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ORIGINAL ARTICLE

An Investigation on Cd and Pb Concentrations of Soils around the Kurdistan Cement Factory in Western Iran

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KEYWORDS

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ABSTRACT: Heavy metals, e.g. Cd and Pb emit and release into the environment during cement production and are deposited into soils. This research was carried out to determine the concentration and spatial distribution of trace elements in top soils around the Kurdistan Cement Factory, west of Iran in order to evaluate the effect of cement factory on the environment. Twenty-four soil samples were collected from surface soils around the factory. Cadmium and lead concentrations in soil samples were determined using acid extraction procedure and atomic absorption spectrophotometric methods. Soils were sampled in four directions of north, south, west and east of cement factory and at intervals of 400 m to 800 m distance from the factory. Ordinary kriging technique in ArcGIS was performed to map the spatial patterns of heavy metals. The results showed that concentrations of Pb and Cd were weakly correlated with each other indicating these metals in soils may be from the different pollution source. No distinct spatial trends of Pb with its low accumulation in the soils demonstrate that Pb content was mainly influenced by soil factors. The spatial pattern of the cadmium showed that the cement factory emission has an impact on the soil's cadmium content, since the highest level in area close to the cement factory. Estimated Pollution Load Index (PLI) showed that the soils around the factory were practically uncontaminated by metals.

INTRODUCTION

The issue of industrial pollution has been a main cause for environmental degradation and continues to be in future [1]. Soil contaminated with metals such as cadmium and lead, is a primary route of toxic element exposure to humans, thus, it is a problem of concern [2]. The origin of heavy metals in the soil is of geogenic or

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anthropogenic sources [3]. The anthropogenic sources of soil heavy metal contamination are industrial emissions, mining activities, fossil fuel combustion, smelting of metal ores applications of insecticides and fertilizers [4]. Industrial activity has contaminated the soil with a several kinds of heavy metals such as cadmium (Cd), lead (Pb), chromium (Cr), copper (Cu), zinc (Zn) and nickel (Ni) in areas that affect crop production [5]. Atmospheric emissions from industrial activities (stationary *and mobile sources*) are one of the important sources of environmental pollution. Cement production is one type of industry that causes particulate matter from various processes [6]. The main impacts of the cement production to the environment are the broadcasts of dusts and gases [7]. Cement dust can spread over a large area with wind and rain, accumulating in plants, animals and soils; so can affect human health badly [8]. Furthermore, the atmospheric particles can have direct consequences for ecosystem services and reduction of biodiversity [9]. Heavy metals are one of the key polluting substances emitted to environment during the process of cement manufacture [10]. Different raw materials, primary (limestone, marl lime, clay stone, sand), or secondary (coal fly ash) substitute of inorganic raw material, as fuels, may contain varying trace element concentrations. Heavy metal pollution in soil around the cement factories is mentioned earlier [3, 9-16]. The heavy metals distribution and speciation was studied in soils around a mega cement factory in north-central Nigeria [3]. Ahiamadjie et al. [9] determined the elemental contents in soils around Diamond Cement Factory, Aflao. Al-Khashman and Shawabkeh [10] investigated the metal distribution in soils around the cement factory in Southern Jordan. The heavy metals contamination of soil and vegetation were evaluated near a cement factory in the Volta Region [12]. Moreover, the pollution loads and the ecological risk assessment of soil heavy metals were investigated around a Mega Cement Factory in Southwest Nigeria [13].

Thus, the determination of the metals in soils around the cement factories is very important in monitoring environmental pollution. No information is available on the distribution of metals around the Kurdistan Cement factory at Kurdistan, Iran.

The present research was designed to evaluate the environmental impact and determine the concentrations of cadmium and lead in the farmland soils near the Kurdistan Cement Factory. Besides, Kriging (geostatistic spatial interpolation method) was applied to generate spatial distribution maps to show the spatial variability of heavy metals in soils around the cement factory.

MATERIALS AND METHODS

Study Area

Kurdistan Cement Factory is located in the northwestern of Bijar City in Kurdistan Province and 5 km from the Bijar-Takab Road. The area under investigation is located between latitude 35º 55'40.89" N and longitude 47 º33'6.59" E with a total land area of 40 ha. It was established by the government of Iran in 1996 as a largest industrial unit in the province. It offers portland pozzolan, special portland pozzolan, and slag portland cement. The prevailing wind direction is from Southwest to Northeast. Mean precipitation is around (619 mm/year). Minimum and maximum temperatures in the study area are -24˚C and 37˚C respectively. The surrounding area is covered by the farmlands.

Sample collection

Twenty four soil samples were collected randomly from different location around the Kurdistan Cement Factory (Figure 1). Composite samples of 1 kg of top soil samples were taken at a depth of 0-20 cm. The soil samples were collected with a spade (a stainless steel) and were stored in a clean polyethylene bags and labeled. Samples were taken from the northern, southern, eastern, western part of the factory. To provide representative samples of the whole study area, soil samples were taken from distances of 400 m and 800 m in four directions (East, West, North, and South) around the Cement factory.

Instrumentation

The instruments applied in this research were Graphite furnace absorption spectrometry (GFAAS), pH meter, EC meter, *heating block*, digestion tubes, sieve, and volumetric flasks and so on.

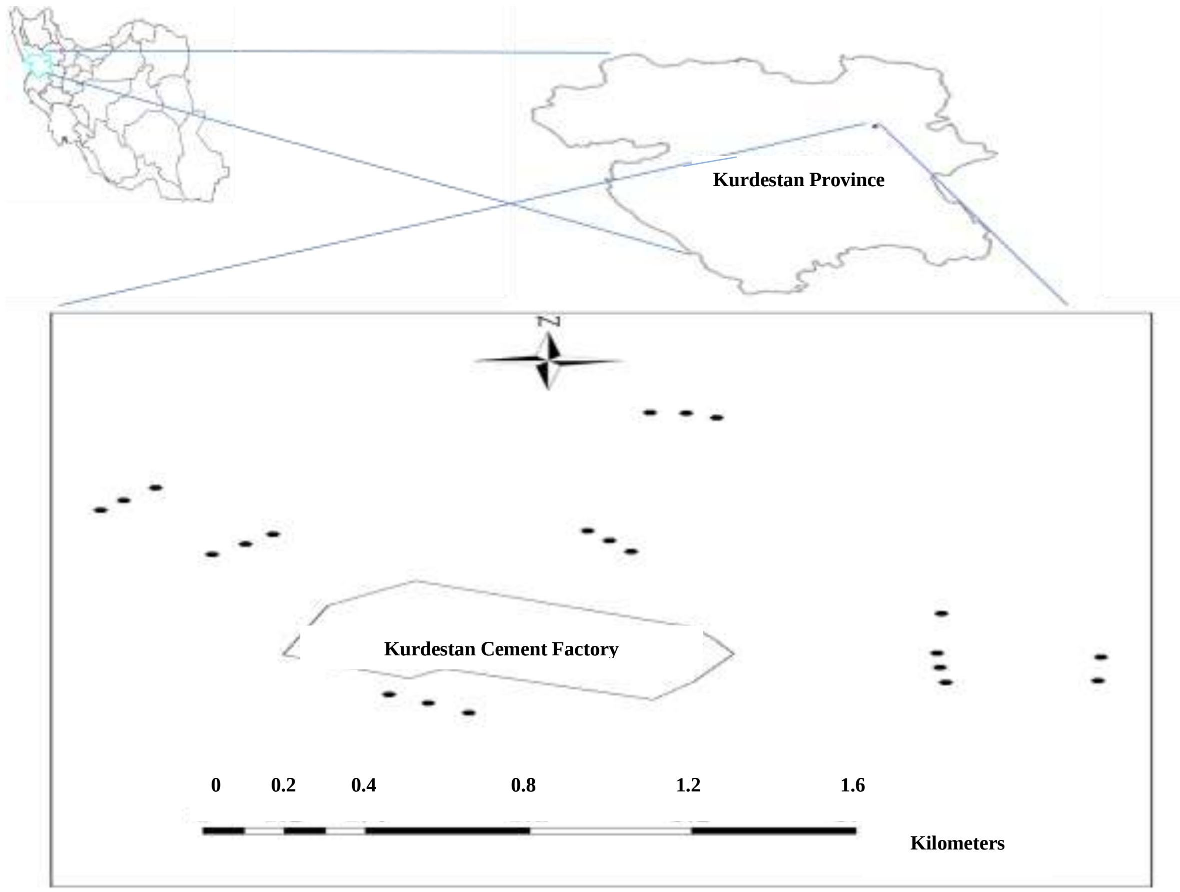

Figure 1. Location map of the investigated area and location of the sampling points

Sample preparation and chemical analysis

The soil samples were homogenized and air-dried at 25 °C for 7 days, then grounded, and sieved to 200 μm and subsequent sieved to 149 μm for chemical analysis. 1g of soil was exactly weighed and digested in digestion tubes with mixture of 9 ml of concentrated HCL and 3 ml of HNO3. Samples were filtered and diluted to 25 ml with distilled water in 50 ml volumetric flasks. The concentrations of Cd and Pb were measured by means of a graphite furnace atomic absorption spectrometry. The concentration of Cd and Pb were extrapolated from the calibration graph prepared. Limit of detection (LOD) of instrument for Pb and Cd was 0.02 and 0.0003 mg/L respectively. Quality assurance and control were evaluated using the duplicates and blanks procedure. The pH and EC (electrical conductivity) values (soil: distilled water =1:5) of soil samples were determined by a pH meter and an EC meter, respectively. All statistical analyses were performed using SPSS 20 for Windows (Chicago, IL, USA).

Calculation the degree of pollution

The degree of contamination in soil was determined with the aid of following parameters Geo-accumulation Index (Igeo), Contamination factor (Cf) and Pollution Load Index (PLI).

Geoaccumulation index (Igeo)

Geo-accumulation index (Igeo) introduced originally by Müller [17] has also been largely used to assessing the degree of metal contamination in soil, sediment as well as dust in comparison to background values. It is mathematically expressed as: Igeo= $\log_2 (C_n/1.5B_n)$, where C_n is the measured concentration of the metal n in the soil, B_n is the geochemical background value and 1.5 is a constant number to include possible variations in the background values that are may be attributed to lithologic variations in soils. Müller [17] allocated seven pollution classes to the Igeo values, ranging from uncontaminated to extremely contaminated (Table 1).

Table 1. Pollution classes of Geo-accumulation Index of metals

Igeo value	Igeo class	Designation of sediment quality
Igeo >5	6	extremely contaminated
4<Igeo≤5	5	strongly to extremely contaminated
3<Igeo≤4	4	strongly contaminated
2<Igeo≤3	3	moderately to strongly contaminated
1<Igeo≤2	2	moderately contaminated
0<Igeo≤1	1	uncontaminated to moderately contaminated
≤0	0	uncontaminated

Contamination factor

The contamination factor (CF) is proposed by Håkanson [18] to assess the contamination of a metal in soil or sediment. Contamination Factor (CF) is defined as the quantifier of degree of contamination relative to measured background values from geologically similar and uncontaminated area or the average crustal composition of the element [19]. Mathematically, it is calculated by the formula: $CF = C_n / B_n$

Where Cn is the mean concentration of metal n in soil and B_n is the background concentration (value) of metal n. Håkanson [18] proposed this classification: Cf<1 represents low contamination factor, 1≤Cf<3 represents to moderate contamination factor, 3≤Cf<6 represents considerable contamination, and Cf≥6 represents very high contamination factor.

Pollution Load Index (PLI)

The pollution load index (PLI), suggested by Tomilson, et al. [20], and estimates the degree of pollution with respect to all heavy metals considered together in a particular sample location. In fact, this index is based on the values of the Concentration Factors (CF) of each metal in the soil. This parameter was expressed using the following formula:

$$PLI = (CF1\times CF2 \times CF3 \times\ldots \times CFn)\ 1/n$$

Where n is the number of studied metals in each location, (two in this study) and CF is the Contamination Factor. The PLI provides simple method but comparative means for assessing a location quality, where a value of PLI < 1 indicating no pollution; PLI = 1 indicating baseline levels of pollutants and PLI > 1 indicating progressive deterioration [21]. The background values (Earth crust averages) of the studied metals were used based on Taylor [22].

Statistical Analysis

Normality of metal distribution was tested with the Shapiro-Wilk test. The Spearman correlation test was applied to check for correlations between heavy metals and soil properties (pH, EC). Differences between the cadmium concentrations in four directions were tested with non-parametric Kruskal Wallis and Mann-Whitney U tests. In addition, analysis of variance (ANOVA) was used to compare lead concentrations of soil in different directions. Two independent sample *t*-tests were used to compare lead concentrations at two distances (400 m and 800 m).

Spatial Analysis

Spatial variability of heavy metals in soils was analysed using the geostatistics method. Geostatistics uses the variogram (semivariogram) to measure the spatial variation of a regionalized variable [23]. Geostatistics uses the technique (or semivariogram) to measure the spatial variability of a regionalized variable, and provides the input parameters for spatial interpolation using kriging [24]. Variogram, γ (h), is calculated as half the average squared differences between pairs of points separated by a certain distance [25]. The function of variogram is expressed as follows:

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} \{Z(xi) - Z(xi + h)\}^2$$

where γ(h) is the variogram value of points with distance interval h, N(h) is the number of sample pairs separated by the lag distance h, Z (xi) is the measured value of the variable at the location (xi); Z (xi + h) is the variable's value measured at the location (xi + h).

According to fitted variogram models, the ordinary Kriging provided by the software Arc/GIS (version 9.3) was applied to map the spatial distribution of heavy metals in soils around the cement factory.

RESULTS AND DISCUSSION

The descriptive statistical parameters of soil pH, soil Electrical conductivity (EC) and concentrations of Cd and Pb in the topsoil around the Cement Factory are presented in Table 2. Soil pH of the topsoil ranges from 6.86 to 8.37 with an average of 7.9. Therefore, soil was observed to be alkaline type. The pH of the soil is a very important parameter that affecting particularly the content of metals in bioavailable forms. Higher proportion of mobile fraction occurs in acidic soils [26]. Electrical conductivity varies from 0.11 to 0.21 dS/m with an average of 0.15 dS/m that high electrical conductivity values were detected close to the cement factory in agreement with Al-Khashman and Shawabkeh [10].

Table 2. Descriptive statistics parameters of soil properties and metals (mg/kg)

	Minimum	Maximum	Mean	Std. Deviation	Variance	Skewness	Kurtosis
Cd	0.02	1.44	0.37	0.37	0.14	1.61	1.9
Pb	0.58	2.49	1.56	0.43	0.19	-0.3	0.459
pH	6.86	8.37	7.9	0.46	0.21	-0.8	-0.279
EC	0.11	0.21	0.15	0.02	0.001	0.78	1.09

The concentrations of cadmium and lead in the soils of the study area are generally low especially for Pb. The concentration of Cd and Pb in the topsoil ranged from 0.02 to 1.44 mg/kg (mean=0.37), 0.58 to 2.49 mg/kg (mean=1.56) dry soil respectively in the soil around the Cement Factory. Similar results were presented in Ghana, from soils around Diamond cement factory of Aflao [9]. The highest lead concentration in the soil samples were recorded close to the Bijar - Takab Road. This high Pb content of the soil mainly could have derived from the synergistic deposition effects from cement production processes and traffic activities. Pb is known to be part of metals released during portland cement manufacturing [27, 28]. Furthermore, the maximum level of cadmium was found to the west of the cement factory. With regard to, in the west of the study area, there is not any obvious source of pollution; therefore this high level of Cd may be related to cement production.

Table 3 summarizes the correlation analysis of Cd and Pb concentrations and soil properties (pH and EC) based on the data set of soil. It shows that soil pH correlated negatively with Cd (P<0.01) and EC (Table 3). Results were supported by the previous work of Ogunkunle and Fatoba [27] that obtained significant (P<0.01) negative correlation between the soil pH and soil content of Cd. So, pH of the soil seemed to be a major factor affecting the amounts of Cd in the soil; any increase in the soil pH reduces the soil content of this metal. *Moreover* significant but relatively weak correlations (r=0.49) were observed between Cd and Pb that may indicate possible same source such as cement production; But low concentration of Pb in the soil could not be related to emissions from the cement factory.

Table 3. Spearman correlations coefficients between topsoil heavy metal concentrations and soil properties

	Cd	**Pb**	**pH**	**EC**
Cd	1.00	0.49*	-0.55**	0.24
Pb	0.49*	1.000	-0.08	0.14
pH	-0.55**	-0.08	1.00	-0.41*
EC	0.24	0.14	-0.41*	1.00

*. Correlation is significant at the 0.05 level.
**. Correlation is significant at the 0.01 level.

To evaluate the influence of the cement factory on the heavy metals accumulation in soil around areas, various distances and directions from the cement factory were regarded. Concentration of heavy metals in soil samples collected from the twenty- four locations decreased with increasing distance from the cement factory (Table 4). Cd and Pb showed a decreasing metal concentration from 400 m to 800 m. Metal concentrations at 400 m Kurdistan Cement Factory was higher than 800 m. Table 4 and 5 present the summarized results of the mean concentrations of soil metals with regard to distance and direction from the cement facility. As can be seen in Table 4, the highest levels of Cd and Pb occur in distance of 400 m and 800 m respectively. The statistical analysis done using *t*-test and Mann-Whitney U tests presented in Fig. 2, these results indicate that there was no statistically significant difference in the cadmium and lead at various distances from the cement factory.

Table 4. Descriptive statistics for heavy metal concentrations (mg/kg) in soil at different distances from the Kurdistan Cement Factory.

		N	Mean	Std. Deviation	Std. Error	Minimum	Maximum
Cd	400m	12	0.41	0.40	0.11	0.10	1.44
	800m	12	0.32	0.34	0.01	0.02	1.07
	Total	24	0.37	0.37	0.07	0.02	1.44
Pb	400m	12	1.65	0.23	0.07	1.18	1.96
	800m	12	1.464	0.60	0.16	0.58	2.49
	Total	24	1.56	0.43	0.09	0.58	2.49

Table 5. Heavy metal concentrations (mg/kg) in soil at different directions from the Kurdistan cement factory.

		N	Mean	Std. Deviation	Std. Error	Minimum	Maximum
Cd	North	6	0.67	0.34	0.14	0.21	1.07
	West	6	0.37	0.53	0.21	0.06	1.44
	South	6	0.29	0.22	0.09	0.13	0.72
	East	6	0.15	0.10	0.04	0.02	0.32
	Total	24	0.37	0.37	0.07	0.02	1.44
Pb	North	6	1.80	0.47	0.19	1.33	2.49
	West	6	1.30	0.28	0.11	0.98	1.72
	South	6	1.74	0.13	0.05	1.51	1.88
	East	6	1.40	0.58	0.24	0.58	1.96
	Total	24	1.56	0.43	0.09	0.58	2.49

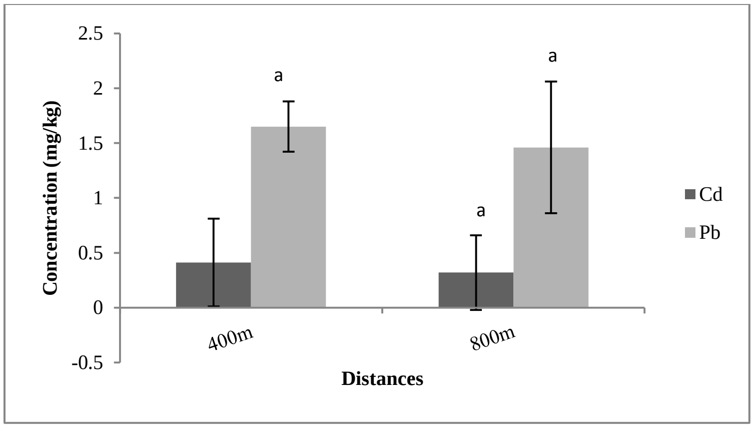

Figure 2. Comparison of metals in different distances from the Kurdistan cement factory

Figure 3 and 4 show comparison of soil heavy metal concentration in all four directions, north, south, west and east, that are significant for cadmium and there is no statistical significance for lead.

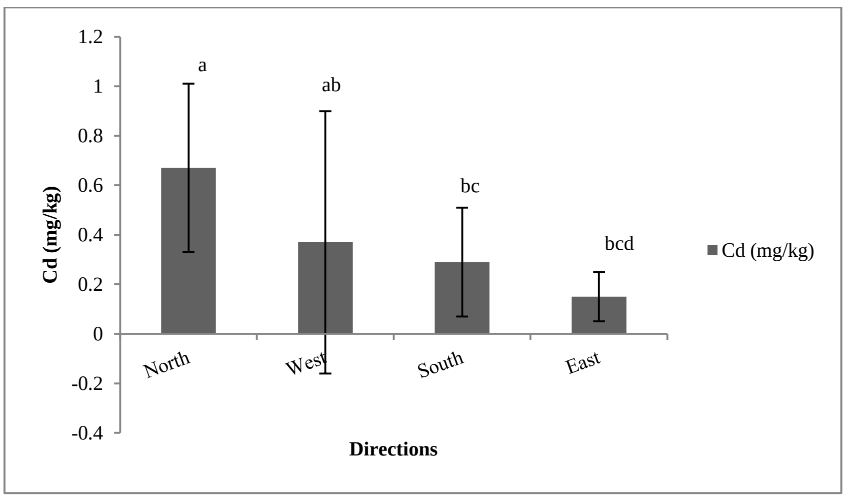

Figure 3. Comparison of cadmium in different directions from the Kurdistan cement factory

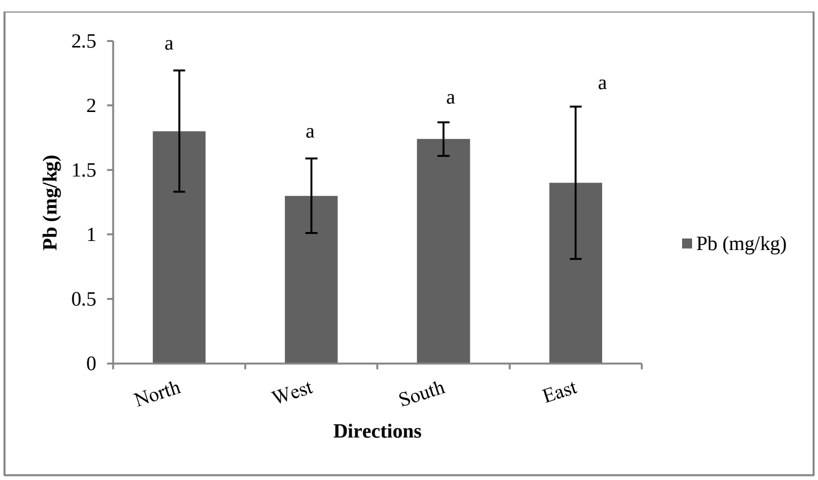

Figure 4. Comparison of lead in different directions from the Kurdistan cement factory

To quantify the degree of metal contamination, various methods were used for soil around the cement factory. Therefore, Index of geoaccumulation (Igeo), Contamination Factor (CF) and Pollution Load Index (PLI) were calculated. The calculated geoaccumulation (Igeo) values are shown in Fig. 5. The Igeo values for Pb exhibited zero class, indicating unpolluted soil quality. The values for Cd, among the 24 locations of the study area, 16 sites exhibited Igeo class 0, 2 sites exhibited Igeo class 1, 5 sites exhibited Igeo class 2 and 1 sites exhibited Igeo class 3 soil quality by Cd. . It is evident from Fig.5 that the uncontaminated to moderately - strongly contaminated Igeo value by Cd and uncontaminated by Pb. CF values for metals recorded at different sampling locations are presented in Fig.6 .As shown in Fig.6, these values varies from one location to another. The contamination factors (CFs) of the heavy metals of environmental concern range as Pb: 0.03–0.13 and Cd: 0.05–4.7. In this study, the highest CF value was obtained for Cd and low contamination factors being recorded for Pb. Based on the mean CF values, the soils may be considered low contamination by Pb and moderate contamination by Cd.

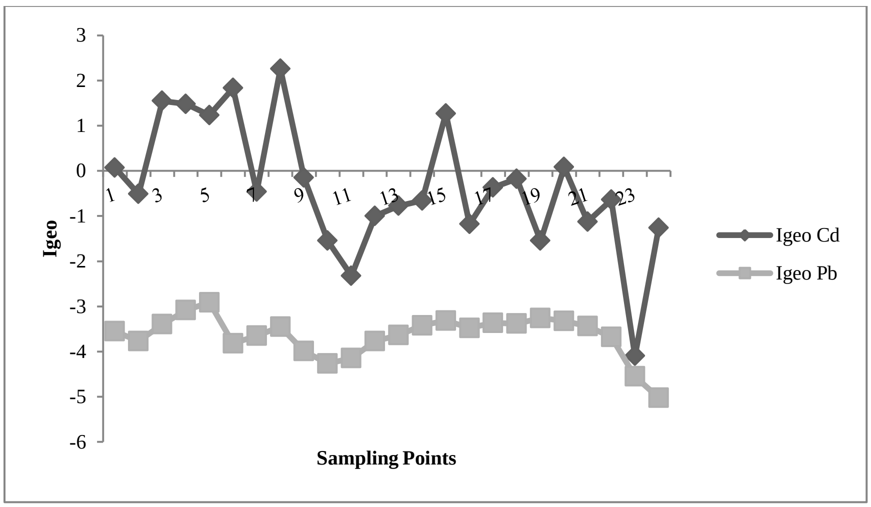

Figure 5. Index of Geoaccumulation (Igeo) of heavy metals in soil samples collected from around the cement factory

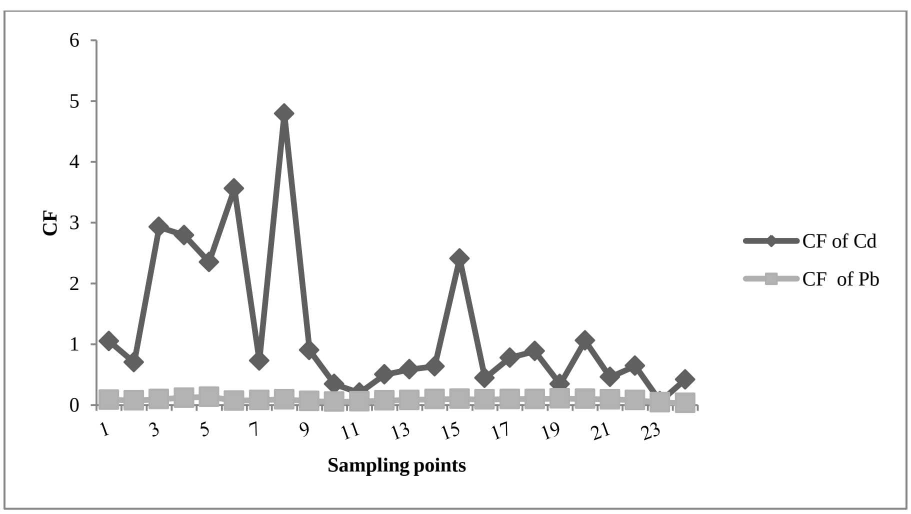

Figure 6. Contamination Factor (CF) of heavy metals in soil samples collected from around the cement factory

The PLI values ranged from 0.05-0.66 with mean value of 0.29 for soil samples collected from 24 locations (Figure 7). All sites had the value <1.0 indicates no pollution load in the study area.

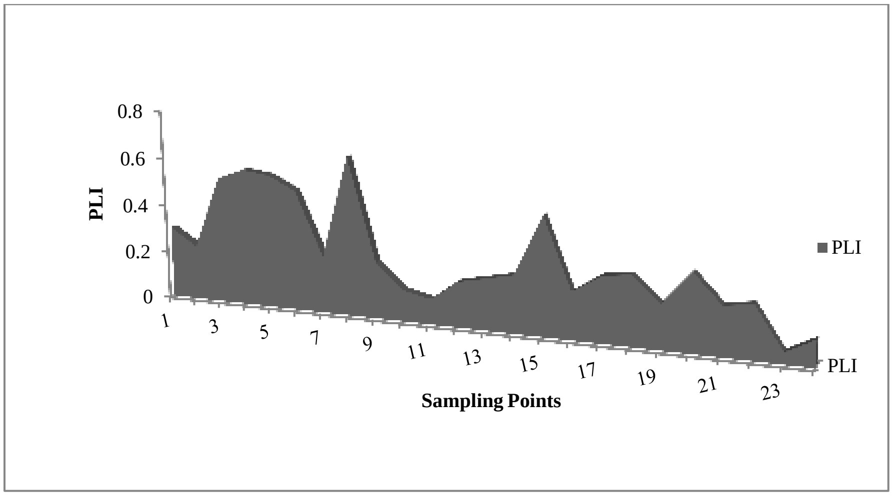

Figure 7. Pollution Load Index (PLI) of heavy metals in soil samples collected from around the cement factory

Map of spatial spread distribution of Cd, Pb, pH and EC using kriging technique of ArcGIS is presented in Figure 8. As observed in the maps, spatial distribution of Cd was different from Pb distribution in the studied area, suggesting different sources. The spatial distribution shows that the concentration of cadmium is high in north and northeastern parts of the study area (Fig.8). The result indicated that cadmium concentration decreases as the distance increases from the cement factory. It seem that, the main source of cadmium concentration is atmospheric deposition from the cement production through the stack [27] and may be carried by winds and deposited even at a distance of about 1 km from the factory at north. Cadmium is present as a trace contaminant in the raw materials used in cement production. The cadmium level in these raw materials has been measured to be around 2 ppm. The amount of cadmium emissions to the atmosphere in the form of dusts will depend on efficiencies in dust collection [29]. Furthermore, Fig. 8 shows the spatial distribution of lead in the study area. No obvious trend could be observed in this map. The lead content of soil is very low and variations are not significantly even in the neighborhood of cement factory. Although there is no obvious enrichment of this metal in the immediate vicinity of the cement factory, but slightly higher values in the north and south areas of cement factory cannot be related to cement production and may be due to vehicular emissions. The distribution map of soil pH prepared by the kriging interpolator is presented in Fig.7. The spatial distribution pattern of soil pH cannot be related to cement factory generally, but must relate to other environmental factors at different spatial scales, such as elevation, terrain attributes, precipitation, soil vegetation type [30]. Soil pH is lower in the north of the factory. The highest soil pH values are distributed in the west and southwest of the cement factory. Our findings are generally consistent with results obtained by Addo et al. [31], in contamination of soils by cement dust pollution that revealed at the environment of the cement facility the pH increased as distance from the cement factory increases.

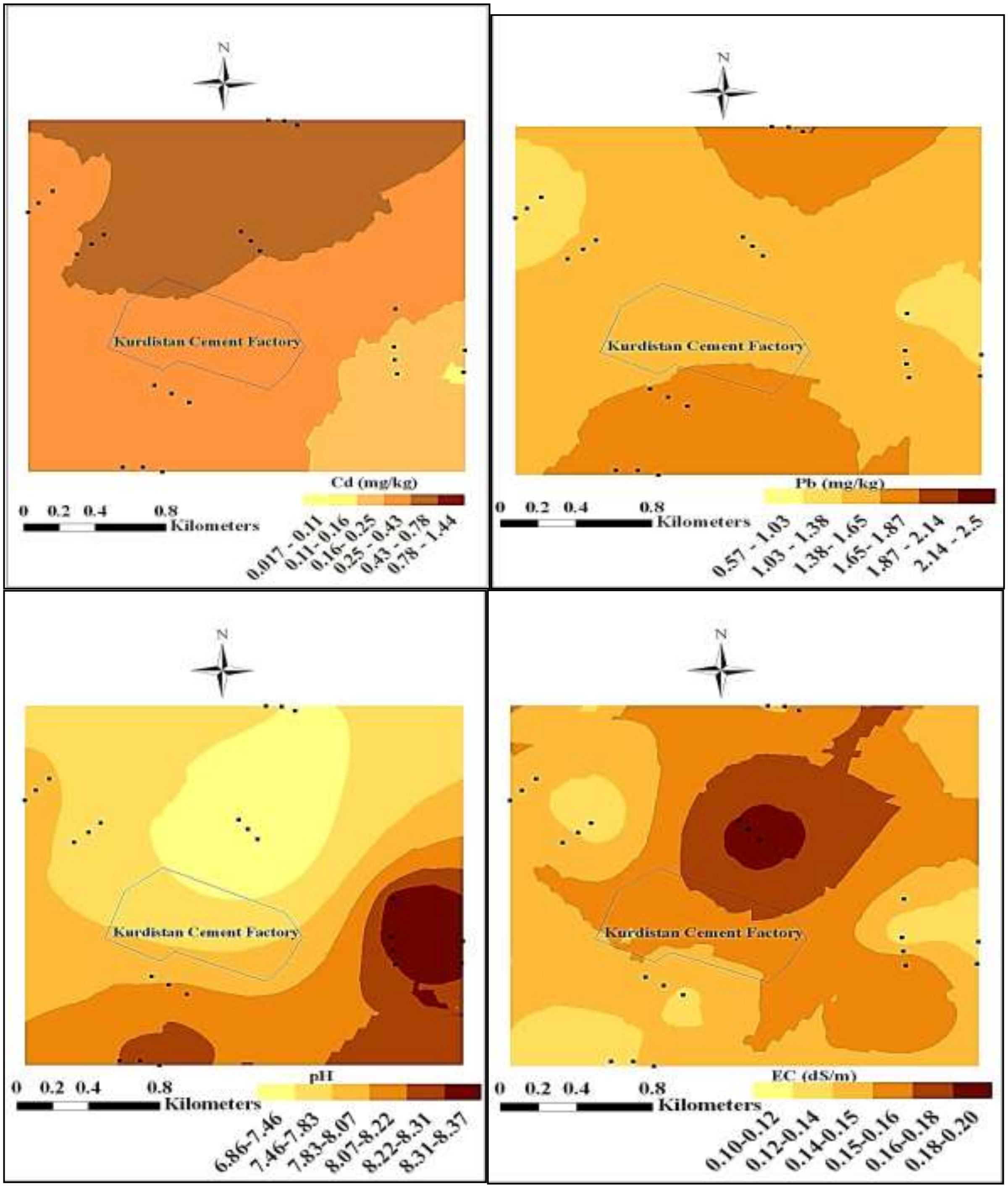

Figure 8. Spatial distribution of soil Cd, Pb, pH and EC

Results of the spatial distribution of EC values, are presented in Fig. 8, show that soil affected by cement factory. This map revealed that, EC values for the soil were increased significantly toward the cement factory. Similarly, it was found that the higher values of soil EC could be associated with the dust emission from the cement factory in Mekelle, Ethiopia [32].

CONCLUSIONS

The characteristics of soils such as EC and metals (Cd) in the study area seem to be influenced by cement dusts that have settled on the soil from the factory. However, other characteristics such as pH and Pb were not affected by cement factory. Moreover, the CF values suggest that soil around the cement factory were low contamination for Pb, and moderate contamination by Cd. The Igeo values showed that the uncontaminated to moderately strongly contaminated by Cd and uncontaminated by Pb. According to PLI, all locations suggest perfection or no overall pollution of site quality. On the other hand, from the spatial distribution maps, it was clear that contamination of the soil by Cd around the cement factory was due to cement production activities while the spatial distribution pattern of soil Pb cannot be related to cement factory. Further research with intensive sampling is required to know about status and extent of metals in soils.

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