Introduction

Contamination of soil with heavy metal and metalloids results mainly from anthropogenic activities including mining, smelting, tanning, draining of sewage and dumping of wastes. Although metals occur naturally in the environment, chemical and metallurgical industries are the most important sources of metal contamination. Heavy metals/metalloids cannot be easily degraded and are continuously being deposited into soil, water and sediment, causing pollution. Metal concentrations are greatest near towns, indicating their urban/industrial origins. Apart from destabilizing the ecosystem, accumulation of these toxic metals in the food web is a threat to public health and their potential long-term impact on the ecosystem cannot be ignored.

Kumasi (6° 40'00" N 1° 37'00" W) is the capital city of the Ashanti Region and covers a land area of 254 km² (98 sq miles). It is the second largest city in Ghana with over 2.5 million inhabitants. The land is dominated by middle Precambrian rocks and the major soil type is forest Ochrosols. On the basis of land use, the study area can be divided into a number of categories: agriculture, human settlement, vegetation cover, water bodies, and industrial. The human population and number of cars have drastically increased during the past few years. In addition, many gas/fuel stations, auto-mechanic/repair workshops, metals fabricators, tanning industries, mining operations (including illegal mining operations popularly known as galamsey), stone quarrying and sand mining industries are located in this region. These and many other anthropogenic factors have led to the release of heavy metals and...
metallic and metalloids into the environment.\textsuperscript{4,5}

There have been a limited number of studies assessing the enrichment/pollution levels and sources of heavy metals and metalloids in the Kumasi metropolis. The objectives of the present study were to determine the concentrations of heavy metals and metalloid in Kumasi soils, determine the levels of metal accumulation compared to a pristine site using enrichment factor and geo-accumulation index, develop distribution maps of heavy metals/metalloid throughout the sample site using geographic information system (GIS), identify the possible sources of metals by multivariate analysis, and evaluate the extent of metal pollution in Kumasi soils using contamination factor and pollution load index.

### Abbreviations

| Abbreviation | Description                                      |
|--------------|--------------------------------------------------|
| CF           | Contamination factor                             |
| EF           | Enrichment factor                                |
| GM           | Geometric mean                                   |
| \( I_{geo} \) | Geoaccumulation index                            |
| KNUST        | Kwame Nkrumah University of Science and Technology |
| PC           | Principal component                              |
| PLI          | Pollution load index                             |
| USEPA        | United States Environmental Protection Agency    |

### Methods

#### Sampling

Soil samples were randomly collected from 31 communities (sample sites) in the Kumasi metropolis. A map showing the sampling sites is presented in Figure 1. The sites were selected to represent a wide area of the town and global positioning system was used to locate the sampling positions. Sampling was done in May, 2011 and a total of 112 soils (0-10 cm top layer) were collected using

![Sampling area/sites (yellow pins indicate sampled communities and white pin indicates reference site, KNUST Botanical Gardens). 1: Kejetia; 2: Central market; 3: Romanhill; 4: Mbrom; 5: Adum; 6: Asafo; 7: Amakom; 8: Afunkwanta; 9: Asokwa; 10: Oforikrom; 11: Racecourse; 12: Bantama; 13: Ashtown; 14: Manhyia; 15: Asawase; 16: Aboabo; 17: Dichemso; 18: Yennyawoso; 19: Tafo Nhyiaso; 20: Tafo; 21: New Suame; 22: Suame; 23: Anomangye; 24: Suntreso; 25: Danyame; 26: Patasi, 27: Ahodwo, 28: Kaase; 29: Atonsu; 30: Ahinsan; 31: Bomso and 32: KNUST Botanical Gardens.](image-url)
After digestion, the solutions were allowed to cool, filtered using ashless filter paper 5B (Advantec, Tokyo, Japan) into Corning tubes (Corning Incorporated, New York, USA). Lanthanum chloride (1 mL, atomic absorption spectrometry grade, 100 g La/L solution, Wako Pure Chemical Industries Ltd., Osaka, Japan) was added to prevent ionization/interference during metal analysis. Samples were diluted to 50 mL with 2% nitric acid prepared with Milli-Q water. Concentrations of heavy metals and metalloids were determined by atomic absorption spectrophotometry (AAS) (Z-2010, Hitachi High Technologies Corporation, Tokyo, Japan) after preparation of calibration standards. Cadmium (Cd), chromium (Cr), nickel (Ni), lead (Pb) and arsenic (As) were analyzed by graphite furnace AAS (argon gas) with Zeeman background correction. Copper and zinc (Zn) were analyzed by flame AAS (acetylene flame) with deuterium background correction.

In addition, total mercury (Hg) was measured by thermal decomposition, gold amalgamation and atomic absorption spectrophotometry (mercury analyzer, MA–3000, Nippon Instruments Corporation, Tokyo, Japan), after preparation of calibration standards. Blanks were prepared using the same procedure. The water content (WC) of each sample was measured after 12 h of oven drying at 105°C. Organic matter (OM) content was determined by loss of weight on ignition at an oven temperature of 600°C for 5 hours. Then pH was measured in a soil deionized water suspension (soil: water, 1:2.5 by volume) with a calibrated pH meter.

Quality Control and Quality Assurance
For quality control, blanks were analyzed after every 10 samples. The instrument was calibrated using standard solutions of the respective metals (to establish standard curves before metal analysis). The detection limits (mg/kg) were 0.5 for Cr, 0.5 for cobalt (Co), 1.0 for copper (Cu), 0.1 for Zn, 0.2 for Cd, 1.0 for Pb, 0.5 for Ni and 2.0 for As. Reference materials, Standard Reference Material 1944 (New York/New Jersey Waterway Sediment) and BCR–320 (Channel Sediment, Institute for Reference Materials and Measurements, Belgium) were used for method validation. Replicate analyses of these reference materials showed good accuracy and recovery rates ranged from 80% to 115%. Recovery rates (%) of Hg for these certified reference materials (BCR–320R and Standard Reference Material 1944) ranged from 92–103. The detection limit of Hg in soil samples was 2.0 pg total Hg.

Data Analysis

Enrichment Factor
A common approach to estimating the anthropogenic impact on soil is to calculate the enrichment factor (EF) for metal concentrations above uncontaminated background levels. The EF method normalizes the measured metal content with respect to a reference metal. The reference material would then represent a benchmark to which the metal concentrations in the polluted samples are compared and measured. Pollution, in this case, will be measured as the amount (or ratio) of the sample metal enrichment above the concentrations present in the reference sample. Similar to the approach by Matthai and Birch, Co was considered a normalizing element for determining anthropogenic pollution sources in this study. The EF was calculated according to Equation 1:

\[
\text{EF} = \frac{C_s}{C_r} \times \left( \frac{M_s}{M_r} \right)
\]
Equation 1

\[ EF = \left( \frac{M_{\text{sample}} \times C_{\text{ref}}}{M_{\text{ref}} \times C_{\text{sample}}} \right) \]

where \( M_{\text{sample}} \) is the geometric mean (GM) concentration of metal in soil, \( C_{\text{ref}} \) is the GM of Co in the reference sample (KNUST Botanical Gardens), \( M_{\text{ref}} \) is the GM of metal in reference sample and \( C_{\text{sample}} \) is the GM of Co in the sample. Classification of EF by Chen et al. was adopted in this study and has been provided in Supplemental Material 1.12

Geoaccumulation Index

This method assesses the degree of metal pollution in terms of seven enrichment classes based on the increasing numerical values of the index. Geoaccumulation index (\( I_{\text{geo}} \)) is calculated using Equation 2:

\[ I_{\text{geo}} = \log_2 \left( \frac{C_i}{1.5B_n} \right) \]

Where \( C_i \) is the GM concentration of the element in the enriched samples, and \( B_n \) is the background or pristine value of the element (KNUST Botanical Gardens). A factor of 1.5 was introduced to minimize the effect of possible variations in the background values which may be attributed to lithologic variations.13 Classification of \( I_{\text{geo}} \) by Muller was used (Supplemental Material 1).14

Contamination Factor

Contamination factor (CF) reflects the anthropogenic input in elemental pollution and is widely used as a measure of overall contamination of soil. CF was calculated using Equation 3:

\[ CF = \frac{C_i}{B_i} \]

Where \( C_i \) and \( B_i \) are GM concentrations of the examined metal, i, in sample and reference (KNUST Botanical Gardens), respectively.15 The contamination grades in an increasing order are rated from 1 to 6 (0 = none, 1 = none to medium, 2 = moderate, 3 = moderate to strong, 4 = strongly polluted, 5 = strong to very strong, 6 = very strong).16

Pollution Load Index

The pollution load index (PLI) for a set of \( n \) polluting elements is defined as a value calculated from the GM of the contamination factors of those elements. PLI was calculated by the following expression given by Tomlinson et al.17

\[ PLI = (CF1 \times CF2 \times CF3 \times ...CFn)^{1/n} \]

A PLI value higher than unity suggests pollution, while values lower than 1 indicate no pollution load.

Statistical Analysis

Statistical analyses were performed using SPSS 20.0 (IBM SPSS Inc., Chicago, USA). Kolmogorov–Smirnov and Shapiro–Wilks tests were used to determine the normality of data and data were considered statistically significant if the p value was less than 0.05. Statistical analyses were carried out after data were log transformed (normalized). Spatial distributions were performed using Arc-GIS 9.3 (ESRI Co., Redlands, USA). Kriging was adopted for the interpolation of geographical data. Geographic Information System coordinates and concentrations of metals obtained in soil were used to create the distribution maps. In order to identify the important parameters that affect the chemistry of soil, Pearson’s correlation matrix was used (at a significance level (p) less than 0.05). Principal component analysis and cluster analysis were carried out to describe the degree of association/possible sources of metals in Kumasi soils. The principal components based on log transformed data were extracted with eigenvalues > 1 through a varimax rotation. Cluster analysis was also performed based on Euclidean distance using Ward’s clustering method.

Results

Heavy Metals and Metalloid Concentrations in Kumasi Soils

Concentrations of eight heavy metals and a metalloid (As) were measured in Kumasi soils and results are shown in Table 1. The metal concentrations from some sample sites exceeded the recommended levels by Kabata-Pendias and Pendias (unpolluted soils), the United States Environmental Protection Agency (USEPA) and the reference site (KNUST Botanical Gardens).5,18 Kolmogorov-Smirnov tests for normality showed a significant variation (p < 0.01) in metal distribution in Kumasi soils (Table 1). As shown in Table 1, Zn was the most abundant metal (107 ± 64.6 mg/kg dry weight (dw)), followed by Cr (97.0 ± 43.7 mg/kg dw) and Pb (52.8 ± 37.9 mg/kg dw). Concentrations of Hg (0.05 ± 0.0363 mg/kg dw) and Cd (0.147 ± 0.159 mg/kg dw) were the lowest.

Enrichment Factor and Geoaccumulation Index

The results of EF revealed that 65, 32, 58 and 93% of soils from the sample sites were moderately to extremely high enriched with Zn, Pb, Cd and Cr, respectively (Supplemental Material 2), suggesting anthropogenic inputs. As shown in Table 2, Yennyawoso and Anomangye were extremely highly enriched with Cd (24.6) and Cr (21.1), respectively, and revealed extreme contamination (\( I_{\text{geo}} \); Supplemental Material 3) in these areas. The \( I_{\text{geo}} \) values for Cr, Zn, Cd, Hg and Pb indicated moderate to extreme contamination (\( I_{\text{geo}} \) classes 3 to 6) in 100, 97, 77, 65 and 45% of the sample.
Table 1 — Geometric Mean Concentrations (mg/kg dw) of Heavy Metals and Metalloid in Soils in Kumasi, Ghana

| Sample Site  | n  | pH  | WC  | OM  | Hg  | Zn  | Cu  | Cd  | Ni  | As  | Co  | Cr  |
|--------------|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Kejetia      | 4  | 7.88| 11.2| 7.8 | 0.15| 217 | 38.7| 0.34| 31.0| 1.11| 5.21| 44.6|
| Ahinsan      | 3  | 8.47| 7.69| 4.8 | 0.05| 81.6| 28.3| 0.11| 19.1| 1.37| 4.25| 71.4|
| Ahodwo       | 3  | 8.74| 7.75| 3.37| 0.01| 51.7| 24.8| 0.05| 16.3| 1.21| 3.78| 95.2|
| Danyame      | 3  | 7.8 | 9.69| 5.61| 0.04| 69.3| 33.8| 0.08| 27.3| 1.92| 4.58| 113 |
| Asawase      | 4  | 8.44| 4.49| 3.93| 0.04| 104 | 36.5| 0.21| 12.8| 1.03| 3.66| 113 |
| Atonsu       | 3  | 8.13| 9.05| 3.96| 0.03| 79.6| 18.9| 0.09| 11.7| 0.73| 2.18| 29.6|
| Mbrom        | 4  | 8.4 | 7.56| 4.39| 0.20| 81.4| 33.5| 0.15| 25.9| 1.47| 5.02| 106 |
| Bantama      | 3  | 8.66| 3.7 | 3.29| 0.02| 58.0| 24.7| 0.14| 8.28| 1.04| 2.94| 49.2|
| Ashtown      | 4  | 8.63| 5.13| 5.53| 0.05| 160 | 26.1| 0.19| 11.4| 0.75| 2.51| 102 |
| Racecourse   | 4  | 8.65| 8.5 | 6.21| 0.05| 158 | 99.8| 0.15| 25.7| 1.14| 5.42| 114 |
| Yennaywoso   | 3  | 8.78| 0.93| 4.34| 0.06| 60.5| 37.0| 0.64| 23.5| 1.94| 3.73| 146 |
| Kaasi        | 3  | 8.98| 7.81| 4.46| 0.02| 127 | 33.3| 0.09| 17.1| 2.68| 3.05| 109 |
| Aboabo       | 5  | 7.98| 1.97| 5.32| 0.04| 81.0| 40.2| 0.09| 26.1| 1.11| 6.02| 249 |
| Romanhill    | 3  | 9.11| 3.1 | 5.55| 0.04| 128 | 68.3| 0.17| 9.72| 0.93| 1.88| 86.9|
| Dicemho      | 3  | 8.88| 2.96| 4.07| 0.14| 54.3| 24.0| 0.07| 18.6| 1.58| 2.65| 81.1 |
| Anomangye    | 3  | 8.76| 3.35| 2.71| 0.02| 48.2| 23.2| 0.03| 10.1| 0.88| 2.28| 173 |
| Asokwa       | 4  | 8.62| 5.53| 8.2 | 0.04| 71.2| 23.3| 0.05| 9.75| 0.91| 1.94| 58.8 |
| Afunkwanta   | 3  | 8.66| 3.84| 3.24| 0.05| 58.9| 23.5| 0.05| 8.38| 0.69| 2.12| 49.9 |
| Suame        | 6  | 8.74| 3.1 | 4.69| 0.06| 229 | 278 | 0.66| 73.9| 7.35| 14.6| 107 |
| Tafo         | 6  | 8.47| 6.03| 4.41| 0.03| 108 | 38.3| 0.08| 19.6| 0.94| 3.77| 106 |
| Adum         | 4  | 8.23| 6.34| 7.56| 0.05| 174 | 46.8| 0.42| 13.4| 1.22| 3.17| 47.7 |
| New Suame    | 3  | 8.6 | 8.48| 4.52| 0.16| 63.5| 29.3| 0.07| 16.4| 1.25| 3.67| 101 |
| Central Market| 4  | 8.11| 5.21| 5.98| 0.08| 119 | 54.7| 0.08| 35.9| 1.14| 5.16| 95.9 |
| Oforikrom    | 3  | 7.85| 12.3| 7.43| 0.04| 60.6| 34.3| 0.03| 54.6| 0.94| 6.51| 144 |
| Asafo        | 5  | 8.69| 5.09| 3.37| 0.05| 212 | 46.7| 0.17| 12.1| 1.52| 3.24| 55.0 |
| Suntreso     | 4  | 9.09| 7.83| 3.97| 0.03| 309 | 33.4| 0.06| 15.4| 2.36| 3.38| 122 |
| Tafo Nhyiaso | 3  | 8.61| 6.58| 5.57| 0.05| 62.5| 34.2| 0.07| 22.1| 1.73| 4.46| 98.8 |
| Patasi       | 3  | 8.55| 4.85| 4.73| 0.03| 62.9| 30.7| 0.05| 24.8| 1.88| 5.24| 100 |
| Manhyia      | 3  | 8.11| 3.58| 4.17| 0.06| 123 | 27.5| 0.06| 10.6| 1.37| 3.27| 117 |
| Amakom       | 3  | 8.18| 5.55| 3.42| 0.03| 78.1| 22.7| 0.08| 8.22| 1.35| 1.87| 75.2 |
| Bomso        | 3  | 8.89| 6.84| 3.09| 0.03| 40.6| 22.3| 0.04| 11.87| 1.39| 2.36| 50.3 |
| GM           | 3  | 8.50| 6.00| 4.82| 0.0506| 107 | 43.1| 0.147| 20.4| 1.51| 3.98| 97.4 |

Abbreviations: n, number of samples; USEPA, USEPA Ecological-Soil Screening Levels; World range, world range of metals in unpolluted soils; Reference, reference values (KNUST Botanical Gardens); nd, not detected; K-S, Kolmogorov-Smirnov test; WC, water content; OM, organic matter; GM, geometric mean; dw, dry weight.

Bold values indicate concentrations higher than limits of the USEPA and/or Kabata–Pendias and Pendias.

**Table 1 — Geometric Mean Concentrations (mg/kg dw) of Heavy Metals and Metalloid in Soils in Kumasi, Ghana**
# Table 2 — Contamination Factor and Pollution Load Index of Heavy Metals in Soils in Kumasi, Ghana

| Sample Site  | Hg  | Zn  | Cu  | Cd  | Ni  | As  | Co  | Cr  | Pb  |
|--------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Kejetia      | 30.0| 29.0| 3.06| 37.4| 7.25| 3.66| 3.86| 9.57| 14.1| 10.3|
| Ahinsan      | 10.0| 10.9| 2.24| 11.7| 4.48| 4.49| 3.28| 15.3| 3.03| 5.90|
| Ahodwo       | 2.00| 6.92| 1.96| 5.48| 3.81| 3.98| 2.92| 20.4| 2.97| 4.18|
| Danyame      | 6.00| 9.26| 2.67| 8.65| 6.40| 6.31| 3.54| 24.4| 6.46| 6.74|
| Asawase      | 8.00| 14.0| 2.88| 23.1| 2.99| 3.40| 2.83| 24.4| 10.1| 7.21|
| Atonsu       | 6.00| 10.6| 1.49| 10.1| 2.74| 2.40| 1.69| 6.36| 5.71| 4.18|
| Mbrom        | 40.0| 10.8| 2.65| 16.4| 6.06| 4.85| 3.88| 22.7| 7.40| 8.93|
| Bantama      | 4.00| 7.74| 1.95| 15.1| 1.94| 3.41| 2.27| 10.5| 8.41| 4.74|
| Ashownt      | 10.0| 21.4| 2.06| 20.8| 2.67| 2.47| 1.94| 21.8| 7.79| 6.47|
| Racecourse   | 10.0| 21.2| 7.87| 16.8| 6.02| 3.75| 4.19| 24.5| 9.46| 9.47|
| Yennyawoso   | 12.0| 8.08| 2.92| 71.1| 5.50| 6.38| 2.88| 31.4| 17.7| 10.1|
| Kaasi        | 4.00| 17.0| 2.62| 10.3| 4.01| 8.81| 2.36| 23.3| 3.10| 6.06|
| Aboabo       | 8.00| 10.8| 3.17| 10.5| 6.11| 3.66| 4.66| 53.4| 6.97| 7.84|
| Romanhill    | 8.00| 17.1| 5.38| 18.8| 2.27| 3.07| 1.46| 18.6| 4.88| 6.16|
| Dichemso     | 28.0| 7.26| 1.89| 7.31| 4.35| 5.20| 2.05| 17.3| 3.31| 5.8 |
| Anomangye    | 4.00| 6.44| 1.83| 2.97| 2.36| 2.91| 1.76| 37.2| 2.42| 3.77|
| Asokwa       | 8.00| 9.52| 1.84| 6.07| 2.28| 2.99| 1.50| 12.6| 2.83| 4.07|
| Afunkwanta   | 10.0| 7.86| 1.85| 6.04| 1.96| 2.28| 1.64| 10.7| 3.07| 3.90|
| Suame        | 12.0| 30.6| 21.9| 73.5| 17.2| 24.1| 11.3| 23.1| 21.6| 22.3|
| Tafo         | 6.00| 14.4| 3.02| 8.48| 4.58| 2.97| 2.92| 22.8| 11.8| 6.60|
| Adum         | 10.0| 23.2| 3.69| 47.1| 3.13| 3.95| 2.40| 10.2| 6.99| 7.60|
| New Suame    | 32.0| 8.48| 2.31| 7.90| 3.84| 4.10| 2.84| 21.6| 3.38| 6.32|
| Central market| 16.0| 15.9| 4.32| 8.85| 8.41| 3.63| 3.95| 20.5| 2.99| 7.46|
| Oforikrom    | 8.00| 8.10| 2.71| 3.69| 12.7| 3.08| 5.03| 30.9| 6.30| 6.63|
| Asafo        | 10.0| 28.3| 3.68| 18.5| 2.83| 4.93| 2.51| 11.7| 13.3| 7.79|
| Suntreso     | 6.00| 41.2| 2.64| 7.01| 3.62| 7.77| 2.61| 26.2| 2.62| 6.58|
| Tafo Nyiaso  | 10.0| 8.35| 2.70| 7.54| 5.18| 5.68| 3.45| 21.1| 3.08| 6.07|
| Patasi       | 6.00| 8.41| 2.42| 5.07| 5.81| 6.19| 4.05| 21.4| 3.97| 5.82|
| Manhyia      | 12.0| 16.4| 2.17| 7.10| 2.48| 4.51| 2.53| 25.1| 3.25| 5.76|
| Amakom       | 6.00| 10.4| 1.79| 9.17| 1.92| 4.44| 1.44| 16.1| 5.26| 4.67|
| Bomso        | 6.00| 5.43| 1.76| 4.01| 2.77| 4.59| 1.83| 10.7| 2.72| 3.77|

**Table 2 — Contamination Factor and Pollution Load Index of Heavy Metals in Soils in Kumasi, Ghana**

**Abbreviations**: PLI, pollution load index; SD, standard deviation

*Bold contamination factor indicates moderate to very strong contamination; Bold PLI indicates values greater than 1 and signifies pollution*
sites, respectively, (Supplemental Material 3) when compared to the reference site. In Suame, all the studied metals showed moderate to extreme contamination with $I_{geo}$ ranging from 2.92 (Co) to 5.62 (Cd) (Supplemental Material 3).

Sources Characterization by Multivariate Analysis

Principal Component Analysis

Principal component (PC) analysis was used to characterize sources of metals in Kumasi soils. From the results, three principal components (PC1, PC2, and PC3) were extracted and accounted for 66.9% of the total variance. As shown in Figure 2, PC1 explained 33.6% of the total variance and was characterized by high loadings of Cu, Pb, Cd, As and Zn. PC2 explained 20.6% of the total variance (Figure 2) and was dominated by high loadings.

Figure 2 — Source characterization of heavy metals and metalloid concentrations by principal component analysis

Figure 3 — Hierarchical dendrogram of heavy metals and metalloid concentrations from the sample sites obtained using Ward’s clustering method
of Ni, Co, and Cr, while PC3 (Hg) explained 12.7% of the total variance.

**Cluster Analysis**
Hierarchical cluster analysis was used in this study to identify the degree of association and/or accumulation pattern of heavy metals from the sample sites (Figure 3). The dendrogram revealed five classes with Suame and KNUST Botanical Gardens in different clusters (Figure 3). Kejetia, Asawase, Mbrom, Ashtown, Racecourse, Yennawoso, Romanhill, Tafo, Adum, Central market and Asafo were in class 1 of the dendrogram (Figure 3), indicating a strong association between metal levels, sources or distribution in soils at these sites.

**Correlation Between Metals and Soil Properties**
The physico-chemical parameters determined in Kumasi soils were soil pH, organic matter and water content. Mean pH values ranged from 7.88 ± 0.49 (Kejetia) to 9.11 ± 0.5 (Romanhill) (Table 1). pH influences the rate of adsorption, retention and the transfer/migration of heavy metals in soil. The organic matter content ranged from 2.71 (Anomangye) to 8.2% (Asokwa) (Table 1). In the present study, concentrations of metals did not correlate with either pH or organic matter (Supplemental Material 4), similar to the results of a previous study.

**Distribution Maps of Heavy Metals and a Metalloid**
The distribution maps of Cd, Ni, As, Co, Cu and Pb highlighted Suame (22 on Figure 1) as hotspot zone, indicating high metal concentrations (Figures 1 and 4). The hotspots identified from the geochemical map for Zn, Cr and Hg indicated high concentrations of these metals in Suntreso, Aboabo/Yennawoso and Mbrom/Kejetia/New Suame, respectively.

**Contamination Factor and Pollution Load Index**
Table 2 shows the CF and PLI of metals in soils from the sample sites. The average CF for all the studied metals were greater than 3, indicating moderate to very strong contamination in Kumasi soils. The highest CF for Cu, Cd, Ni, As, Co and Pb were in Suame, while the highest CF for Hg was in Mbrom, Zn (Suntreso), and Cr in Aboabo (Table 2). In this study, the PLI of heavy metals and a metalloid revealed Suame (22.3) as the sample site most polluted with metals, followed by Kejetia (10.3) ≥ Yennawoso (10.1) > Racecourse (9.47) > Mbrom (8.93) > Aboabo (7.84) ≥ Asafo (7.79) ≥ Adum (7.60) ≥ Central market (7.46) > …, Afunkwanta (3.90) ≥ Bomso (3.77) = Anomangye (3.77). The study showed that all study sites (average PLI = 6.89 ± 3.38; range: 3.77 to 22.3) were polluted with metals when compared to KNUST Botanical Gardens (Table 2).

**Discussion**
**Metal Enrichment and Accumulation in Kumasi Soils**
The concentrations, EF and Igeo of heavy metals and a metalloid from some sample sites within the Kumasi metropolis were higher and this could be due to the fact that the sampling sites in Kumasi were located within an area with heavy vehicular movement/traffic and industrialization. In addition, the high soil metal enrichment could be attributed to differences in the magnitude of input for each metal and/or differences in the removal rate from soil. The moderate to extreme metal contamination in Suame could have resulted from the many auto mechanical/repair workshops and vehicles in the area.

**Principal Component Analysis**
As shown in Figure 2, PC1 showed an association with Cu, Pb, Cd, As and Zn and inputs of these metals and metalloid could have resulted from industrial activities and discharges such as mining and smelting processes. Cd is soft, ductile and is obtained as a by-product from the smelting of Zn ores. In mining contexts, Cd can also be found in the form of the greenockite mineral, cadmium sulfide. Cadmium in soils from the study area may come from the mining and processing of Zn and chalcophilic metals. The presence of Zn in the environment is associated with mining and smelting, which pollutes the air, water and soil and ultimately undergoes oxidation to release Zn2+ ions into water bodies.

Processing ore after blasting gold bearing rock involves roasting, and this results in the production of arsenic trioxide gas which is distributed throughout the study area by air currents. Arsenic is toxic and could accumulate in surface soils because of its non-biodegradable nature. Cadmium and As concentrations could also be associated with industrial activities/discharges, sewage sludge and municipal solid waste.

Large amounts of vehicular/industrial emissions and improper disposal of wastes could have contributed to the Cu, Pb, and Zn levels in Kumasi. Although no longer in use, previous use of leaded fuel could have accounted for the levels of Pb in soils. Lead is considered immobile in sub-surface soil and generally gets accumulated and remains strongly bound to soil mineral or organic components when deposited.

Ni, Co and Cr were grouped in the same principal component. The high EF and Igeo from the sample sites, especially for Cr, suggest an
anthropogenic input from industrial sources. Ghana, including the Kumasi metropolis, is filled with many tanning industries where animal skin is converted into leather, a practice considered to be an environmental threat. During this process, a variety of chemicals are used along with large volumes of water which are discharged as effluents containing liquid and solid wastes, and a significant amount of Cr. An average tannery uses approximately 65,000 tons of chemicals, including Cr (as chromium sulfate), annually, only to be discharged as effluents. The processes involved in the treatment of skin/hides are highly associated with sodium, potassium, magnesium and Co in effluents. Similarly, tanning processes are highly associated with Cr in soil.

Artisanal and small-scale gold mining, production of cement and non-ferrous metals (including Cu, Pb, Zn, aluminum and large-scale gold production) and disposal of Hg wastes are some of the main sources of environmental Hg contamination. Artisanal and small-scale mining is highly practiced in some sample sites in Kumasi, and during this process Hg is used to amalgamate gold. This practice, although simple and inexpensive, could contribute to the concentrations of metals, including Hg levels, in the environment. Other sources of Hg in Kumasi soils could include discarded thermometers, batteries and fluorescent lamps, as these accounted for 40% of Hg emissions in North America. In addition, the use of barometers releases Hg into the environment. In agricultural systems, pesticides, fertilizers, sewage sludge and irrigation water were some of the main sources of Hg contamination.

Cluster Analysis
KNUST Botanical Gardens (reference site) was grouped in a different cluster of the dendrogram (Figure 3) and this trend could be attributed to the low metal concentrations compared to other sites and the world range for unpolluted soils. This trend, again, suggests that metals detected in KNUST Botanical Garden soils originated from natural/geological processes. On the other hand, high levels of metals were detected in Suame (Table 1) which was in class 4 of the dendrogram (Figure 3) and, EF and Igeo indicated moderate to extreme contamination at this site (Supplemental Material 1 and 3). Differences in metal sources or the higher level of soil metal contamination could have contributed significantly to the present results.

Sampling sites such as Kejetia, Asawase, Mbrom, Ashtown, Racecourse, Yennyawoso, Romanhill, Tafo, Adum, Central market and Asafo were grouped in class 1 of the dendrogram (Figure 3), implying a similar/single source of metal pollution at these sites. Sources of metals in Mbrom and Central market, and Adum and Asafo were closely related and showed a strong association with metals levels in Racecourse, Kejetia and Yennyawoso (Figure 3). As shown in Figure 1, the sampling sites grouped in class 1 are
Close together, with the exception of Yennawosso (site # 18) and Tafo (site # 20), which are about 1.3 km apart. This trend could possibly be due to effects of artisanal and small-scale gold mining in some sample sites.

Correlation Between Metals and Soil Properties

Lack of significant correlation between soil properties and heavy metals could be attributed to a continuous input, since the release and transport of heavy metals are governed by complex processes.

Another possible reason could be variations in soil type within the sampled area.

Distribution Maps of Heavy Metals and a Metalloid

As shown in the distribution maps (Figure 4), the high metal concentrations in Suame could also be due to heavy vehicle traffic and the large amount of metal scrap in the area. The “Suame Magazine” is one of Africa’s largest light-industrial clusters. It is a 200 hectare area filled with polluted industrial waste, auto-mechanic workshops and saw mills, with frequent burning of tires generating a significant amount of waste. The hotspots identified from the distribution maps for Zn (Suntreso), Cr (Aaboob and Yennawosso) and Hg (Mbrum, Kejetia and New Suame) could be due to the fact that some of these sampling sites are densely populated with vehicles and light (small scale) industries, including many tanneries.

Conclusions

Concentrations of heavy metals and a metalloid were studied in Kumasi soils and Zn, Pb, Cd and Cr were found to be enriched in some of the sample sites, suggesting anthropogenic inputs. Based on the obtained Igeo values, Cr, Zn, Cd, Hg and Pb showed moderate to extreme contamination in 100, 97, 77, 65 and 45% of the sample sites, respectively. Distribution maps and pollution load index values highlighted Suame as the most significantly polluted site, followed by Kejetia ≥ Yennawosso > Racecourse > Mbrum > Aaboob ≥ Asofo ≥ Adum ≥ Central market > …, Afunkwanta ≥ Bomso = Anomangye. Finally, the present study indicates that industrial activities, including mining, are the major sources of metals in Kumasi soils, as observed at the most contaminated site of Suame.

Acknowledgements

This work was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan awarded to M. Ishizuka (No. 24405004 and No. 24248056) and Y. Ikenaka (No. 26304043, 15H0282505, 15K1221305), and the foundation of JSPS Core to Core Program (AA Science Platforms) and Bilateral Joint Research Project (PG36150002 and PG36150003). We also acknowledge the financial support by The Mitsu Co., Ltd. Environment Fund. We are grateful to Mr. Takahiro Ichise (Laboratory of Toxicology, Graduate School of Veterinary Medicine, Hokkaido University) for technical support.

Copyright Policy

This is an Open Access article distributed in accordance with Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0/).

References

1. Navarro MC, Perez-Sirvent C, Martinez-Sanchez MJ, Vidal J, Tovar PJ, Bech J. Abandoned mine sites as a source of contamination by heavy metals: a case study in a semi-arid zone. J Geochem Explor [Internet]. 2008 Feb-Mar [cited 2016 Oct 12];96(2-3):183-93. Available from: http://www.sciencedirect.com/science/article/pii/S0375674207000519 Subscription required to view.

2. Linnik PM, Zubenko JB. Role of bottom sediments in the secondary pollution of aquatic environments by heavy metal compounds. Lake Reserv: Res Manag [Internet]. 2000 Mar [cited 2016 Oct 12];5(1):11-21. Available from: http://onlinelibrary.wiley.com/doi/10.1440/1770.2000.00094.x/full Subscription required to view.

3. Ogoyi DO, Mwita CJ, Nguu1 EK, Shiundu PM. Determination of heavy metal content in water, sediment and microalgae from Lake Victoria, East Africa. Open Environ Eng J [Internet]. 2011 [cited 2016 Oct 12];4:156-61. Available from: http://erepository.utoronto.ca/bitstream/1807/49403/1/er08047.pdf

4. 2010 population and housing census [Internet]. Accra, Ghana: Ghana Statistical Service; 2012 May [cited 2016 Oct 12]. 117 p. Available from: http://www.statsghana.gov.gh/docfiles/2010phc/Census2010_Summary_report_of_final_results.pdf

5. Akoto O, Ephraim JH, Darko G. Heavy metals pollution in surface soils in the vicinity of abundant railway servicing workshop in Kumasi, Ghana. Int J Environ Res [Internet]. 2008 Autumn [cited 2016 Oct 12];2(4):359-64. Available from: https://tspace.library.uottawa.ca/bitstream/1807/49403/1/er08047.pdf

6. Kabata-Pendias A, Pendias H. Trace elements in soils and plants. 2nd ed. Boca Raton, Florida: CRC Press; 1991 Dec 7. 384 p.

7. Bortey-Sam N, Akoto O, Ikenaka Y, Nakayama SM, Ishizuka M. Determination of benzo[a] pyrene levels in ambient air and the source of polycyclic aromatic hydrocarbons using a diagnostic ratio method in Ghana. Ipn J Vet Res [Internet]. 2013 Feb 1 [cited 2016 Oct 12];61 Suppl:S72-4. Available from: http://europepmc.org/abstract/med/23631159 Subscription required to view.

8. Bortey-Sam N, Ikenaka Y, Nakayama SM, Akoto O, Yohannes YB, Baidoo E, Mizukawa H, Ishizuka M. Occurrence, distribution, sources and toxic potential of polycyclic aromatic hydrocarbons (PAHs) in surface soils from the Kumasi Metropolis, Ghana. Sci Total Environ [Internet]. 2014 Oct 15 [cited 2016 Oct 12];496:47-1-8. Available from: http://dx.doi.org/10.1016/j.scitotenv.2014.07.071 Subscription required to view.

9. Bortey-Sam N, Ikenaka Y, Akoto O, Nakayama SM, Yohannes YB, Baidoo E, Mizukawa H, Ishizuka M. Geochemical Control Study of Heavy Metal Levels and a Metalloid in Surface Soils in Ghana: A Case Study in a Semi-Arid Zone. J Geochem Explor [Internet]. 2010 Feb-Mar [cited 2016 Oct 12];106:26-36. Available from: http://www.sciencedirect.com/science/article/pii/S0375674210000059 Subscription required to view.
14. Mulier G. Index of geoaccumulation in sediments of the Rhine River. Geol J. 1969;2(3):109-18.

15. Hakanson L. An ecological risk index for aquatic pollution control, a sedimentological approach. Water Res. [Internet]. 1980 Apr [cited 2016 Oct 12];14(4):975-1001. Available from: http://www.sciencedirect.com/science/article/pii/0043135080901438 Subscription required to view.

16. Varol M. Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. J Hazard Mater [Internet]. 2011 Nov [cited 2016 Oct 12];195:355-64. Available from: http://www.sciencedirect.com/science/article/pii/S0304389411010697 Subscription required to view.

17. Tomlinson DL, Wilson JG, Harris CR, Jeffrey DW. Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. Helgol Meeresunters [Internet]. 1980 [cited 2016 Oct 12];33:566-75. Available from: http://hmn. biomedcentral.com/articles/10.1007/BF02414780

18. Guidance for developing ecological soil screening levels: OSWER-directive 9285.7-75 [Internet]. Washington, D.C.: United States Environmental Protection Agency; 2003 Nov [revised 2005 Feb; cited 2016 Oct 12]. 85 p. Available from: https://www.epa.gov/chemical-research/guidance-developing-ecological-soil-screening-levels

19. de Matos AT, Fontes MPF, da Costa LM, Martinez MA. Mobility of heavy metals as related to soil chemical and mineralogical characteristics of Brazilian soils. Environ Pollut [Internet]. 2001 Oct [cited 2016 Oct 12];111(3):429-35. Available from: http://dx.doi.org/10.1016/S0269-7491(00)00088-9 Subscription required to view.

20. Al-Khashman OA, Shawabkeh RA. Metals distribution in soils around the cement factory in southern Jordan. Environ Pollut [Internet]. 2006 April [cited 2016 Oct 12];140(3):387-94. Available from: http://dx.doi.org/10.1016/j.envpol.2005.08.023 Subscription required to view.

21. Bortey-Sam N, Nakayama SM, Akoto O, Ikenaka Y, Baidoo E, Mizukawa H, Ishizuka M. Ecological risk of heavy metals and a metalloid in agricultural soils in Tarkwa, Ghana. Int J Environ Res Public Health [Internet]. 2015 Sep [cited 2016 Oct 12];12(9):11448-65. Available from: http://www.mdpi.com/1660-4612/12/9/11448.htm

22. Obiri S. Determination of heavy metals in water from boreholes in Dumasi in the Wassa west district of the western region of the Republic of Ghana. Environ Monit Assess [Internet]. 2007 Jul [cited 2016 Oct 12];130(1-3):455-63. Available from: http://link.springer.com/article/10.1007/s10661-006-9345-y Subscription required to view.

23. Amonoo–Neizer EH, Nyamah D, Bakiamoh SB. Mercury and arsenic pollution in soil and biological samples around mining towns of Obuasi, Ghana. Water Air Soil Poll [Internet]. 1996 Oct [cited 2016 Oct 12];91(3-4):363-73. Available from: https://link.springer.com/article/10.1007/BF00666270 Subscription required to view.

24. Zhao L, Xu Y, Hou H, Shangguan Y, Li F. Source identification and health risk assessment of metals in urban soils around the Tanggu chemical industrial district, Tianjin, China. Sci Total Environ [Internet]. 2014 Jan [cited 2016 Oct 12];468-469:654-62. Available from: http://www.sciencedirect.com/science/article/pii/S0048969713010218 Subscription required to view.

25. McLean JE, Bledsoe BE. Behavior of metals in soil. In: Ground water issue [Internet]. Washington, D.C.: United States Environmental Protection Agency; 1992 Oct [cited 2016 Oct 12]. 25 p. Available from: https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=1000D5STX

26. Bai J, Xiao R, Cui B, Zhang K, Wang Q, Liu X, Gao H, Huang L. Assessment of heavy metal pollution in wetland soils from the young and old reclaimed regions in the Pearl River Estuary, South China. Environ Pollut [Internet]. 2011 Mar [cited 2016 Oct 12];159(3):817-24. Available from: http://dx.doi.org/10.1016/j.envpol.2010.11.004 Subscription required to view.

27. Tariq SR, Shah MH, Shaheen N, Khalique A, Manzoor S, Jaffar M. Multivariate analysis of selected metals in tannery effluents and related soil. J Hazard Mater [Internet]. 2005 Jun 30 [cited 2016 Oct 12];122(1-2):17-22. Available from: http://www.sciencedirect.com/science/article/pii/S0304389605001238 Subscription required to view.

28. Landgrave J. A pilot plant for removing chromium from residual water of tanneries. Environ Health Perspect [Internet]. 1995 Feb [cited 2016 Oct 12];103(Suppl 1):63-5. Available from: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC1519324/

29. Mason RP, Choi AL, Fitzgerald WF, Hammerschmidt CR, Lamborg CH, Soerensen AL, Sunderland EM. Mercury biogeochemical cycling in the ocean and policy implications. Environ Res [Internet]. 2012 Nov [cited 2016 Oct 12];119:101-17. Available from: http://www.sciencedirect.com/science/article/pii/S0013935112001132 Subscription required to view.

30. Rajaee M, Long RN, Renne EP, Basu N. Mercury exposure assessment and spatial distribution in a Ghanaian small-scale gold mining community. Int J Environ Res Public Health [Internet]. 2015 Sep [cited 2016 Oct 12];12(9):10755-82. Available from: http://www.mdpi.com/1660-4612/12/9/10755/htm

31. Hutchison AR, Atwood DA. Mercury pollution and remediation: the chemist's response to a global crisis. J Chem Crystallogr [Internet]. 2003 Aug [cited 2016 Oct 12];33(6):631-45. Available from: http://link.springer.com/article/10.1023/A:1024906212586 Subscription required to view.

32. Hsu ZY, Su SW, Lai HY, Guo HY, Chen TC, Chen ZS. Remediation techniques and heavy metal uptake by different rice varieties in metal-contaminated soils of Taiwan: new aspects for food safety regulation and sustainable agriculture.
33. Lu AX, Wang JH, Qin XY, Wang KY, Han P, Zhang SZ. Multivariate and geostatistical analyses of the spatial distribution and origin of heavy metals in the agricultural soils in Shunyi, Beijing, China. *Sci Total Environ* [Internet]. 2012 May 15 [cited 2016 Oct 12];425:66-74. Available from: http://www.sciencedirect.com/science/article/pii/S0048969712003348 Subscription required to view.

34. Grant C, Sheppard S. Fertilizer impacts on cadmium availability in agricultural soils and crops. *Hum Ecol Risk Assess* [Internet]. 2008 Apr [cited 2016 Oct 12];14(2):210-28. Available from: http://dx.doi.org/10.1080/10807030801934895 Subscription required to view.

35. Dartey E, Adimado AA, Agyarko K. Evaluation of airborne lead levels in storage battery workshops and some welding environments in Kumasi metropolis in Ghana. *Environ Monit Assess* [Internet]. 2010 May [cited 2016 Oct 12];164(1-4):1-8. Available from: https://www.ncbi.nlm.nih.gov/pubmed/19357980 Subscription required to view.