ASSESSMENT OF SPATIAL VARIABILITY OF HEAVY METALS IN SOILS UNDER THE INFLUENCE OF INDUSTRIAL SOAP AND DETERGENT WASTE WATER DISCHARGE

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ABSTRACT

Soil heavy metals have been a very useful indicator of environmental quality worldwide. The present study was conducted to investigate the levels, sources, distribution and spatial variability of heavy metals (Cu, Mn, Cd, Pb, and Zn) in soils in close proximity to an industrial area. Hierarchical Cluster Analysis (HCA) was applied to test the similarities between sampled elements based on nearest neighbour method. Mean concentrations (mg/L) of heavy metals in the sampled soils were as follows: Mn (19.90), Cu (15.23), Zn (9.06), Pb (6.19) and Cd (0.13). ANOVA showed that the concentrations of individual heavy metals in soils were significantly higher ($P < 0.05$) than the background reference soils indicating that the effluent discharge from the industry has increased the heavy metal concentrations in these soils. A strong positive correlation was found between Cu, Zn, Pb and Cd whereas Mn was positively correlated somewhat less strongly to Zn and Pb. Mn was negatively correlated with Cu and Cd. The results indicate that the concentrations of all metals except Cd exhibited weak spatial autocorrelations (ratios ranging from 0.80 to 11.94) confirming that spatial variability was affected by the industrial effluent discharge. These results suggest the need to develop proper management strategies to contend with heavy metal contamination in industrial areas.

Keywords: *Trace Metals; Atomic Absorption Spectroscopy; Effluents; Kriging; Geostatistics; Contamination*

1. INTRODUCTION

The activities of human society via industry in urban areas influences biogeochemical cycles and this has led to various irreversible changes in our environment [1; 2]. As a result, the undesirable effects of poor environmental circumstances on human health are most manifest in urban environments, predominantly in developing countries where urbanization, industrialization and rapid population growth are taking place on an unprecedented scale [3; 4; 5]. The soil environment is a boundary point, diverse, and dynamic, and the fundamental characteristics of soil contamination are different from those of air and water, such as concealment and hysteresis, accumulation, and irreversibility [6; 7]. Heavy metal content of soil is of major significance in relation to their fertility and nutrient status. Soil heavy metals have been a very useful indicator of environmental quality worldwide and been the subject of much attention because of their peculiar characteristics.

Regarding most heavy metals particularly Pb, Cu and Zn, anthropogenic origins put in more to pollution than natural sources [8]. These heavy metals in the terrestrial environment visibly constitute a significant risk to the quality of soils [9], plants [10], natural waters [11] and human health [12]. Waste water from industrial processes may contain an important load of zinc, copper, chromium and nickel [13]

Given the investigation of soil metal distribution and their influencing factors in topsoil could present a model approach to monitor and assess the pollution of soil in particular, and environmental quality on the whole as seen in soils [14; 15], investigations of heavy metal contamination in urban soils is receiving a growing body of literature. For instance regarding soil quality, various studies have been carried out in wide-ranging geographic regions including Ibadan [16], Cartagena [17], Hyderabad [18], Uppsala [18], Guangzhou [19], Yixing [20] and Xuzhou [21]. These studies notwithstanding, the geospatial variability and speciation of heavy metals in soils under different environmental conditions is not fully understood. Soil pollution assessment becomes very complicated when diverse sources of contamination are present and their products are variably distributed [22; 23]. In these cases the spatial variability of the heavy metal concentrations in soils is fundamental information for identifying the potential sources of contamination and to outline the strategies of site remediation [13; 24].

Multivariate geostatistics has been applied in quite a few studies to present a more objective account on the source of some heavy metals in the topsoil [25; 26]. Source identification of heavy metals should not only be derived from visual examination of the metal concentration maps [27] but it must also based on the quantitative analysis of the spatial variability of the elements and their interaction at different spatial scales [13]. Furthermore, multivariate methods have been used to compare the results coming from the principal component analysis carried out on the concentration data with the experimental indicator variogram applied to some categorical information, in order to relate the concentration of heavy metals to the geology and land use of the area [28; 29]. The spatial variability of soil heavy metals is therefore an important part of environmental supervision and ecosystem evaluation. Consequently, this study set out to assess the concentration and distribution of selected heavy metals in soils near a manufacturing industry in Cape Coast; identify the possible sources of these heavy metals, and determine the variability of these heavy metals via multivariate geostatistics.

The industrialization rate of Cape Coast is relatively low compared to Accra and Kumasi; however, urbanization rate is high [30]. Apart from two main industries, there are no significantly large industrial establishments in Cape Coast [31]. One of the main industries is involved in the manufacture of soap and brake bands [32]. However, there are several small-scale enterprises located throughout the metropolitan area. These include soap making, oil extraction (coconut, palm kernel and palm oil), garages, and quarrying [32]. It is public knowledge that bad odour particularly at night, is characteristic of the study area.

2. MATERIALS AND METHOD

Site characteristics

Soil samples was collected from sites close to the industrial area (Fig. 1) in the Cape Coast Metropolis (5° 14" 0' N to 5° 5" 30' N and 1° 14" 30'W to 1° 22" 30W) in the Central Region of Ghana [32]. The metropolis covers an area of about 122 km^2. The vegetation is mainly coastal savanna grassland. The area has a bi-modal rainy season from May to June and August to October with an annual rainfall range of between 750mm and 1000mm. The soils at the research site are Acrisols. The specific study site consists of browned and withered vegetation which exhibit obvious signs of toxicity [32]. Effluent discharge with remaining sludge layer on the surface of the soil was evident at the site.

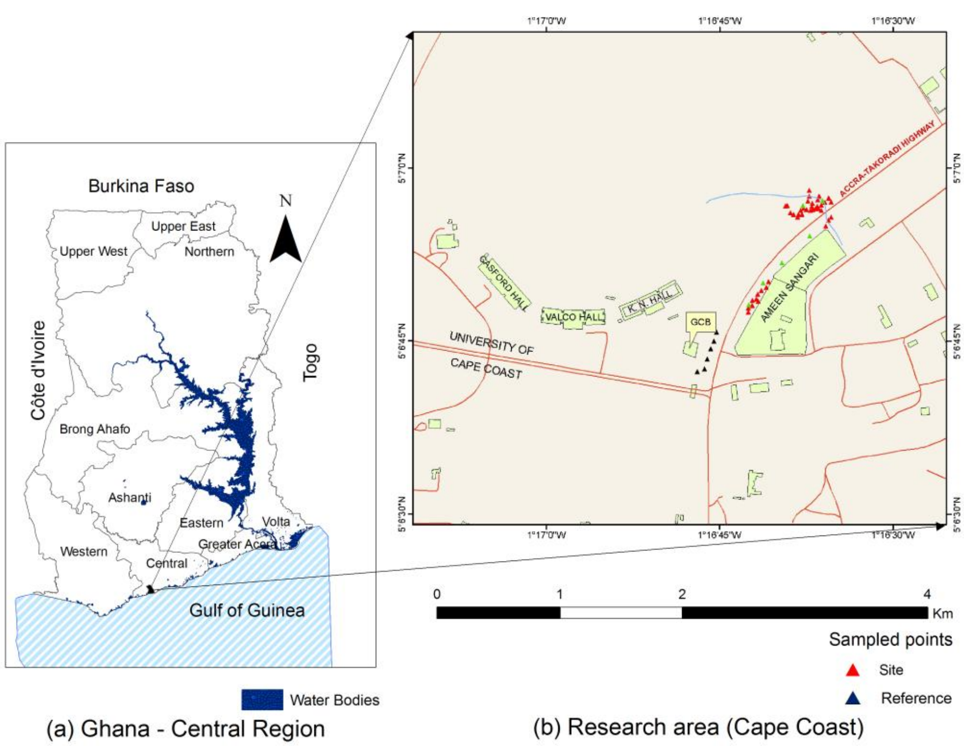

Fig.1: Location map with (a) the Central Region in Ghana, and (b) the study area, Cape Coast, with sampled sites.

Ground sampling and chemical analysis

A random sampling scheme for field measurements was generated using Hawth's tool (ArcGIS 9.3) consisting of a total of 41 geographical coordinates. On the ground the sample points were located from April to May 2010, using a GPS communicating with an iPAQ palm computer (ArcPad software). The location of the sampling points is shown in Fig. 1. Soils were sampled using a 30cm auger. Soil samples were also taken upstream from locations uninfluenced by the operations of the industry, and analyzed for metal concentrations. The samples were stored in self-locking polythene containers and transported to the laboratory.

Laboratory analysis

The soil samples were air-dried and sieved to <0.25mm, then stored in desiccators prior to analysis of heavy metals. About 0.5 g of the dry sample was weighed and digested with a mixture of nitric acid (HNO_3) and perchloric acid ($HClO_4$).

A 2 g sample was transferred to a Teflon beaker and 25 mL of distilled water was added. About 2 mL of concentrated HNO_3 was added the contents of the beaker and this was allowed to evaporate to dryness. Subsequently, three drops of concentrated H_2SO_4 and 10 mL of HF were added. The sample was then placed on a sand bath while the temperature slowly increased to 200 ◦C and was allowed to evaporate to dryness. This was followed by the addition of 15 mL of concentrated HNO_3, 2 mL of H_2SO_4, and 5 mL of $HClO_4$. Heating continued until strong fumes of SO_3 were produced. The Teflon container was cooled and the solution transferred quantitatively to a 50 mL volumetric flask by adding distilled water. A comprehensive description of this digestion method is given by [33]. Concentrations of Mn, Cu, Cd, Pb and Zn were determined by flame atomic absorption spectrometry (Shimadzu model 6401F) after preparation of appropriate calibration standards. All samples were digested and analyzed in replicate.

Data analysis

The descriptive statistical parameters were calculated with SPSS17.0 software package (SPSS Inc., Chicago, IL), and the correlations between heavy metals were assessed by using Pearson correlation analysis. One-way analysis of variance (ANOVA) was performed to test the significance of differences in total metal concentrations and soil properties in different soil series and mean values were grouped by Tukey test [34] for comparison ($P<0.05$). The Hierarchical Cluster Analysis (HCA), which is suitable for environmental analysis was applied to test the similarities between sampled elements based on nearest neighbour method. Using ArcGIS 9.2 Ordinary kriging was employed for geostatistic interpolation. Geostatistics uses the technique of semivariogram to measure the spatial variability of a regionalized variable, and provides the input parameters for the spatial interpolation of kriging [35].

3. RESULTS

Heavy metal concentrations

Descriptive statistics of the data including soil parameters (nugget, sill, range, root mean square) of the five metal concentrations are shown in Table 1. There was a distinct variation in the contents of heavy metals among the sampled soils; Mn, Cu, Zn, Pb and Cd varied between 1.67 and 71.07, 0.29 and 56.88, 0.75 and 15.05, 0.96 and 13.57, and 0.01 and 0.45 mg/L respectively, with mean concentrations of 19.90, 15.23, 9.06, 6.19 and 0.13 respectively. Concentrations of Mn, Cu, Zn, Pb and Cd determined for soils not impacted by the industrial activities were 17.85, 2.85, 2.21, 3.74 and 0.02 mg/L, respectively.

The ratios of mean concentrations to background values for all metals were larger than 1.0, and are ranked in the following order: Cd>Cu>Zn>Pb>Mn. This means that the effluent discharge from the industry has significant effects on the concentrations of metals in soils over the area, and the soil is contaminated by these metals. The ANOVA analysis showed that the concentrations of individual heavy metals in soils were significantly higher ($P < 0.05$) than the background reference soils indicating that the effluent discharge from the industry has increased the heavy metal concentrations in soils.

Table 1: Descriptive statistics of the elements in soil samples in the degraded area (n = 41).

	pH	COD	Cl	Na	K	NO_3	PO_4	Ca	Mg	Co	**Mn**	**Cu**	**Zn**	**Pb**	**Cd**
Min	3.90	0.01	6.8	0.0	3.20	0.0	0.50	9.22	164.91	0.05	1.67	0.29	0.75	0.96	0.01
Max	7.93	9.76	499.8	384.4	30.60	654.5	248.34	18.29	317.55	3.15	71.07	56.88	15.05	13.57	0.45
Mean	6.50	2.35	90.3	106.4	12.20	70.3	32.84	15.97	252.20	0.87	19.90	15.23	9.06	6.19	0.13
SD	0.82	1.94	96.7	77.6	7.92	127.8	45.05	2.06	31.49	0.76	16.57	13.97	3.79	3.45	0.13
Background value	5.30	0.20	3.07	4.10	2.15	12.39	0.87	12.32	149.00	0.02	17.85	2.57	2.21	3.74	0.02

Heavy metals in soil usually have relationships between them and other soil parameters. Table 2 indicates the Pearson correlation coefficients calculated for each pair of variables. There was a high interdependence of total metal concentrations and selected soil parameters. Mn and pH are strongly correlated (r = 0.382) at the 0.05 level. COD is strongly correlated with Cd (r = 0.367) and Cu (r = 0.352) at the 0.05 level. Cd and Cl are strongly correlated (r = 0.317) at the 0.05 level. Cu and Na are strongly correlated (r = 0.383) at the 0.05 level. K is strongly correlated with Zn (r = 0.379) and Pb (r = 0.372) at the 0.05 level. K and Cu are strongly correlated (r = 0.481) at the 0.01 level whereas Ca is strongly but inversely correlated with Cu (r = 0.382) and Zn (r = 0.331) at the 0.05 level. Again, Mg is strongly correlated with Cu (r = 0.380) and Pb (r = 0.363) at the 0.05 level. Also, Mg and Zn are strongly correlated (r = 0.538) at the 0.01 level. Co is strongly correlated with Zn (r = 0.435) and Pb (r = 0.456) at the 0.01 level. These strong correlations point to common origin for these metals. From Table 3, a strong positive correlation was found between Cu and Zn (r = 0.584), Cu and Pb (r = 0.509), Zn and Pb (0.707). The high correlations between soil heavy metals may reflect the fact that these heavy metals had similar pollution levels and similar pollution sources [28]. The strongest correlation exists between Pb and Zn and this is also evident from the dendrogram (Fig. 2).

Table 2: Pearson correlation coefficients matrix of total metal concentrations versus selected soil chemical properties (n = 41).

	Mn	**Cu**	**Zn**	**Pb**	**Cd**
pH	**.382***	-.181	-.184	-.031	.079
COD	.034	**.352***	.225	.105	**.367***
Cl	.029	.095	.037	-.123	**.317***
Na	-.265	**.383***	.223	.261	.328*
K	-.056	**.481****	**.379***	**.372***	.163
NO_3	-.138	-.032	.102	-.315*	.121
PO4	-.163	.096	.178	-.184	.113
Ca	.161	**-.382***	**-.331***	-.136	-.124
Mg	.210	**.380***	**.538****	**.363***	.207
Co	.145	**.374***	**.435****	**.456****	**.289**

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

Table 3: Pearson correlation coefficients matrix of total metal concentrations (n = 40).

	Mn	**Cu**	**Zn**	**Pb**	**Cd**
Mn	1.00				
Cu	-.011	1.00			
Zn	.124	.584**	1.00		
Pb	.171	.509**	.707**	1.00	
Cd	-.044	.265	.313*	.323*	1.00

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

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                   0         5        10        15        20        25
Label     Num      +---------+---------+---------+---------+---------+

Pb          1       -+-----------+
Zn          4       -+           +-----------------+
Cu          5       -------------+                 +-----------------+
Cd          2       -------------------------------+                 |
Mn          3       -------------------------------------------------+
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Fig. 2: Hierarchical clustering results (dendrogram) of the heavy metal concentrations in soil samples.

Spatial Analysis

The semivariograms of soil heavy metal concentrations are shown in Fig. 3a-e. Key parameters of these semivariograms are given in Table 4. The range represents the average maximum distance over which two samples are related. At distances less than the range, measured properties of two samples became similar with decreasing distance between the two points. Thus, the range presents an estimate of areas of similarity. The ranges of the studied heavy metals were in the order of Cu= Pb> Mn= Zn>Cd. The zones of influence for Cu and Pb range from 2.487 to 2.491m. The zones of influence for Mn and Zn were the same (0.571m); however for Cd, the distance was much less (0.058m). The low ranges for the metals suggested that anthropogenic factors such as industrial effluent discharge could have affected the concentrations of these heavy metals.

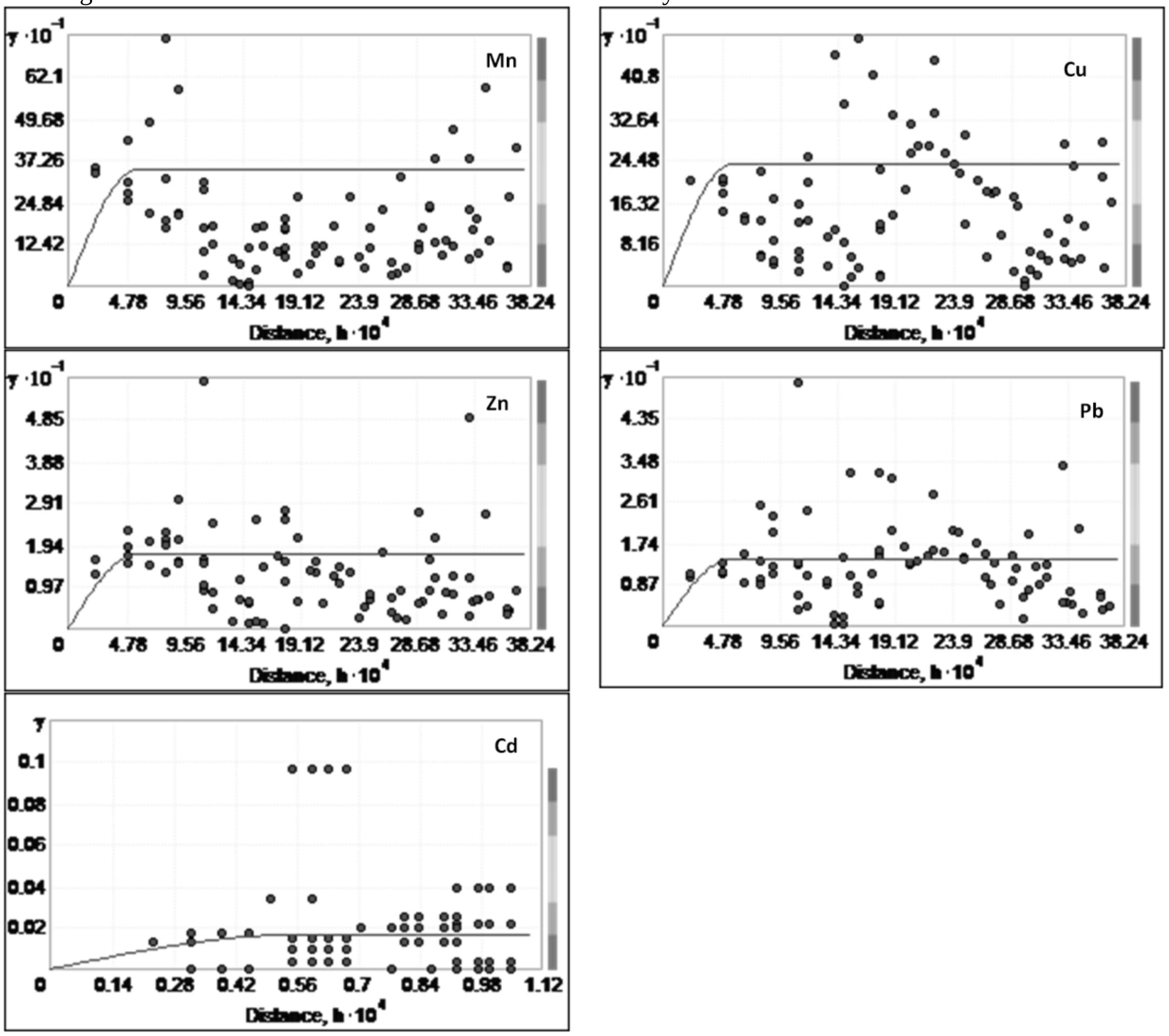

Fig. 3a-e: Semivariograms of soil heavy metals with fitted models.

Table 4: Semivariogram models and parameters of heavy metals.

Elements	**Range (m)**	**Nugget (C_0)**	**Sill (C_0+ C)**	**C_0/(C_0+ C)**	**Prediction errors Root-Mean-Square (RMS)**
Mn	0.571	274.68	343.76	0.80	12.69
Cu	2.491	187.25	15.684	11.94	14.61
Zn	0.571	14.342	17.211	0.83	3.63
Pb	2.487	10.174	3.3008	3.08	3.57
Cd	0.058	0.0009	0.0167	0.05	0.14

Fig. 4a-e is the spatial variability distribution map generated based on the semivariograms of all heavy metals under study. High concentration of Cu was distributed over the whole study area. Close examination of the maps reveals that Mn and Cd have similar spatial distribution pattern except that higher concentrations of Cd appear to be slightly widely dispersed than Mn. Zn and Pb also showed similar spatial distribution pattern and belonged to one group in the Hierarchical clustering analysis.

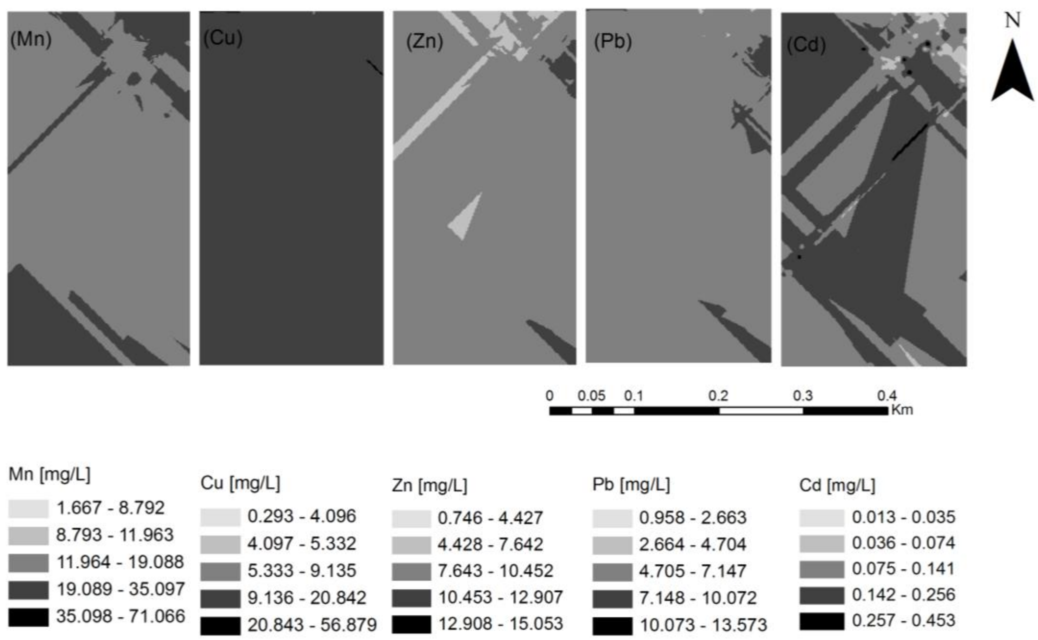

Fig. 4. The spatial interpolation distribution maps of heavy metal concentrations in soil.

4. DISCUSSION

According to [27], Soap and detergent industrial effluents contribute to high level of Biochemical Oxygen Demand (BOD), chemical oxygen demand (COD), Total Dissolved Solids (TDS) and some heavy metals like Pb, Cd and Mn. The COD levels obtained in this study were higher than what was obtained by [27] in Ilorin, Nigeria. The study area is noted for bad odour particularly at night. According to [27], high BOD and COD are responsible for the odorous nature of industrial areas where effluent discharge are widespread. Consequently, the bad odour in the study area could be attributed to high COD. In this study, levels of Cu, Mn and Zn were 10, 60 and 4 times respectively more than their corresponding background values. The levels of Mn, Pb and Cd were by far higher than that obtained at the soap and detergent industrial area in Ilorin. These findings therefore do not support the result of [27]. The nugget to sill ratio ($C_0/(C_0 + C)$) indicates the proportion of random components to system spatial heterogeneity. The ratio of <0.25, 0.25–0.75, and >0.75 could be used to describe the proportion of the spatial structure that showed strong, moderate, and weak spatial autocorrelation, respectively [36]. To some extent, this indicator reflects predominant factors which impact the spatial variability of soil heavy metals between intrinsic factors (natural factors, such as soil parent materials) and extrinsic factors (anthropogenic factors, such as agricultural practices and industrial effluent discharge). In general, weak spatial dependence of soil heavy metals can be ascribed to extrinsic factors, and strong spatial dependence can be ascribed to intrinsic factors [36]. The concentrations of all metals except Cd in this study exhibited weak spatial autocorrelations (ratios ranging from 0.80 to 11.94) confirming that their spatial variability were affected by the industrial effluent discharge (Table 4). Studies have shown that high concentrations of heavy metals in soils are mostly due to industrial effluent and sewage sludge from chemical, metal processing and mining industries [37; 38]. The results of this study confirm the findings of [37; 38]. [39] in their study concluded that even very low levels of heavy metals in soils may influence plant growth and reproduction. Since the study site serves as a grazing field, high doses of accumulated toxic metals in edible plants are not only harmful to animals when used as animal feed but also to humans. Heavy metals are taken up by plants and the subsequent transfer to humans through plant or animal food. The bioavailability and toxic impact of heavy metals on plants is determined by soil temperature, soil pH, soil hydrous metal oxide content, water hardness, clay content and type and dissolved organic carbon content [40]. Plants growing in metal polluted locations exhibit altered metabolism, growth reduction, lower biomass production, and metal accumulation. Various physiological biochemical processes in plants are affected by metals.

5. CONCLUSION

The levels, sources, distribution and spatial variability of heavy metals (Cu, Mn, Cd, Pb, and Zn) in soils in close proximity to a soap and detergent industrial area were investigated in this study using geo-statistical techniques. The concentrations of Cu, Mn and Zn in soils were significantly higher than the background reference soils indicating that the effluent discharge from the soap industry may have increased the heavy metal concentrations in these soils. The concentrations of all metals except Cd exhibited weak spatial autocorrelations indicating that spatial variability of these metals was affected by the industrial effluent discharge.

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