Geostatistical Analysis of Contamination of Soils in an Urban Area in Ghana

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Open Science Index, Mathematical and Computational Sciences Vol:12, No:6, 2018 publications.waset.org/10009292.pdf

***Abstract*—**Urbanization remains one of the unique predominant factors which is linked to the destruction of urban environment and its associated cases of soil contamination by heavy metals through the natural and anthropogenic activities. These activities are important sources of toxic heavy metals such as arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), and lead (Pb), nickel (Ni) and zinc (Zn). Often, these heavy metals lead to increased levels in some areas due to the impact of atmospheric deposition caused by their proximity to industrial plants or the indiscriminately burning of substances. Information gathered on potentially hazardous levels of these heavy metals in soils leads to establish serious health and urban agriculture implications. However, characterization of spatial variations of soil contamination by heavy metals in Ghana is limited. Kumasi is a Metropolitan city in Ghana, West Africa and is challenged with the recent spate of deteriorating soil quality due to rapid economic development and other human activities such as "Galamsey", illegal mining operations within the metropolis. The paper seeks to use both univariate and multivariate geostatistical techniques to assess the spatial distribution of heavy metals in soils and the potential risk associated with ingestion of sources of soil contamination in the Metropolis. Geostatistical tools have the ability to detect changes in correlation structure and how a good knowledge of the study area can help to explain the different scales of variation detected. To achieve this task, point referenced data on heavy metals measured from topsoil samples in a previous study, were collected at various locations. Linear models of regionalisation and coregionalisation were fitted to all experimental semivariograms to describe the spatial dependence between the topsoil heavy metals at different spatial scales, which led to ordinary kriging and cokriging at unsampled locations and production of risk maps of soil contamination by these heavy metals. Results obtained from both the univariate and multivariate semivariogram models showed strong spatial dependence with range of autocorrelations ranging from 100 to 300 meters. The risk maps produced show strong spatial heterogeneity for almost all the soil heavy metals with extremely risk of contamination found close to areas with commercial and industrial activities. Hence, ongoing pollution interventions should be geared towards these highly risk areas for efficient management of soil contamination to avert further pollution in the metropolis.

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***Keywords*—**Coregionalization, ordinary cokriging, multivariate geostatistical analysis, soil contamination, soil heavy metals, risk maps, spatial distribution.

I. Introduction

THERE are growing public concerns world-wide in recent times over the spate of environmental degradation due to rapid urbanization. Although urbanization leads to economic growth and development [42], its negative impact on biodiversity poses serious health implications. Soil is a fundamental and important natural resource and also vital to human survival; however, there are numerous industrial and other anthropogenic activities sited in urban areas which are the key sources of toxic heavy metals such as As, Cd, Cr, Cu, Fe, Mn, Pb, Ni and Zn which contaminate the soil and its environment [1]-[4]. Human activities including agricultural practices, indiscriminate burning of substances, disposal of electronic/ electrical appliances and domestic/industrial waste as well as atmospheric deposition, combine with the naturally occurring heavy metals, derived from the geological parent mineral to increase the contamination of soil to endanger the environment [5]-[9]. High concentration levels of heavy metals reduce soil quality and also increase human exposure to the metals, which can threaten food safety and also pose potential health risks [10]-[13]. These environmental challenges are not different in Ghana. Its natural environment is being degraded, threatening water bodies and ecosystems coupled with poor sanitation across the country. This has led to a national crusade against the small scale illegal mining activities, popularly known as "Galamsey", and indiscriminate disposal of domestic and industrial rubbish to protect the environment and also improve the sanitation issue in the country. Environmental risk assessment involves provision of valuable information on spatial and temporal variations of the pollutants and their possible sources of risk to aid effective management control [3], [14]-[16].

Geostatistical analysis is a powerful spatial statistical technique which contributes immensely to prediction of random processes distributed over space and time [16], [17]. It is widely applied in environmental monitoring to analyze spatial and temporal distributions of pollutant concentrations from soil and groundwater resources [3]-[4], [7]-[9], [18]-[24]. References [3] and [4] used various geostatistical techniques including indicator kriging (IK) and ordinary kriging (OK) to explore spatial distribution and hazard assessment of four heavy metals (Cr, Cd, Ni and Pb) in soils at a coal mining and paper mill industrial areas in north-eastern India. The two separate studies produced variogram models and risk maps to

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describe the range of auto-correlations of the observed soil contaminations and probability of exceeding the maximum permissible limit value for each heavy metal. Other studies combine the classical multivariate modelling approach with geostatistical analysis to characterise urban soils and groundwater quality. Reference [9] performs factor analysis coupled with OK to quantify and establish potential sources of various heavy metals in an agricultural basin in Spain, while the principal component analysis is applied with OK in [19]-[21] to investigate heavy metal contamination in various farmland and industrial areas in China to facilitate management strategies to control soil pollution. Geostatistical multivariate techniques via linear model of coregionalisation (LMC) have been used to establish joint spatial variations in soil physiochemical properties and other natural resources [14]-[16]. References [25] and [26] use various cokring techniques to estimate Cu grade and cobalt by accounting for correlated covariates to delineate areas of high risk of excess of these heavy metals, while prediction performances of simple cokriging and ordinary cokring estimators using environmental dataset on concentrations of five heavy metals (Cd, Cu, Pb, Ni and Zn) have been compared in [27]. Reference [28] applies factorial kriging to study spatial relationships among some soil phyiochemical properties in central Italy, while similar kriging methodology via cokring is used in [29] to characterize the spatial variability of microbiological and soil attributes.

Multivariate assessments of soil metals and water quality have extensively been explored in various parts of Ghana [5]-[6], [10], [30]. However, none of these studies have or adequately explored the use of geostatistical analysis. Previous analysis of topsoil quantifying the risk levels of heavy metals in [5], [6] lacks detailed statistical analysis to properly characterize the risk levels and their sources of pollution. The second study in [6] showed risk maps of soil contamination but did not produce the structural analysis report to ascertain the prediction accuracy and uncertainty of risk levels at various local areas. This study applies multivariate geostatistical analysis to further characterize the contamination levels of four soil heavy metals (As, Cr, Cu and Zn) and to identify their potential health hazards for local residents in an urban area in Ghana.

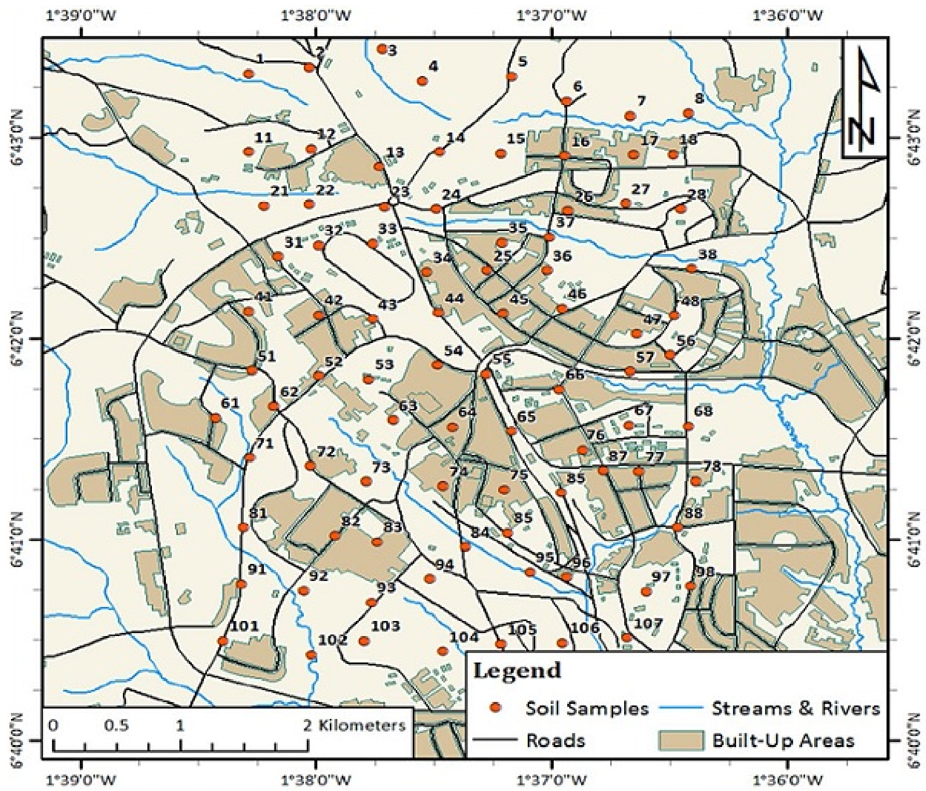

Fig. 1 Map of Kumasi showing topsoil sample locations [5]

II. Materials and Methods

A. Study Area and Data

Point referenced data on some main toxic heavy metals in topsoil samples in previous studies conducted in Kumasi [5], [6] were collected. Kumasi is the second largest metropolitan city and also serves as the regional capital of Ashanti Region of Ghana in West Africa. It lies between longitudes 1°35′W and 1°40′W and latitudes 6°40′N and 6°44′N with a total land area of about 229 km^2. It is relatively warm in the metropolis with annual temperatures varying within 20-30 °C, while the annual rainfall is about 1,400 mm. Kumasi is densely populated with an estimated inhabitants of over 2 million [31] and also characterised with various commercial and industrial activities. It has the Kejetia Market with over 45,000 shops,

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the largest market in the country, and Suame Magazine, a large industrial area designated for auto-mechanic workshops for metal engineering, fabrication and vehicle repairs [32]. New built up areas, mostly with unauthorised structures, are sprinkling up, while the city is also interspersed with streams and rivers, where local residents often engage in unorthodox crop farming and illegal mining activities. These human activities have resulted to indiscriminate disposal and burning of substances to pollute the soil and other natural resources in the environment with heavy metals being among the major pollutants of these sources [33]. The data for analysis in this study were the contamination levels (in mg/kg) of four heavy metals, Ar, Cr, Cu and Zn in topsoil samples in the city. The topsoil samples were collected within a 0.5×0.5 km^2 regular grid of 94 locations across the city and its immediate environs as described in the surveys in [5] and [6]. Part of the data collected has been obtained for further assessment of soil pollution of these heavy metals. Fig. 1 shows the study area, indicating the sampling locations and other land features.

B. Multivariate Geostatistical Analysis

1. Preliminary Concepts

Geostatistical analysis is based on the theory of a regionalised variable $Z(\mathbf{u})$ that varies continuously over the domain $\mathbf{D} \subseteq \mathbb{R}^d$ and assumes spatial auto-correlation such that samples closer in space are more alike than those further apart [34], [35]. The collection of such random variables in space $\{Z(\mathbf{u}) : \mathbf{u} \in \mathbf{D} \subseteq \mathbb{R}^d\}$ is called *random function*, with a well-defined joint distribution function (1), which models the joint uncertainty of the unsampled values of $Z(\mathbf{u})$ at locations $\mathbf{u}$ and a variogram (2), the main structural tool for describing the spatial dependence of $Z(\mathbf{u})$ by assuming the much weaker intrinsic stationarity assumption:

$$F(z_1,...,z_n;\mathbf{u}_1,...,\mathbf{u}_n) = P[Z(\mathbf{u}_1) \le z_1,...,Z(\mathbf{u}_n) \le z_n], \tag{1}$$

for every collection $\mathbf{u} = \mathbf{u}_1,...,\mathbf{u}_n \in \mathbf{D}$.

$$\begin{aligned} 2\gamma(\mathbf{h}) &= Var(Z(\mathbf{u}+\mathbf{h}) - Z(\mathbf{u})) \\ &= E[\{Z(\mathbf{u}+\mathbf{h}) - Z(\mathbf{u})\}^2], \end{aligned} \tag{2}$$

$\forall\, \mathbf{u} \in \mathbf{D}$ and $\forall\, \mathbf{h} \in \mathbb{R}^d$ where $\mathbf{h}$ is the distance vector separating the paired observations $Z(\mathbf{u}+\mathbf{h})$ and $Z(\mathbf{u})$.

Geostatistical kriging techniques are used to model the spatial patterns, predict values at unmeasured locations, and assess the uncertainty associated with a predicted value at these locations. Kriging is a generalized least-squares interpolation method, which predicts random attribute(s) values at unmeasured locations by using $n(h)$ neighboring sampled observations $\{Z(\mathbf{u}_\alpha); \alpha = 1,2,...,n(h)\}$ and spatial correlation information obtained by a variogram model [15]. Geostatistical kriging techniques include the ordinary kriging (OK) and ordinary cokriging (OCK), which are used for predicting a single and multiple random attributes, respectively.

In this study, the observed contamination levels of the heavy metals in topsoil samples at the n locations were transformed via the unit normal-score probability distribution. The transformed dataset at locations $\mathbf{u}_1, \mathbf{u}_2, ..., \mathbf{u}_n$ is denoted by $\{Z_i(\mathbf{u}_\alpha) : i = 1,2,...,k\}$, where $Z_1(\mathbf{u}), Z_2(\mathbf{u}), ..., Z_k(\mathbf{u})$ are the concentration levels of the four heavy metals (Ar, Cr, Cu, and Zn). The contamination levels of the heavy metals were then modelled as realisation of $k = 4$ random functions $\{Z_i(\mathbf{u}) : i = 1,2,...,k; \mathbf{u} \in \mathbf{D}\}$ occurring in space. To predict values for each $Z_i(\mathbf{u})$ at $n_i(\mathbf{u})$ unsampled locations, the semivariogram $\gamma_i(\mathbf{h})$, which charactrises the spatial dependence via the average variability between paired sampled observations separated by a lag distance $\mathbf{h}$, is defined following (2). The semivariograms for all the soil heavy metals were computed from the observed sample data using the experimental semivariogram following the Matheron's estimator (3) proposed by [35].

$$\hat{\gamma}_i(\mathbf{h}) = \frac{1}{2n(h)} \sum_{\alpha=1}^{n(h)} \left(Z_i(\mathbf{u}_\alpha + \mathbf{h}) - Z_i(\mathbf{u}_\alpha) \right)^2 \tag{3}$$

where $Z_i(\mathbf{u}_\alpha)$ and $Z_i(\mathbf{u}_\alpha + \mathbf{h})$ are values for the soil heavy metal observed at locations $\mathbf{u}_\alpha$ and $\mathbf{u}_\alpha + \mathbf{h}$, respectively, while $n(h)$ is the number of paired observed values separated by distance vector $\mathbf{h}$. The experimental semivariograms were then modelled as isotropic process, depending only on the magnitude of the separation vector, and fitted using a theoretical spherical model nested with nugget effect (4):

$$\gamma(h;\theta) = \begin{cases} 0 & ; h = 0 \\ a_0 + a_1 \left\{ (3/2)(h/r) - (1/2)(h/r)^3 \right\} & ; 0 < h \le r \\ a_0 + a_1 & ; h \ge r \end{cases} \tag{4}$$

where $\theta = (a_0, a_1, r)^{\mathrm{T}}$ contains the nugget (a_0), the sill (a_1) and the range (r) being the main parameters used to characterise the spatial autocorrelation structure of the soil heavy metals under investigation.

The estimation of each soil heavy metal $Z_i(\mathbf{u})$ was performed using the ordinary kriging optimal estimator (5), which assumes a locally constant mean but unknown to predict an unknown location $\mathbf{u}_0$ using a linear combination of $n(u)$ data values within the local neighborhood.

$$\hat{Z}_{ok}(\mathbf{u}) = \sum_{\alpha=1}^{n(u)} \lambda_\alpha Z_i(\mathbf{u}_\alpha); \text{ such that } \sum_{\alpha=1}^{n(u)} \lambda_\alpha = 1 \tag{5}$$

where the weights λ_α were optimally assigned to the observed values $Z_i(\mathbf{u}_\alpha)$ by minimising the prediction error variance

$\sigma_e^2 = Var(\hat{Z}_{ok}(\mathbf{u}) - Z_i(\mathbf{u})) = E[(\hat{Z}_{ok}(\mathbf{u}) - Z_i(\mathbf{u}))^2]$ such that weights sum to 1 to ensure its best linear unbiased estimator (BLUE) property. This leads to solving the following OK system of equations (6) via the method of Lagrange multipliers for the weights λ_α to be determined:

$$\begin{cases} \sum_{\beta=1}^{n(u)} \lambda_\beta^{ok} \gamma(\mathbf{u}_\alpha - \mathbf{u}_\beta) - \mu_{ok} = \gamma(\mathbf{u}_\alpha - \mathbf{u});\ \alpha = 1,\ldots,n(u) \\ \sum_{\beta=1}^{n(u)} \lambda_\beta^{ok} = 1 \end{cases} \tag{6}$$

where μ_{ok} is the Lagrange multiplier for optimal weights (7) to be obtained [15], [36]:

$$\boldsymbol{\lambda}_{ok}^{\mathrm{T}} = \boldsymbol{\Gamma}^{-1}\boldsymbol{\gamma} \tag{7}$$

where $\boldsymbol{\Gamma}$ is a $n(\mathbf{u}) \times n(\mathbf{u})$ matrix whose components are $\gamma(\mathbf{u}_\alpha - \mathbf{u}_\beta)$ for $\beta = 1,2,\ldots,n(u)$; $\boldsymbol{\gamma}$ is a vector with components $\boldsymbol{\gamma} = [\gamma(\mathbf{u}_0 - \mathbf{u}_1), \gamma(\mathbf{u}_0 - \mathbf{u}_2), \ldots, \gamma(\mathbf{u}_0 - \mathbf{u}_{n(u)})]^{\mathrm{T}}$ and $\mathbf{I}$ is a vector with entries 1. The optimal weights in (7) result in the OK estimator in (5) with minimum prediction variance estimated by (8):

$$\sigma_e^2 = \sum_{\beta=1}^{n(u)} \lambda_\beta^{ok} \gamma(\mathbf{u}_\alpha - \mathbf{u}_\beta) - \mu_{ok} = \boldsymbol{\lambda}_{ok}^{\mathrm{T}} \boldsymbol{\gamma} \tag{8}$$

where $\boldsymbol{\lambda}_{ok}^{\mathrm{T}} = (\lambda_1^{ok}, \lambda_2^{ok}, \ldots, \lambda_{n(u)}^{ok}, \mu_{ok})^{\mathrm{T}}$.

2. Linear Model of Coregionalisation and Cokriging

The geostatistical OK estimator in (5), as presented in the previous section, implements the quantification and mapping of a single attribute (soil heavy metal) $Z_i(\mathbf{u})$ through a linear model of regionalisation of the experimental semivariogram in (3) using (4). However, each soil heavy metal can also be predicted through its jointly interactions with the other soil heavy metals observed at same locations for better insight of spatial variations of the various soil heavy metals at same or different scales. This then extends the ordinary kriging to the multiple random variables $Z_1(\mathbf{u}), Z_2(\mathbf{u}), \ldots, Z_k(\mathbf{u})$ for the multiple spatial variations to be studied simultaneously through a linear model of coregionalisation (LMC) to pave way for the ordinary co-kriging (OCK) estimation of each soil heavy metal Z_i, accounting for the spatial correlations with the other heavy metals.

As with the univariate case, the multivariate random function $\{\mathbf{Z}(\mathbf{u}); \mathbf{u} \in \mathbf{D}\}$, defined over the domain $\mathbf{D}$, has the components $Z_1(\mathbf{u}), Z_1(\mathbf{u}), \ldots, Z_k(\mathbf{u})$ as vectors of the random functions which are characterised by the semivariogram matrix in (9) whose components are the semivariograms $\gamma_{ij}(\mathbf{h})$ for all pairs $(i,j) = 1,\ldots,k$:

$$\boldsymbol{\Gamma}(\mathbf{h}) = \frac{1}{2} E[(\mathbf{Z}(\mathbf{u}+\mathbf{h}) - \mathbf{Z}(\mathbf{u}))(\mathbf{Z}(\mathbf{u}+\mathbf{h}) - \mathbf{Z}(\mathbf{u}))^{\mathrm{T}}] \tag{9}$$

where the diagonals are called direct-semivariograms for $i = j$ as in (3), and the off diagonals are called cross-semivariograms for $i \neq j$, which is estimated by the experimental semivariograms in (10):

$$\hat{\gamma}_{ij}(\mathbf{h}) = \frac{1}{2n(\mathbf{h})} \sum_{\alpha=1}^{n(\mathbf{h})} \left(\mathbf{Z}_i(\mathbf{u}_\alpha + \mathbf{h}) - \mathbf{Z}_i(\mathbf{u}_\alpha)\right)\left(\mathbf{Z}_j(\mathbf{u}_\alpha + \mathbf{h}) - \mathbf{Z}_j(\mathbf{u}_\alpha)\right)^{\mathrm{T}} \tag{10}$$

for $i = 1,..,k$, where $n(\mathbf{h})$ is the number of pairs of sample locations separated by the lag vector $\mathbf{h}$. To account for the spatial dependence between the k attributes a permissible LMC (11) consisting of nugget effect and a spherical model (4) was used to fit to all the $k(k+1)/2$ direct- and cross-experimental semivariograms in (10) [15], [26], [37], [38].

$$\Gamma(\mathbf{h}) = \gamma_{ij}(\mathbf{h}) = \sum_{l=0}^{k} \mathbf{B}_l g^l(\mathbf{h}), \forall i, j \tag{11}$$

where $\mathbf{B}_l = (b_{ij}^l)$ is a positive semi-definite matrix.

The OCK estimator is the multivariate version of the OK estimator (5) where the random variables $Z_i(\mathbf{u}); i = 1,2,\ldots k$ are collocated with observations $\{Z_i(\mathbf{u}_\alpha); i = 1,2,\ldots k; \alpha = 1,2,\ldots,n\}$. The OCK unbiased estimator for kriging the soil heavy metal $Z_i(\mathbf{u})$, correlating spatially with the other covariates via LMC (10), (11) and using $n_i(u)$ neighborhood observations is given by (12):

$$\hat{Z}_{(i)ock}(\mathbf{u}) = \sum_{i=1}^{k} \sum_{\alpha_i=1}^{n_i(u)} \lambda_{\alpha_i} Z_i(\mathbf{u}_{\alpha_i});\quad i = 1,2,\ldots k \tag{12}$$

where the kriging weights λ_{α_i} are computed by minimising the prediction error variance subject to the unbiased constraints (13), for $(i,j) = 1,2,\ldots k$:

$$\sum_{\alpha_i=1}^{n_i(u)} \lambda_{\alpha_i} = 1 \text{ and } \sum_{\alpha_j=1}^{n_j(u)} \lambda_{\alpha_j} = 0 \tag{13}$$

from which the OCK system is expressed in terms of the direct- and cross-semivariograms (14):

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$$\begin{cases} \sum_{j=1}^{k}\sum_{\beta_j=1}^{n_i(u)} \lambda_{\beta_j}^{ock}\gamma_{ij}(\mathbf{u}_{\alpha_i}-\mathbf{u}_{\beta_j})-\mu_i=\gamma_{ij}(\mathbf{u}_{\alpha_j}-\mathbf{u});\ j=1,\ldots,k \\ \sum_{\beta_j=1}^{n_i(u)} \lambda_{\beta_i}^{ock}=1;\ \sum_{\alpha_j=1}^{n_i(u)} \lambda_{\alpha_j}^{ock}=0;\ j=1,\ldots,k; \end{cases} \quad (14)$$

for the optimal cokring weights λ_{α_i} to be computed for each i as in (7).

III. Results and Discussion

A. Descriptive Statistics of Heavy Metals

The summary statistics of the four topsoil metals (As, Cr, Cu and Zn) considered in this study are summarised and shown as in Table I. The mean values exceed the medians, which shows that the distributions of soil contamination of the four heavy metals were all positively skewed. Higher mean amounts of Zn (96.64 mg/kg) and Cr (44.95 mg/kg) were observed in topsoil samples of the study area as compared with the lower mean values for Cu (27.79 mg/kg) and As (18.65 mg/kg). The variation in distribution relative to the mean was highest for Cu with a coefficient of variation (CV) of 2.12, while As has the least variation in distribution with CV of 1.43. Correlation analysis between paired heavy metals was also performed and the results as presented in Table II. There were relatively positively weak (but significant α=0.05) correlations (0.280-0.390) between As and the other three heavy metals as indicated by the Spearman correlation coefficients. On the other hand, the correlations among pairs of the remaining three heavy metals (Cr, Cu and Zn) suggest very strong positive correlations (0.810-0.871) and significant at α=0.001.

The observed values of heavy metals in topsoils were transformed using the unit normal-score distribution approach to achieve more symmetric distributions [15], [39] for further analysis. The shapes of the distributions for the normal-score transformed topsoil metals as shown in Fig. 2 are more symmetrical compared to that of the original values.

TABLE I
DESCRIPTIVE STATISTICS OF HEAVY METALS (AS, CR, CU AND ZN) CONTAMINATION IN SOIL (MG/KG)

Statistic	As	Cr	Cu	Zn
Minimum	1.0000	0.1000	0.5700	0.7000
Maximum	190.98	478.00	377.00	912.00
Mean	18.650	44.950	27.790	96.640
Standard Deviation	26.630	83.410	58.930	179.89
Lower Quartile	4.8000	1.3300	1.4300	2.3100
Median	11.980	3.1000	2.2850	5.8900
Upper Quartile	23.120	59.880	22.980	109.50
Coefficient of Variation	1.4300	1.8700	2.1200	1.8600

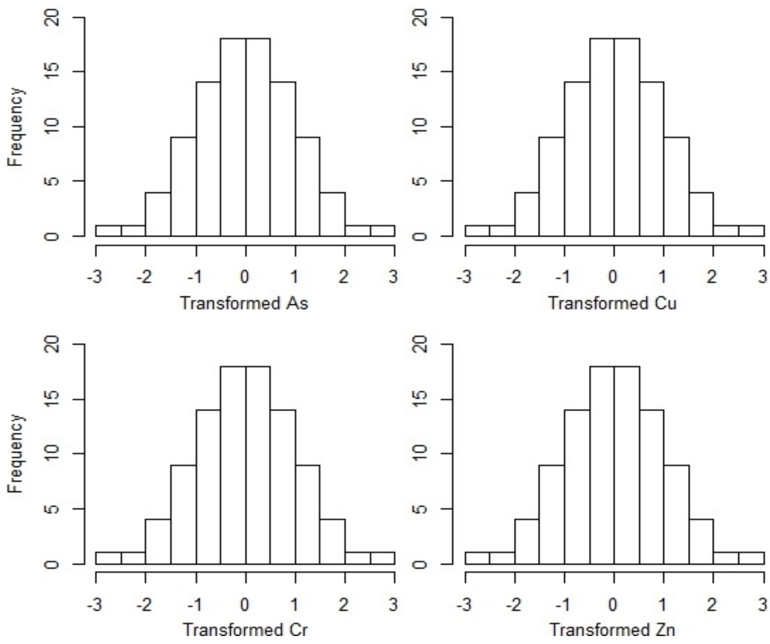

Fig. 2 Histogram of normal-score transformed of As, Cr, Cu and Zn

TABLE II
CORRELATION MATRIX SHOWING THE SPEARMANS'S CORRELATION COEFFICIENTS BETWEEN HEAVY METALS: AS, CR, CU AND ZN

Symbol	As	Cr	Cu	Zn
As	1.000			
Cr	0.280[a]	1.000		
Cu	0.340[a]	0.840[b]	1.000	
Zn	0.390[b]	0.810[b]	0.871[b]	1.000

[a]Significant at 0.05; [b]Significant at 0.001

B. Spatial Variability of Heavy Metals

The spatial structure of the observed four soil heavy metals were modelled singly and jointly as an isotropic process as discussed in Section II *B*. The experimental semivariograms for the individual (3) and multiple (10) soil heavy metals were constructed using 10 lags at lag distance spacing of 60 meters. The univariate experimental semivariograms were modelled by an isotropic spherical variogram model nested with (or

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without) a nugget effect (4) while a linear model of coregionalisation (11) was fitted to the direct-semivariogram of each soil heavy metal and its cross-semivariograms in (10) using the same nested model (4). The results obtained from the fitted univariate and multivariate semivarigrams models are as presented in Tables III and IV, respectively, while the corresponding semivarigram graphs are as displayed in Figs. 3 and 4.

TABLE III
PARAMETERS' VALUES OF THE FITTED LINEAR MODEL OF COREGIONALISATION OF HEAVY METALS: AS, CR, CU AND ZN

Variable	As	Cr	Cu	Zn
Nugget Effect:				
As	1.03			
Cr	0.01	0.48		
Cu	0.27	0.38	0.59	
Zn	0.40	0.53	0.64	0.87
Spherical model (range = 300 m):				
As	0.12			
Cr	0.26	0.69		
Cu	0.12	0.49	0.55	
Zn	0.05	0.26	0.24	0.18

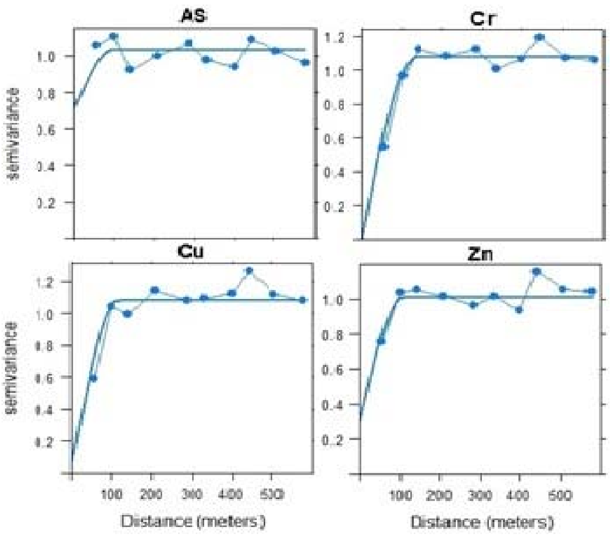

Fig. 3 Experimental semivariograms (line with dots) with the fitted isotropic spherical model nested with nugget (solid line) for each normal-score transformed of As, Cr, Cu and Zn

The linear models of regionalization and coregionalisation, each comprising a spherical variogram model nested with nugget effect (4), appeared well-fitted and acceptable (see Figs. 3 and 4), having satisfied the semi-positive definite condition [16], [39] in all cases. The autocorrelation structures indicate spatial variations of distributions of the four soil heavy metals. The experimental direct-semivariograms, particularly for Cr and Cu, showed relatively smaller nugget effect values of 0.48 and 0.59, respectively, compared with much smaller values of 0.00 and 0.07 from the univariate semivariogram models of same soil heavy metals. The nugget effect parameter, indicating the semivariance values at short distance varied between 0.01 and 1.03 for both direct- and cross-semivariograms, while the sill parameter, indicating the semivariance values at very large distance, varied between 0.27 and 1.15 for the univariate and multivariate semivariograms. The correlation structure of the experimental cross-semivariograms shows positive spatial correlations among all the four soil heavy metals. The range parameter, representing the distance of influence of a heavy metal contamination, ranged 100–135 meters for the univariate models whereas the range of autocorrelations for multivariate semivariograms was found to be within 300 meters for all the soil heavy metals. The nugget-sill ratios, indicate the strength of spatial autocorrelations among the observations for the multiple autocorrelations model were quite high, ranging 0.41–0.90, compared with the univariate semivariograms' nugget-sill ratios of 0.297-0.699, except that for Cr with a ratio of 0.

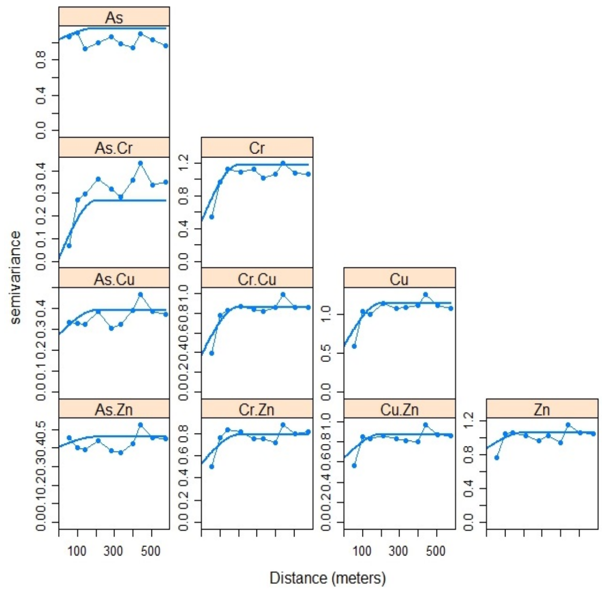

Fig. 4 Experimental direct- and cross-semivariograms (line with dots) with the fitted linear model of coregionalisation (solid curve) for normal-score transform of As, Cr, Cu and Zn

C. Estimation and Risk Maps

Based upon the spatial structure as described by the fitted univariate and multivariate semivariogram models, the estimates of the four soil heavy metals were obtained by performing both OK (5) and OCK (12) over a 10×10 meter grid spacing created to cover the study area. The kriged normal-score values at the unsampled locations of the study area for each heavy metal were back-transformed. The descriptive summary of the predicted values of the soil heavy metals are presented in Table V to be compared with the observed values. The prediction performance of the OK and OCK estimators are compared using the three error measures, mean error (ME), mean absolute error (MAE) and mean square error (MSE) in a cross-validation analysis as shown in Table VI.

Averagely, the predicted values of soil heavy metal contamination were lower but more variable (except As)

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compared with the observed data. The spatial risk maps of soil heavy metal contamination produced from the predicted values by the OK and OCK estimators are displayed in Figs. 5 and 6, respectively. The predictions, as observed from the spatial risk maps, suggest highly contaminations of soil by Ar, Cr, Cu and Zn, which are mainly found in the northern, southern and eastern parts of the study area, while some patches of high contaminations, particularly by Cr and Cu, are seen in the central part of the study area. The risk maps show globally similar spatial distribution pattern of contamination but differ locally in levels of contamination.

TABLE V
DESCRIPTIVE STATISTICS OF PREDICTED AND OBSERVED VALUES OF SOIL HEAVY METALS

Metal	Count	Min	Max	Mean	StdDev	Median	CV
OK Predicted (mg/kg):							
As	7568	1.00	191	11.97	2.93	12.00	0.25
Cr	7568	0.10	478	23.13	44.63	2.84	1.93
Cu	7568	0.57	377	9.59	22.93	2.28	2.39
Zn	7568	0.70	912	21.47	51.16	5.99	2.38
OCK Predicted (mg/kg):							
As	7568	1.00	191	11.76	3.48	11.99	0.96
Cr	7568	0.10	478	13.01	25.91	2.86	1.96
Cu	7568	0.57	377	5.82	13.06	2.27	2.24
Zn	7568	0.70	912	7.61	16.82	5.83	2.21
Observed (mg/kg):							
As	94	1.00	191	18.65	26.63	11.98	1.43
Cr	94	0.10	478	44.59	83.41	3.10	1.87
Cu	94	0.57	377	27.79	58.93	2.29	2.12
Zn	94	0.70	912	96.64	179.89	5.89	1.86

TABLE VI
CROSS-VALIDATION OF OK AND OCK PREDICTION ACCURACY OF SOIL HEAVY METALS

Statistic	ME	MAE	MSE
Ordinary kriging			
As	0.000	0.807	1.018
Cr	-0,005	0.823	1.019
Cu	-0.005	0.819	0.979
Zn	0.000	0.801	1.004
Ordinary Cokriging			
As	0.001	0.806	1.060
Cr	0.001	0.829	1.066
Cu	0.000	0.842	1.079
Zn	0.000	0.822	1.021

TABLE IV
DESCRIPTIVE STATISTICS OF PREDICTED AND OBSERVED VALUES OF HEAVY METALS

Metal	Count	Min	Max	Mean	StdDev	Median
Predicted (mg/kg):						
As	7568	1.00	191	11.76	3.48	11.99
Cr	7568	0.10	478	13.01	25.91	2.86
Cu	7568	0.57	377	5.82	13.06	2.27
Zn	7568	0.70	912	7.61	16.82	5.83
Observed (mg/kg):						
As	94	1.00	191	18.65	26.63	11.98
Cr	94	0.10	478	44.59	83.41	3.10
Cu	94	0.57	377	27.79	58.93	2.29
Zn	94	0.70	912	96.64	179.89	5.89

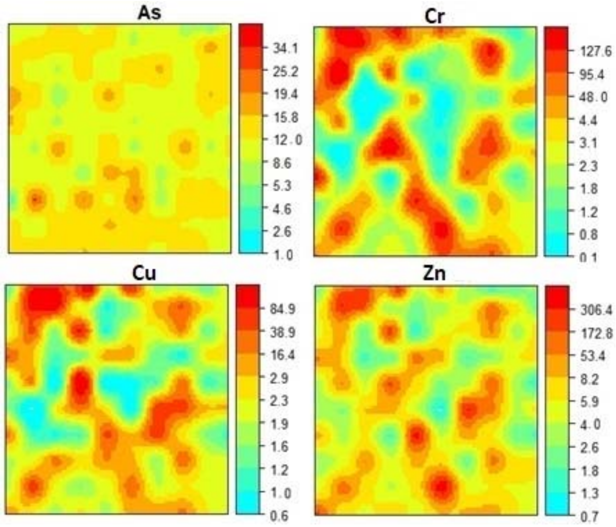

Fig. 5Spatial distribution of ordinary kriging (OK) estimates of As, Cr, Cu and Zn risk of soil contamination in the study area

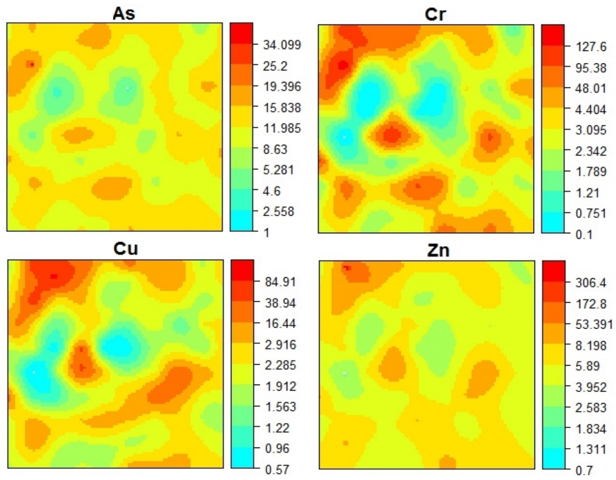

Fig. 6 Spatial distribution maps of ordinary cokriging estimates of As, Cr, Cu and Zn showing risk of soil contamination in the study

The prediction error values for the soil heavy metals indicate that the OCK estimator predicts slightly better than the OK estimator with relatively smaller ME values but approximately equal MAE and MSE values. The OCK produced risk maps show smoother kriged surface, covering a larger area to spread the heterogeneity compare with the OK risk maps which appear more spotted in levels of contamination.

D.Discussion

Mapping the distribution of heavy metals' concentrations in soils in human settlement areas is essential for environmental protection agencies to monitor and delineate hazardous areas for remediation [40]. In this paper, the spatial distribution of heavy metals, namely As, Cr, Cu and Zn measured from topsoil samples collected from human settlements in Kumasi Metropolis and its environs in Ashanti Region of Ghana were studied. Previous studies [5], [6] found some of the soil

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samples of these heavy metals to have exceeded the international environmental soil quality guidelines [41], which is a cause for concern. Thus, mapping the spatial distribution of these topsoil heavy metals will allow demarcation of highly contaminated areas for efficient management of soil pollution. The present study describes the spatial distribution of these topsoil heavy metals using multivariate geostatistical techniques which account for the spatial cross-correlations among the heavy metals. The cross-correlations allow us to account for different sources of spatial variations which is important for accurate prediction of spatial distribution of regionalized variable [15], [38].

The results of both univariate and multivariate semivariograms models showed that there exists spatial variation in the distribution of the soil heavy metals. The spatial variation was particularly high for Cr and Cu in the study area. In addition, there was positive spatial cross-correlations among the heavy metals, which indicates that areas with high concentration of one heavy metal happens to be the areas with high concentration of the other metals. The cross-correlations among the metals indicate that these heavy metals may have originated from the same sources and have similar level of pollution [5], [20] while high values of the nugget-sill ratios can be to attributed human activities in that vicinity. The range of the heavy metals contamination of soil in this urban area was found to be short, ranging between 100 and 300 meters, which is an indication of spatial heterogeneity of all the soil heavy metals.

The OCK estimator predicted accurately better than the OK estimator with smaller prediction errors and also smoother predicted surfaces. As indicated by the predicted values of the topsoil heavy metals, the spatial patterns of soil contamination are highly concentrated at the northern, southern and eastern parts of the study area with some spotted areas in the central part. The distribution risk maps of these heavy metals show globally similar spatial pattern but the magnitude in term of levels of contamination vary locally. The patchiness at the central part of the study area was found to be highly contaminated with Cr. In general, the magnitude of Zn was found to be higher compared to the other metals. High concentration levels of these heavy metals, particularly, As, Cu and Zn, in the topsoil of the study area could be mainly attributed to anthropogenic sources due to high proportions of the nugget effects. The northern parts of the study area are surroundings of the largest mechanic and spare parts shops in Ghana as well as vehicle garages [5]. The soil pollution by Cr and Cu in the central part of the study area could be influenced by vehicular emissions from heavy traffic movements [20] coupled with indiscriminate disposal of waste substances and quack car-mechanic activities. Reference [20] observed considerable release of Cu and Zn from vehicle exhausts in Beijing.

IV. Conclusion

In conclusion, the case study presented here shows the importance of mapping heavy metals concentration in urban soils to support environmental monitoring process. The spatial risk maps of the predicted topsoil heavy metals suggest that all the four soil heavy metals studied showed signs of spatial heterogeneity and highly contaminated at the central and border areas of the study area. The predicted values far exceeded the maximum acceptable values based on the national and international risk soil quality guidelines [41]. The results could be incorporated into decision-making making process regarding environmental safety and monitoring as well as contaminated area delineation and remediation.

Acknowledgment

The authors are grateful to Dr. Godfred Darko of Department of Chemistry, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana, for providing them the required data for the study.

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