is a transfer of contaminants to other environmental components and could pose a threat to human health through the food chain or water supply systems [3]. Heavy metals, due to their non-biodegradable nature and their long half-lives for elimination in biological systems present a formidable risk. In the soil, heavy metals are usually immobile, and hence accumulation occurs over time [4].

Rapid population growth in many urban communities has led to a growing sprawl in communities on the fringes of these urban areas. As such, peri-urban communities are witnessing increasing commercial activities such as auto mechanic shops, increasing vehicular activities, and increased agricultural activities [5]. The increase in population invariably leads to increased generation of municipal waste and sewage. All these factors contribute to heavy metal pollution in soils of such communities. In the residential areas of many peri-urban communities, children are most likely to be exposed to heavy metals. Due to their frequent mouth-to-hand behaviour, children are in more frequent contact with soils in comparison to most adults. Children may deliberately or involuntarily ingest soils by mouthing dirty hands and objects and thus increasing their risk of exposure. Children are also more vulnerable than adults to the potential negative health effects of metal ingestion. While their smaller body mass increases the relative exposure to a given quantity of contaminants (per kg body mass), they also have a higher gastrointestinal absorption of metals [6]. Moreover, because their nervous system is not fully developed, they are more sensitive to neurotoxic metals such as Pb and Hg.

The potential risk due to metal intake is dependent on the amount of metal ingested and the bioaccessibility of that metal [7]. Metals in the soil are in different chemical and physical forms with different solubilities, which affect their bioaccessibility in the gastrointestinal tract [8]. Metals from anthropogenic emissions are commonly present in a more reactive form than those naturally occurring in minerals. This is because while added metals are sorbed on surfaces in initial stages, metals of natural origin may be incorporated into soil particles, which slows down the desorption process considerably [4,9]. The sorption of metals in soil is, however, a scale of different processes occurring at the same time and at different rates [10]. Characteristics of soil such as pH, organic matter, and clay content affect the sorption strength of metals. Low soil pH enhances the mobility of the metals, while the presence of organic matter and clay generally lowers the mobility and increases the metal content because more attractive binding sites are provided [11].

Kumasi is the second-largest city in Ghana. The metropolis is well-noted for its industrial and commercial activities [12]. The peri-urban areas of Kumasi are, however, without any significant industrial and commercial activities. Most of these communities are thus used mainly for agriculture and residential purposes. This work evaluated the levels of heavy metals in topsoils from peri–urban communities in the Kumasi metropolis. The environmental risks associated with the exposure to the metals were estimated from various hazard indices. Finally, oral bioaccessibility levels determined were used to assess the potential risk the metals pose to humans through ingestion.

Methods

Study area

Kumasi is a city in the Ashanti Region and is among the largest metropolitan areas in Ghana. The metropolis, which lies between latitude 6.35–6.40° and longitude 1.30–1.37° is a major commercial, industrial, and cultural centre in Ghana. The metropolis serves as a major commercial centre with commercial activities centred on trading with both financial and non-banking financial institutions also offering ancillary services for residents of the metropolis. The metropolis is approximately 500 km north of the Equator and 200 km north of the Gulf of Guinea. Kumasi features a tropical wet and dry climate, with relatively constant temperatures throughout the year [13]. The major geological formation in the metropolis is the middle Precambrian rock, with forest ochrosol as the major soil type. In most of the peri–urban communities, the soils are either granites (which are acidic) or phyllites (less acidic) [14].

Soil sampling

A total of 73 soil samples were collected during the sampling campaign in December 2016. The sites were in a systematic grid net map using a regular 2 km × 2 km over the survey area (Fig. 1). The points of intersection of the various longitude and latitude coordinates on the grid map were selected as the specific sampling points. For locations where sampling was impossible due to interference such as tarred roads, rivers, and houses, sampling was done by moving to the nearest accessible location within the same sample cell. Soil samples were taken from the topsoil (0–10 cm depths) at all locations using a plastic trowel. The position of sampling sites was recorded using a hand-held global positioning system. At every 5th point, duplicate samples were collected. Soil samples were placed into labelled Ziploc bags, sealed, and transported to the laboratory.

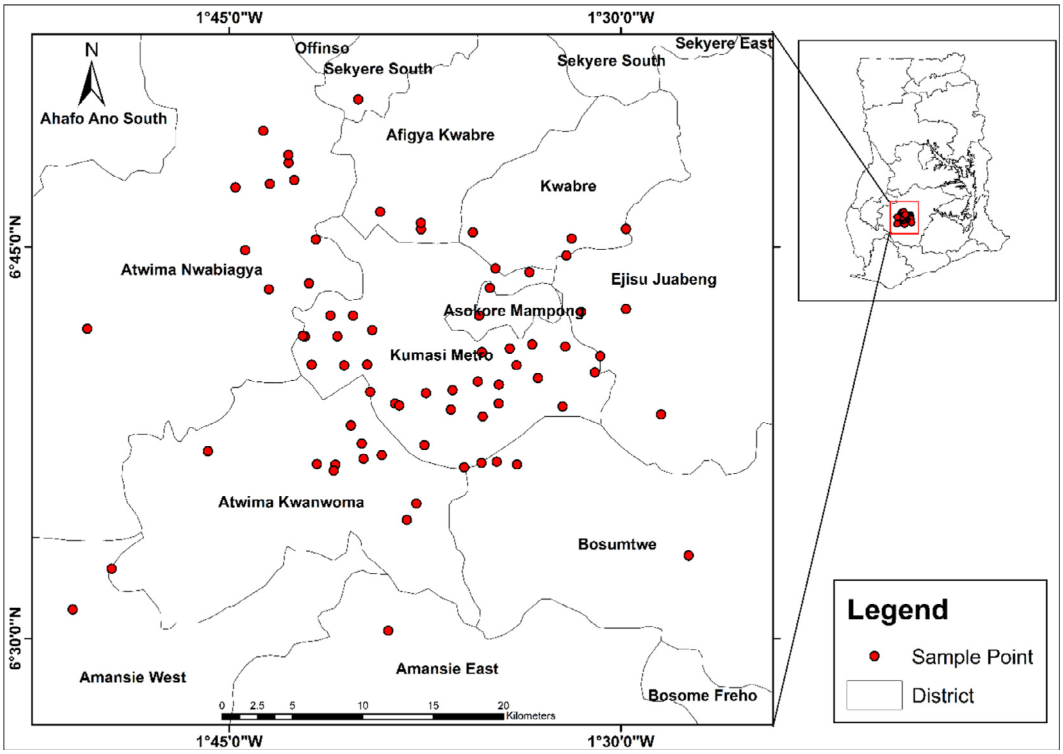

Fig. 1. Map of Kumasi showing sampling locations.

Sample preparation and analysis

Drying and sieving

The soil samples were air-dried to get a uniform mass and sieved to <250 µm using USA Standard Testing Sieve ASTM E11 for homogeneity and packed into coded Ziploc bags.

Soil pH and electrical conductivity

To determine soil pH and electrical conductivity, 40 mL of distilled water was added to 20 g of dry soil sample (1:2 ratio of soil to water), shaken vigorously, and allowed to stand for 1 h. A multi-parameter probe (Oakton Waterproof Multiparameter PCSTestr35) was then used to read the pH and electrical conductivity of the supernatant liquid [15].

Soil organic carbon

The loss on ignition method was used to evaluate soil organic carbon content. One gram of soil sample was placed in a porcelain dish and heated at 105 °C in an oven. After 2 h of heating, the porcelain dish was removed from the oven and cooled to room temperature for an hour in a desiccator. Samples were then heated again at 550 °C for 4 h in a Thermolyne muffle furnace, cooled to room temperature in a desiccator, and re-weighed. Organic matter content was calculated as the difference between the initial and final weights of samples divided by the initial sample weight and multiplied by 100% [16,17].

Sample metal analysis by XRF and ICP-MS

Soil samples were analysed for metals using a Niton XL3t GOLDD+ field portable X-ray fluorescence (FP-XRF) spectrometer following the United States Environmental Protection Agency Method 6200 for metal analysis [18]. A check sample (NIST 2709a) was run prior to analysis and this was done at the beginning of each working day. Sample analyses were performed in triplicates. The average recovery obtained by running the check sample (NIST 2709a) was always ≥75±5%. Analysis of 9 replicate sample samples in reproducibility tests resulted in mean relative percent differences less than 21% for each of the metals analysed in this study (As: 21%, Cr: 11%, Cu: 7.5%, Ni: 9.2%, Pb: 13%, Zn: 7.7%). The results indicated satisfactory reproducibility [15,19]. To prepare samples for ICP-MS analysis, sieved soil samples were digested by adding 10 mL of 1:1:1

$HCl-HNO_3-H_2O$ mixture to 1.0 g of soil sample and heating at 95 °C for 1 h. Heated samples were allowed to cool and then centrifuged at 5000 xg for 20 min. An aliquot of the supernatant was pipetted and made to volume with 5% HCl. Inductively coupled plasma mass spectrometry (ICP-MS) analysis followed the USEPA SW 846 test method 6020B, as described elsewhere [16,20].

In vitro *bioaccessibility assay*

Bioaccessibility was evaluated using the standard operating procedure for the *in vitro* bioaccessibility assay of arsenic and lead in soil. [21] The protocol used was the same as those reported elsewhere and involved extraction with glycine-HCl at a pH of 1.5 [22,23].

Estimation of contamination

Determining the level of pollution by a given heavy metal requires the pollutant concentration to be compared with a reference material, which would then be used as a benchmark for the representation of data. The processing, analyses and communication of raw environmental data as well as distinguishing the source of contaminants requires the use of pollution indices. Various methods for quantifying the degree of metal enrichment in soils and sediments have been suggested [24,25]. Pollution impacts ranging from 'low' to 'high' intensity have been proposed to convert the calculated results into bands of pollution. The level of heavy metal contaminants in soils was evaluated using the enrichment factor, contamination factor, and potential ecological risk index. Additionally, levels were compared with similar works conducted in urban parts of Kumasi and other areas.

Enrichment factor

Enrichment factor (EF) was used to assess the degree of heavy metal pollution due to anthropogenic sources and to differentiate the source of metal pollution, whether it is anthropogenic or naturally occurring. Iron was used for normalization due to the relatively high natural concentrations of iron. The EF was calculated as in Eq. (1).

$$EF = \frac{M_s \times F_{er}}{M_r \times F_{es}} \tag{1}$$

where: M_s and F_{es} were heavy metal and Fe concentrations in the soil sample respectively, M_r and F_{er} were the concentrations of the heavy metal and Fe in shale [26,27]. An EF>1 means the metal concentration in the soil sample is enriched relative to the average shale values and the source may be anthropogenic whereas EF<1 indicates that the metal is not enriched and maybe from a natural source. An EF=1 indicates that the metal concentration and its reference value are the same [28].

Contamination factor

Contamination factor (CF) is the ratio of metal concentration in the soil sample to the background concentration of the corresponding metal [29]. The CF accounts for the metal enrichment in the soil and it was calculated using Eq. (2).

$$CF = \frac{Ms}{Mr} \tag{2}$$

where M_s and M_r are the mean concentrations of the metal contaminants in the soil samples and the metals' background concentrations found in pristine soils taken from the KNUST Botanical Gardens in Kumasi. Based on the magnitude of the CF, sample contamination is described as either low ($CF \leq 1$), moderate (1–3), considerable (3–6), or very high ($CF \geq 6$) [28,30].

Pollution load index

The pollution load index (PLI) of metal contaminants was calculated to estimate the overall pollution status for a sample. The PLI for a particular sample location was calculated from the CF of each of its constituent samples [31,32]

$$PLI = (CF1 \times CF2 \times CF3 \times \ldots \times CFn)^{1/n} \tag{3}$$

Where CF represents the contamination factor of the corresponding metal, n represents a specific metal's contamination factor. The PLI values are classified as unpolluted ($PLI \leq 1$), moderately polluted (1–3), highly polluted (3–5), or very highly polluted ($PLI > 5$) [25,30].

Potential ecological risk

The degree of metal pollution in soils based on metal contamination factor and the response of the environment to the contaminant (T_{rf}) was evaluated with the potential ecological risk index (PERI). PERI was computed as the sum of individual risk indices as shown in Eq. (4) [29].

$$PERI = \sum_{i}^{n} (T_{rf} \text{ x } CF) \tag{4}$$

Toxic response factor for metals are in the order; Zn = 1, Cr = 2, Cu = Pb = 5, Ni = 6, As = 10 and Cd = 30 [25,33]. The degree of ecological risk can be classified as; PERI < 40 (low risk), 40 ≤ PERI < 80 (moderate risk), 80 ≤ PERI < 160 (considerable risk), 160 ≤ PERI < 320 (high risk), and PERI ≥ 320 (very high risk) [12,28].

Potential human health risk

The average daily intake of metal based on incidental soil ingestion was estimated using Eq. (5) [34].

$$CDI_{metal} = (M_{soil} \times IngR \times EF \times ED \times CF)/(BW \times AT) \tag{5}$$

where CDI_{metal} = metal daily intake (mg kg^{-1} day−1); M_{soil} = metal concentration in soil (mg kg^{-1}); IngR = ingestion rate of soil (mg day^{-1}); EF = exposure frequency (day $year^{-1}$); ED = exposure duration (year); BW = body weight (kg); AT = averaging time (days); and CF = conversion factor (10^{-6} kg mg^{-1}).

Eq. (5) assumes that the ingested metal is 100% bioavailable. Metal bioavailability, however, depends on soil properties such as pH, texture and organic matter as well as metal speciation. Eq. (5) can thus be modified to include a relative bioavailability factor as shown in Eq. (6) [12]. The relative bioavailability factor was estimated from *in vitro* bioaccessibility assay.

$$CDI_{adjusted} = (M_{soil} \times IngR \times EF \times ED \times CF \times RBA)/(BW \times AT) \tag{6}$$

where RBA = relative bioavailability (unitless).

Eq. (7) was used to estimate the carcinogenic risk [34].

$$Risk = CDI_{adjusted} \times SF \tag{7}$$

Where Risk = probability of carcinogenic effect (unitless) and SF = cancer slope factor (mg kg^{-1} $day^{-1})^{-1}$. For non-cancer risk, the hazard quotient (HQ) was calculated using Eq. (8) [34]

$$HQ = CDI_{adjusted}/RfD \tag{8}$$

Where RfD = reference dose (mg kg^{-1} day^{-1}).

Results and discussions

Physicochemical analysis

Soil pH for all samples analysed ranged between 6.50 and 8.50. About 10% of soil samples were slightly acidic with pH < 7. The rest of the soil samples were slightly neutral to basic with pH ranging from 7.01 to 8.50. Soil samples with lower pH values were from locations with high vehicular activities such as Asokore Mampong and Edwenase. Soil pH can affect plant growth since cation mobility is pH-dependent [35]. Soil samples with neutral to basic pH values probably have high levels of carbonates in them [36,37]. In comparison to a similar study conducted in the commercial areas of Kumasi [12], soil samples from the commercial areas were generally more acidic. This may be due to pronounced anthropogenic activities in commercial areas. A pH range of 7.4–8.0 was obtained in another study on peri-urban soils from New Delhi in India [38]. The electrical conductivity of the soil samples was in the range of 153 to 8990 µS/cm with an average value of 1133.2 ± 139.40 µS/cm. This is an indication of soils with high levels of inorganic ions [39], including metals. Anthropogenic activities such as farming, light industrial activities, vehicular deposits, and waste disposal may have contributed to the presence of these inorganic ions in the soils.

Comparison between ICP-MS and FP-XRF data

A comparison of the field-portable X-Ray Fluorescence (FP-XRF) data to the ICP-MS results showed a linear correlation between the two methods for most of the metals. The R^2 values for As, Cr, Fe, and Mn were between 0.3789 and 0.8666 indicating good comparability of the confirmatory laboratory data to the XRF data, suggesting that little data correction would be needed to match the FP-XRF data to confirm laboratory data [40]. However, correction of the FP-XRF data was required to match the confirmatory data for Pb due to the low R^2 value of 0.0513. From the data obtained, FP-XRF is a useful analytical instrument for screening many samples of soil for most metals prior to the use of a more sensitive analytical instrument especially when the concentrations are high.

Table 1
Descriptive statistics of metal concentrations (mg/kg) using XRF and Physicochemical parameters ($n = 73$).

Metal	Maximum	Minimum	Average	Standard Deviation	CCME (CCME,2007)	Dutch Target VROM,2000	
						Target	Intervention
As	55.18	2.54	10.12	1.15	12	29	55
Cd	27.79	7.68	12.91	0.55	10	0.8	12
Cr	275.71	9.67	77.93	7.41	64	100	380
Cu	41.27	9.79	20.20	0.91	63	36	190
Pb	55.65	7.50	18.60	1.88	140	85	530
Ni	55.85	20.01	29.33	1.01	50	35	210
Mn	969.43	34.15	158.68	13.36	–		–
Sn	22.53	4.27	8.83	0.46	–		–
V	202.48	10.96	78.22	4.12	130	42	250
Fe	166,298.00	3031.00	23,031.00	2846.54			
Zn	419.23	13.10	49.27	5.90	200	140	720
EC	8990	153	1133.21	139.40	–		–
pH	8.50	6.50	7.50	0.14	–		–
% TOC	15.20	0.45	8.85	1.79			

EC – Electrical Conductivity; TOC – Total Organic Carbon.

Heavy metal concentration

Soil samples were obtained from the topsoil as this was assumed to be the layer human beings are most exposed to during their daily activities [41] and likely to provide human exposure risk estimates. The FP-XRF was used to screen all samples for the presence of 11 heavy metals including arsenic, cadmium, chromium, copper, iron, lead, manganese, nickel, tin, vanadium, and zinc. The descriptive statistics of metal concentrations, as well as the Dutch [42] and Canadian [43] guidelines, are summarized in Table 1.

The mean concentration of arsenic obtained in this study was 10.12 ± 1.15 mg/kg, which was greater than the 4.59 mg/kg recorded in soils in the commercial hubs of the Kumasi metropolis [12,44]. Agricultural chemicals including fertilizers and pesticides may contain arsenic [45,46]. The mean arsenic level is lower than the requirements of both the Canadian [43] and Dutch [42] standards. However, since the concentrations at some locations exceeded the limits, it is important to monitor the levels to limit any possible impacts to humans, plants, and other organisms. The levels of arsenic obtained in soils from peri–urban areas in eastern China [47] were much lower than the average of this study probably due to differences in the land-use type in the study areas.

Concentrations of Cu were generally low, with a mean concentration of 20.20 ± 0.91 mg/kg. For all areas sampled. Sampling points in the eastern and southwestern parts of the map (Fig. 1) recorded very high Cu levels. According to Ansari and co-workers, Cu levels in non-contaminated soils are usually below 50 mg/kg [48]. This suggests that the soils of peri–urban Kumasi are not contaminated with respect to Cu. The mean Cu concentration was also lower than that of the Canadian and Dutch standards. Agricultural and domestic use of pesticides and fungicides may be the source of Cu. High Cu levels in the soil are usually associated with anthropogenic activities. The low Cu levels observed may be because industrial activities are minimal in the peri–urban areas.

Levels of Pb recorded in this study were low, with an average of 18.60 ± 1.88 mg/kg. This is lower than the 53.5 mg/kg found in soils in urban areas of Kumasi [12,44] or the peri-urban soils in eastern China [47]. Lead, a highly bioavailable metal with low mobility and high toxicity, has a long residence time in surface soils [49]. Anthropogenic release of Pb may be from the application of leaded paints, historical use of leaded gasoline, and metallurgical industrial activities.

Concentrations of cadmium were much higher in this study (average of 12.91 ± 0.55 mg/kg) than in the corresponding studies in urban Kumasi (0.5 mg/kg) [12]. The levels of cadmium obtained were also much higher than studies on peri-urban soils in eastern China [47] and New Delhi [38]. Cd could be introduced into the environment through municipal waste disposal, nickel-cadmium batteries, sewage sludge, and fertilizer use. These are all activities present in the peri-urban parts of Kumasi and could be contributing factors for the high Cd levels.

Chromium levels ranged between 9.67 and 275.71 mg/kg with an average of 77.93 ± 7.41 mg/kg. The mean Cr level was higher than both Dutch and Canadian target values. Chromium changes its form in soil depending on conditions such as pH, soil adsorption properties, and redox potentials [48]. Toxic effects of chromium include alterations in the germination and physiological processes of plants and the generation of reactive oxygen species in living tissues. Vehicular emissions, wood processing, and burning of municipal waste could all introduce chromium to the soil. Sokoban, a site for major wood processing industries, had very high Cr levels in its soils. In addition, this could be attributed to the use of Cr compounds such as chromated copper arsenate in wood preservation. Average levels of Zn, V, and Ni were much lower than Canadian and Dutch guidelines. In general, metal levels recorded in this study were lower than those from the urban parts of Kumasi (Fig. 2).

Fig. 3 shows the spatial distribution of metals across the study area. Generally, the western part of the metropolis recorded higher metal concentrations. These areas are sites for wood processing industries and heavy agricultural activi-

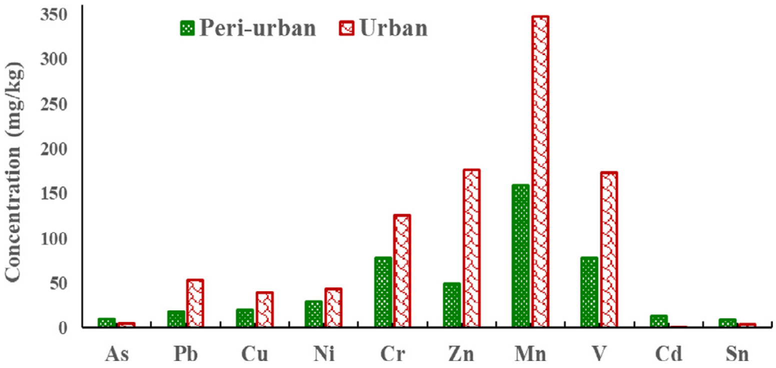

Fig. 2. Comparison of metal concentration across commercial (urban) (Darko, et al. 2017) and non-commercial (peri-urban) hubs of Kumasi metropolis.

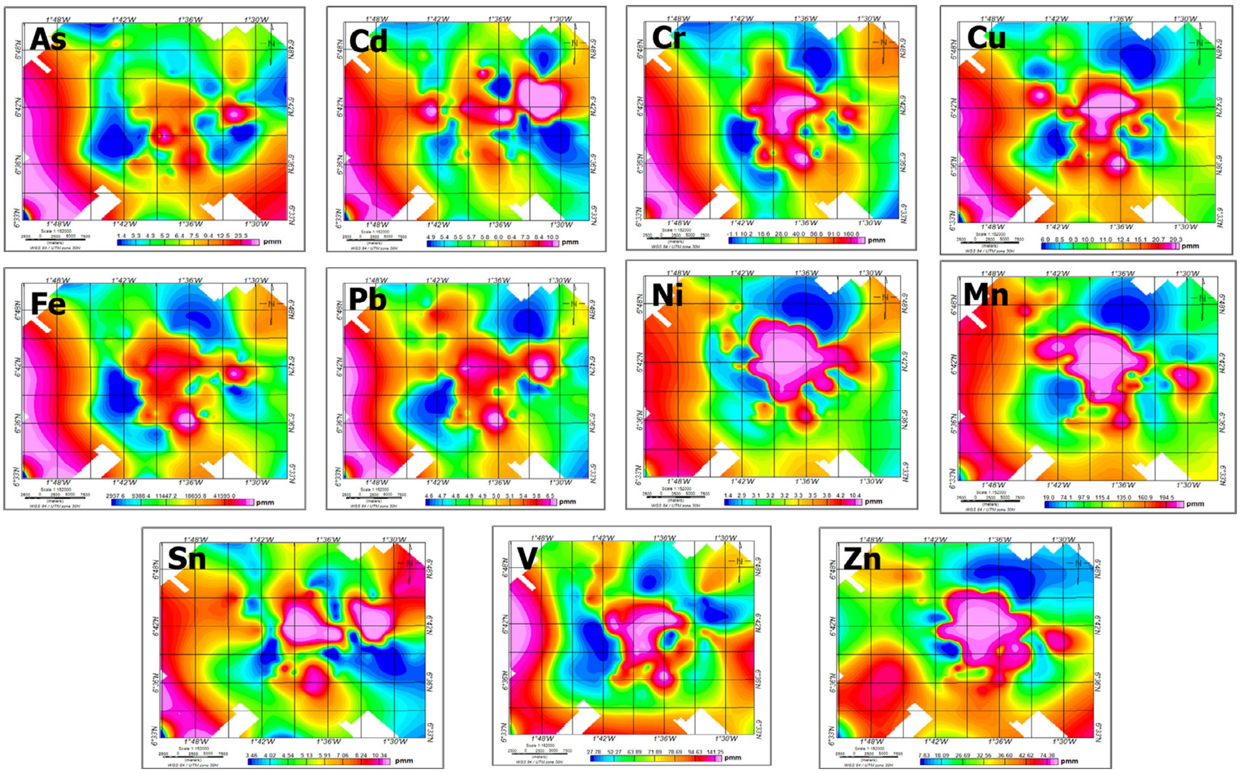

Fig. 3. Heavy metals distribution pattern in the peri-urban areas of the Kumasi metropolis.

ties and these may be the major contributors to the high metal concentrations recorded [50]. The highest levels of metals were concentrated in the middle belts where communities such as Suame and Tafo are located. These communities are sites of intense artisanal industrial activities such as welding, metal fabrication, car spraying, painting, and vehicle repairs. These activities usually result in the release of metals into the environment [51]. Spillage and disposal of used motor oils and paints, spraying of automobiles in the open, and filing of metals are ubiquitous activities and are likely sources of heavy metals in the soil.

Correlations between metals and physicochemical parameters

Table 2 shows the correlations amongst toxic metals and physicochemical parameters in peri-urban topsoils of the Kumasi Metropolis. Elements from a common source would usually exhibit strong correlations among some of their quantitative variables or properties [52]. Very strong positive correlations were found between the concentrations of the metals such as Fe and As, Fe and Cr, Cu and Cr, Fe and Cr, Ni and Cr as well as Ni and Pb (all at α =0.01). Concentrations of Co and V also correlated very strongly with other elements such as Cr, Cu, Fe, Ni, and Pb (α = 0.01). With respect to the

Table 2
Correlations amongst toxic metals and physicochemical parameters in peri-urban topsoils of the Kumasi Metropolis.

	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn	Co	TOC	pH	EC
As	1													
Cd	−0.044	1												
Cr	.711*	.282	1											
Cu	.441	.285	.891**	1										
Fe	.798**	.249	.964**	.778**	1									
Mn	−0.200	.210	.340	.674*	.132	1								
Ni	.692*	.112	.917**	.858**	.917**	.277	1							
Pb	.083	.531	.732*	.851**	.564	.749*	.579	1						
V	.506	.430	.959**	.887**	.893**	.445	.832**	.867**	1					
Zn	−0.001	−0.517	−0.165	.010	−0.306	.216	−0.059	−0.139	−0.282	1				
Co	.354	.079	.781**	.934**	.668*	.616	.857**	.728*	.750*	.190	1			
TOC	.057	.013	.335	.294	.429	.110	.359	.259	.397	−0.721*	.227	1		
pH	.440	−0.035	.579	.402	.629	.016	.678*	.295	.561	−0.089	.404	.268	1	
EC	.902**	.040	.564	.306	.639*	−0.231	.594	.019	.370	.099	.244	−0.132	.419	1

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

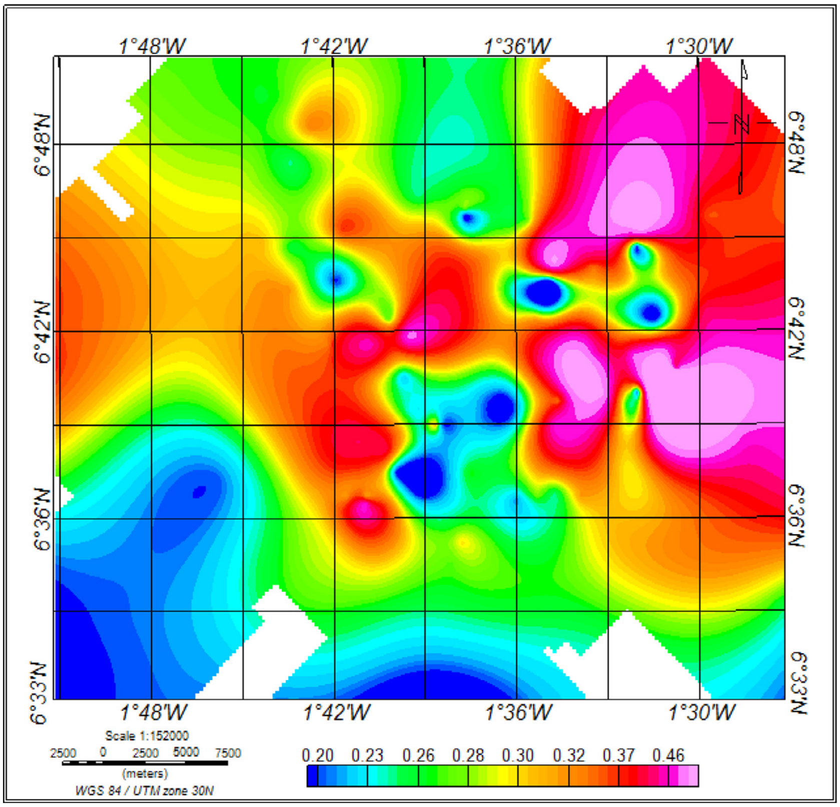

Fig. 4. Grid map of pollution load indices of the selected metals from the study area.

physicochemical parameters and metals concentrations, very strong correlations were found between electrical conductivity and arsenic (0.902; α=0.01; 2-tailed) and between pH and Ni as well as EC and Fe.

Assessment of heavy metal contamination

Several contamination and pollution assessment tools were used to monitor the level of soil contamination. In this study, the enrichment factor (EF) and contamination factor (CF) were used to determine whether the sources of metal contamination were anthropogenic or due to natural processes. Both EF and CF show low pollution of metals in the soil. Pollution load index (PLI) values were between 0.07 - 0.63 which confirms the low level of pollution of the peri-urban soils. Fig. 4 illustrates the PLI grid map of selected metals from the study area. The overall highest metal pollution was found around the

Table 3
Mean Enrichment Factor, Mean Contamination Factor of Metals, Potential Ecological Risk Index, Hazard Index and Carcinogenic Risk Index for Children and Adults in the Per-Urban Areas of Kumasi.

Metal	EF	CF	PERI	HI_{Adult}	$HI_{children}$	CRI_{Adult}	$CRI_{children}$
As	0.06	0.44	4.43	1.34E−08	1.20E−08	3.20E−09	2.40E−09
Pb	0.03	0.01	0.65	2.30E−09	1.40E−09		
Cu	0.07	0.10	0.54	2.00E−09	1.30E−09		
Ni	0.28	0.17	2.8	4.02E−08	2.40E−08	2.30E−09	1.50E−09
Cr	0.64	0.25	1.59	3.20E−08	1.50E−08	3.00E−10	2.50E−10
Zn	0.14	0.99	0.99	1.50E−09	1.04E−09		
Fe	1	2.13	2.34	2.50E−08	1.05E−08		
Mn	0.04	0.18	0.18	2.30E−09	1.30E−09		
V	0.48	0.60	0.78	7.80E−09	5.30E−09		
Sn	0	0.13	4.01	3.40E−08	2.01E−08		
Cd	0	0.30	1.02	5.30E−09	3.20E−09		

EF – Enrichment Factor; CF – Contamination Factor; RI – Risk Index; HI – Hazard Index; CRI – Carcinogenic Risk Index.

Table 4
Mean Bioaccessibility for Total Metals.

Metal	Soil (mg/kg) (n = 73)	% Bioaccessibility (n = 10)
As	57.10 ± 5.01	35.93 ± 0.55
Cd	0.03 ± 0.00	NC
Cr	211.54 ± 1.45	9.16 ± 0.81
Cu	24.06 ± 0.13	60.8 ± 0.00
Fe	90,496.49 ± 36.78	5.79 ± 0.14
Mn	284.20 ± 1.55	99.23 ± 14.57
Ni	9.240 ±0.13	100.00 ± 22.32
Pb	28.36 ± 1.59	100 ± 11.56
V	100.77 ± 2.43	15.19 ± 1.10
Zn	46.44 ± 1.01	NC

NC – Not computed.

north-eastern and the central portions of the study area where human activities such as siting of auto-mechanic workshops are rampant and vehicular traffic is dense.

Ecological risk assessment

Potential ecological risk indices (PERI) characterize the overall contamination of the study area [29]. The PERI, as shown in Table 3, ranging from 0.18 to 4.43. The low values agree with the other pollution assessment indicators used in this study and confirm the low level of pollution of the peri–urban soils. The mean potential ecological risk index was computed to be 19.33 and suggests that the metals at their present levels are not a threat to the disruption of the ecology of the study areas and hence can be classified as being at low ecological risk [25,33].

Human health assessment

Human health risk assessment of metal contaminants was analysed by calculating hazard and carcinogenic risk indices [28]. Since adults and children respond differently to metal contaminants, the carcinogenic risk index was estimated separately for both classes. Results of the hazard index and carcinogenic risk index are shown in Table 3. Metal daily intake was adjusted using the bioaccessibility data.

The mean bioaccessible fractions of the metals ranged from 9.16 ± 0.18% to 100.00 ± 22.32% (Table 4). Arsenic and copper recorded a mean bioaccessibility of 35.93 ± 0.55% and 60.80 ± 0.00 respectively. Bioaccessibility of the other metals including Mn, Ni, and Pb were ≥99.23% meaning the total amount of metals in the soils will be adsorbed into the bloodstream upon ingestion. Whereas the XRF analysis provides the total metal concentration in soil samples, bioaccessibility provides insight into the fraction of the total metal concentration available to biological tissues and its use is, therefore, more accurate in estimating risk than the total metal concentration in the soil. Average carcinogenic risk values incorporating the bioaccessible concentrations for adults and children were 2.83×10^{-9} and 2.13×10^{-9} respectively. It is estimated that risks exceeding 1×0^{-4} are regarded as unacceptable, whilst risks below 1×10^{-6} are not considered to pose significant health effects [53]. Carcinogenic risk levels of heavy metals in topsoil across the peri–urban areas of the Kumasi metropolis are therefore considered not to pose significant health effects to both children and adults.

Conclusion

Metal concentrations (As, Pb, Cu, Ni, Cr, Zn, Fe, Mn, V, Sn, and Cd) in surface soil from peri–urban areas in the Kumasi metropolis were assessed in this study. The levels of metals recorded were, in general, lower than those reported for the urban parts of the city of Kumasi. The mean metal concentrations were in the order: Fe (23,031) > Mn (158.68) > V (78.21) > Cr (77.97) > Zn (49.27) > Ni (29.33) > Cu (20.20) > Pb (18.60) > Cd (12.91) > As (10.11) > Sn (8.83). Metals concentrations were generally higher in the central and southwestern regions of the study area. Assessment of the level of pollution using various tools such as enrichment factor, contamination factor, pollution load index, risk index, and potential ecological risk index indicated low levels of pollution and no threat to the environment at the present levels. Additionally, the levels of metals in the soils of the study area pose no significant risk to humans at these concentrations. However, due to the ability of these metals to bioaccumulate and biomagnify in the food chain, regular monitoring is needed to ensure levels do not become threatening.

Declaration of Competing Interest

All authors declare no competing financial, professional, or personal interests that might have influenced the performance or presentation of the work described in this manuscript.

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Author contributions

LSB, GD and MD conceived the study and designed all experiments. Samples were collected by NK. All experiments were carried out by NK and MD. Data analysis was by LSB, NK, GD and MD. All authors read and approved the final manuscript.

Data Availability

All data generated or analysed during this study are included in this published article.

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