

## ***Geo-statistical Distribution of Heavy Metals in Karoon River's Soil by Geographic Information System***

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### **ABSTRACT**

**Introduction:** Soil has an important role in nutrient cycle and an important function in storage, refinement, and movement of nutrients for the living and non-living parts. Soil pollution of heavy metals and elements is one of the common pollution impacts of human activities, especially industry. Realization of distribution pattern of these elements and their anthropogenic sources is a major part of environmental protection plans. In the present study, concentration of two major heavy metals were investigated and mapped using geostatistical methods throughout western part of Karoon river in Ahwaz city. Four land areas including urban areas, agricultural, industrial, and bare soils were applied.

**Materials and Methods:** In this research, at first, 40 sample plots were determined randomly from the study area and soil samples were taken from surface layer with the depth of 20 centimeters. Afterwards, the data were entered into SAS 9.3 and Arc GIS 10.2 applications for data analysis and mapping.

**Results:** Results showed that Pb and Cd concentrations had the lowest standard rate in western parts of city while their highest rate was in river shores, south-west, and northern parts. Hence, the soil is over polluted in these areas comparing to WHO standards.

**Conclusion:** A significant correlation was observed between Pb and Cd elements. Regarding results achieved by the semi-variance model, it is concluded that pollutions have anthropogenic sources in this area. According to the results, most important factors of pollution in this area were smelting and steel factories as well as agricultural pesticides.

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### **Introduction**

As a part of biogeochemical system, soil has an important role in nutrient cycle and an important function in storage, refinement, and movement of nutrients for the living and non-living parts. Soil pollution by heavy metals and elements is one of the common pollutions caused by human activities, especially industry. Realization of distribution

pattern of these elements and their anthropogenic sources is a major part for environmental protection plans<sup>1</sup>.

Soil is the most important reservoir of heavy metals in the terrestrial ecosystem the content of heavy metals in which is an important indicator of environmental quality<sup>2,3</sup>.

Heavy metals are regarded as nonessential and toxic trace elements in the environment <sup>4</sup>.

Certain heavy metals like zinc and copper are essential for normal metabolism of aquatic organisms in low concentrations, while cadmium, lead, and mercury are nonessential with no recognized role in biological systems <sup>2-5, 6</sup>. Even essential metals could be toxic for biological activities of organisms in high concentration <sup>7</sup>.

Heavy metals are known to have adverse effects on human health, mostly because of their persistence and toxicity <sup>8</sup>. Since the industrial revolution smelters have polluted their surroundings by heavy metal dust emissions. Although, dust inhalation is primarily dangerous for human health, heavy metal dust also concentrates in soils and may become a secondary environmental danger in two respects: (1) contamination of crops and vegetables, when soils are used for agriculture; and (2) contamination of groundwater by metal migration <sup>9</sup>.

High concentrations of heavy metals in fruits and vegetables are related to high prevalence of upper gastro-intestinal cancer <sup>10</sup>. The genetic and epigenetic effects of these elements are associated with an increased risk of different types of cancer <sup>11</sup>.

The concentrations of metals in soil surface, size of the contaminated area, distance from the smelter plant, the period of soil exposure to heavy metals contamination, as well as their concentration, depend on numerous factors such as: concentration, size, distribution, rate, and duration of emission of airborne particles from the smelter chimney stack, stack height, atmospheric stability, wind speed and direction, as well as terrain configuration <sup>12</sup>.

Numerous studies have been conducted on Cd, Pb, Cr, and Hg in soils. Teng et al. in China stated that approximately 10% of planting land is contaminated by heavy metals (Cd, Pb, Hg, Cr, etc.) and approximately 10 million tons of grains are contaminated every year <sup>13</sup>.

Most studies on pollution of heavy metals such as assessment of their environmental impact begin

with determining their distribution. In this context, the need to use advanced statistical methods are necessary <sup>14</sup>.

Due to their potential toxicity, soils are the main source of heavy metals in plants. Recently, the issue of heavy metals pollution in agricultural soils and plants has become increasingly serious <sup>15</sup>.

Therefore, the objective of this study was to investigate heavy metals (Cd & Pb) in the soil of western part of Karoon River in Ahwaz. To do this, four land areas of urban, agricultural, industrial, and bare soils were investigated using geo-statistic and GIS techniques.

## Materials and Methods

### Studied area

The western part soil of Karoon River in Ahwaz city, located in 31° 18' 12" N and 48° 37' 27" E was analyzed.

The land is mainly used for agricultural, urban, rural, and industrial purposes in which different steel and pipe plants and other industrial companies exist.

### Methods

At first, 40 samples of soil in studied area were analyzed randomly on GIS layers. Then, the points of samples were found on the floor with GPS set. The soil samples were taken from a depth of 20 cm in the summer. The samples for chemical analysis and measurement of heavy metals were transported to the laboratory. Later, the samples were dried at room temperature.

Further, lumps were fully crushed and converted into powder until the maximum homogeneity in the samples was obtained at the time of analysis. To measure the weight of dry soil, samples were passed through a 2 mm sieve and placed for 24 hours at 105 ° C in the oven. After weighing the samples using HNO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub>-HCl, they were analyzed according to 3050B method. Also, by applying ICP and graphite atomic absorption set, concentrations of lead and cadmium were measured.

After measurement of heavy metals' concentration, to calculate the mean, standard deviation, and other quantitative criteria data were analyzed through Excel and SAS 9.3 software. In addition, the distribution and correlation between the two elements were measured in the region.

Zoning map of the lead and cadmium were provided via kriging method in ArcGIS software. In the first, all spatial data were transferred to SAS 9.3 software. Range and stationary value (for semi variance of both cadmium and lead elements) (Sill) were calculated by the equation 1.

$$\gamma(h) = \frac{1}{2n(h)} \sum_{i=1}^{n(h)} [z(x_i) - z(x_i + h)]^2 \quad (1)$$

$$= \frac{1}{2n(h)} \sum_{i=1}^{n(h)} [z(x_i) - z(x_i + h)]^2$$

In this changing view data are ( $\gamma$ ), number of samples ( $n$ ), step ( $h$ ), measured variables ( $z$ ), and the sample is  $x_i$ .

In order to estimate the half-changing view of the spherical model (Spherical), equation 2 was used. (2)

$$\gamma(h) = \begin{cases} c \left\{ \frac{3h}{2a} - \frac{1}{2} \left( \frac{h}{a} \right)^3 \right\} & \text{for } h \leq a, \\ c & \text{for } h > a. \end{cases}$$

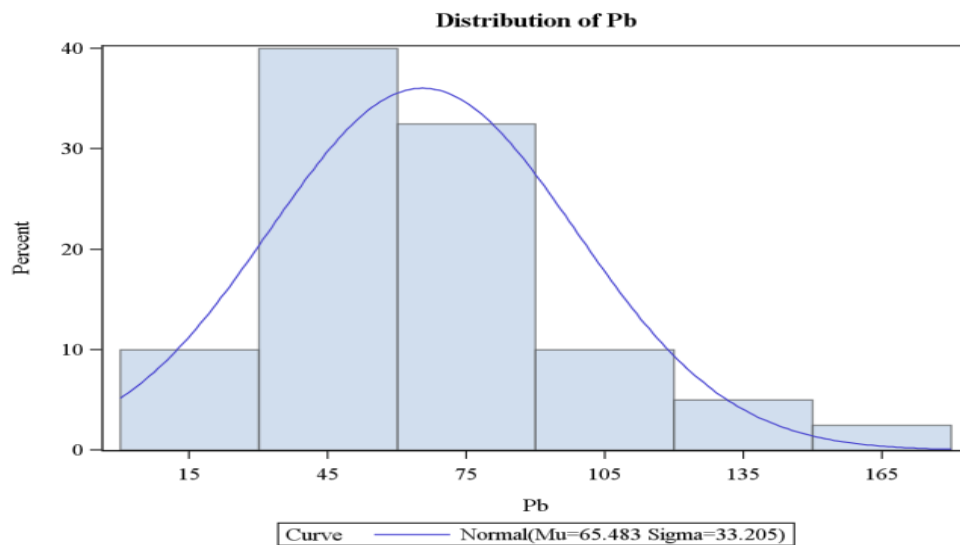
In this formula ( $a$ ) is the range and  $c$  is the rest point. Because of the spatial variation in the data, in this process  $\gamma$  was removed by bivariate quadratic regression and the model residuals were analyzed by vario-gram procedures. (Model 3).

$$Z(X) = \mu + \varepsilon(X) \quad (3)$$

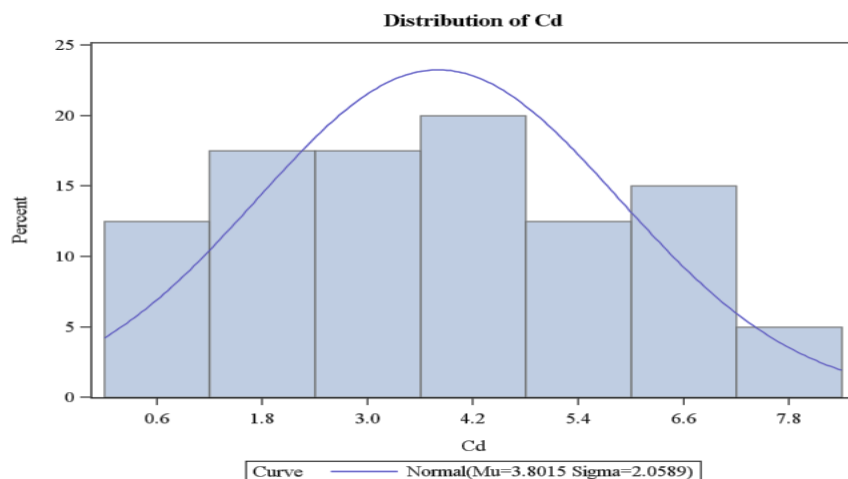
After calculating the half-changing facade and kriging parameters, zoning maps were developed using kriging tool in the tool box of spatial analysis software in ArcGIS. Finally, the area's soil had a lead concentration of greater than 50 mg/kg and a cadmium concentration of higher than 2 mg/kg (standard amount)<sup>16</sup> which were then identified as pollution areas.

## Results

The results of this study achieved through experiments, are presented by figures and tables below. Frequency distribution of lead and cadmium concentrations in the studied area is represented in histograms of figure 1 a and b , respectively.



**Figure 1a:** Histograms of lead concentration frequency distribution in the region (mg/kg)



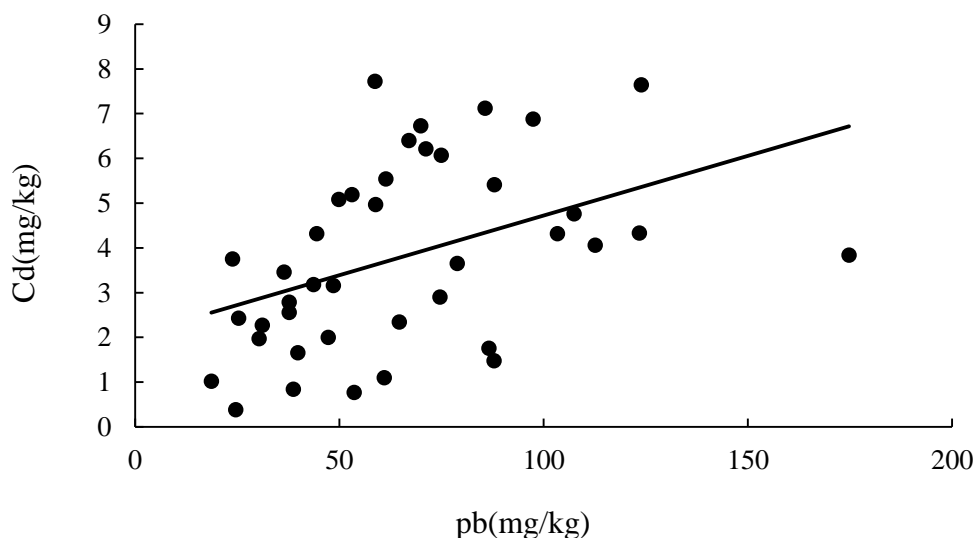
**Figure 1b:** Histograms of cadmium concentration frequency distribution in the region (mg/kg)

Histograms of Figure 1a show that the range of lead has changed from 0.38 to 174.8 mg/kg and distribution of soil concentration plots follow a normal pattern.

Figure 1b shows that the concentration of cadmium in the soil varies between 0.38 to 7.72

mg/kg and it has a more uniform distribution ration than Pb in the soil but it has a normal distribution.

Diagram correlation between the lead and cadmium concentrations is represented in figure 2.



**Figure 2:** Diagram correlation between lead and cadmium concentrations

Results of Regression test indicate that there is a highly significant correlation between the elements of lead and cadmium with a correlation coefficient of 0.43 ( $p < 0.01$ ). Figure 2 shows a significant positive correlation between the two elements.

Cadmium regression model is as follows:

$$Ca(x, y) = -0.05x + 0.0041x^2 + 9.2 \times 10^{-8}y - 6 \times 10^{-10}y^2 + \epsilon$$

Lead regression model is as follows:

$$L(x, y) = -1.13x + 0.0092x^2 + 2.07 \times 10^{-6}y - 1.4 \times 10^{-8}y^2 + \epsilon$$

Figures 3a and 3b show respectively value of Semvariance of the lead and cadmium changes regression model.

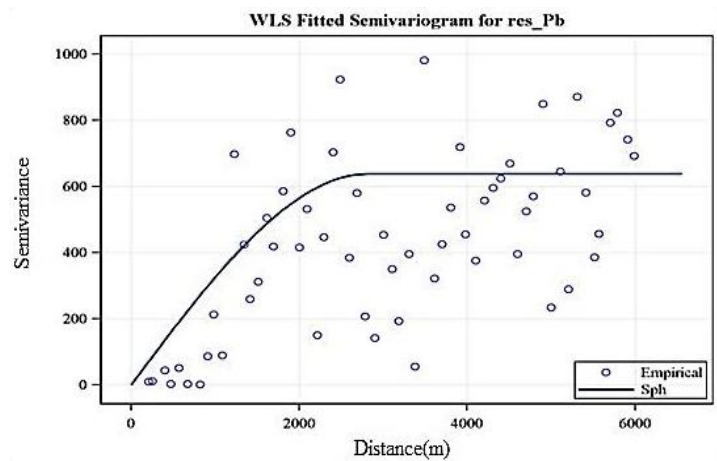


Figure 3a: Semivariance of the residuals of the regression model of lead changes

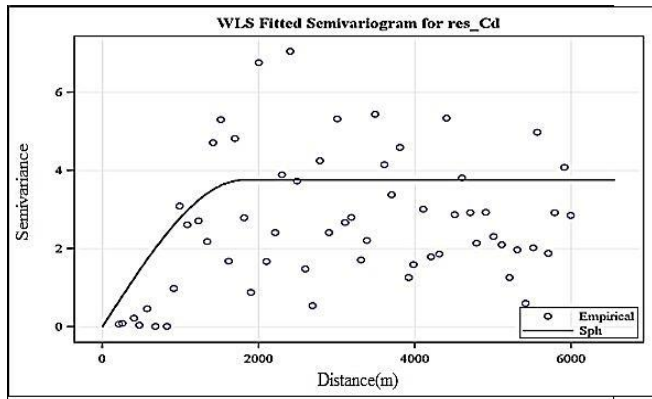


Figure 3b: Semivariance of the residuals of the regression model of cadmium changes

Figure 4a show that concentration of lead in the soils of Karoon River was above the limit, with increase of distance from the river pollution has

decreased substantially and finally in the central and western regions it was close to the standard.

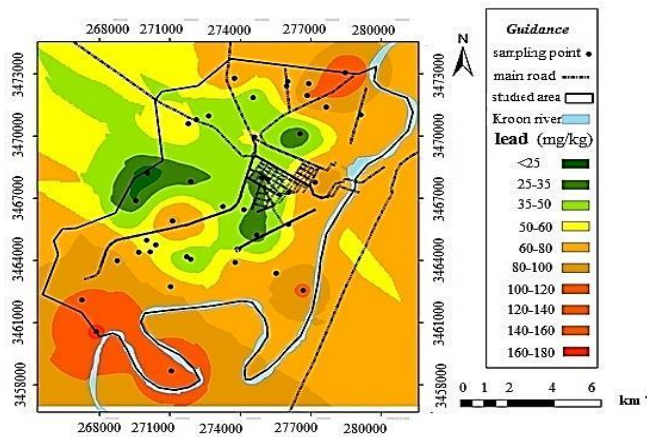


Figure 4a: Zoning map of lead in the studied area by kriging method

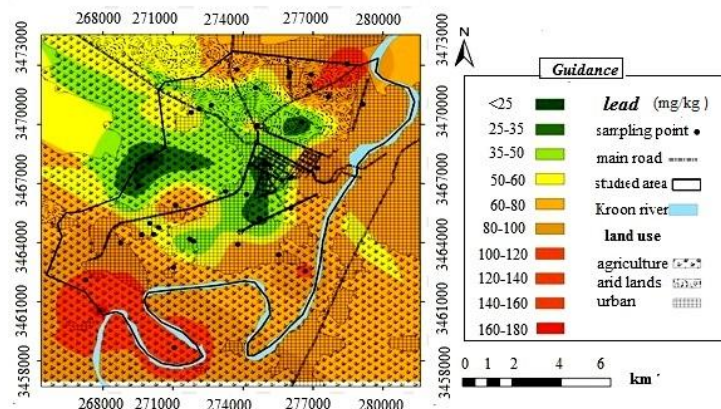
The highest lead concentration was in the northeast and southwest part of the studied region.

Map of lead concentration shows that land use has little effect on soil lead concentrations since all

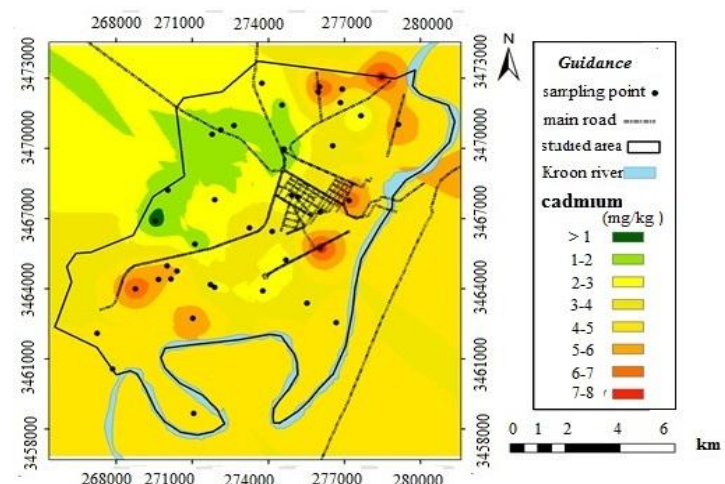


three types of pollution can be observed in varying degrees for lands under different uses. Figure 4b shows an overlaying of the zoning map of lead element and land use in the studied area. figures 5a shows the zoning map by kriging

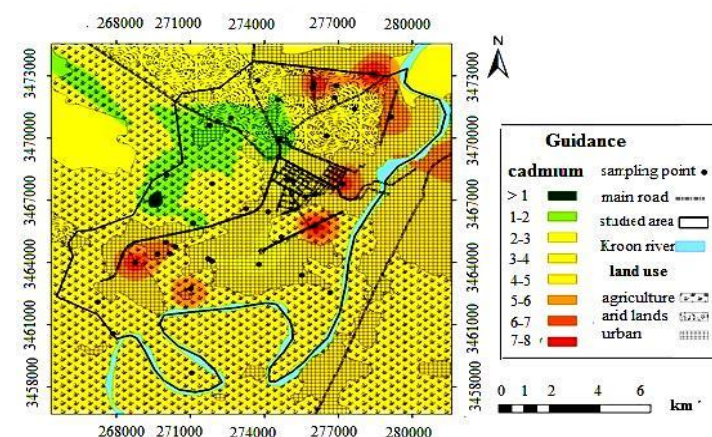
method and figure 5b represents overlaying of cadmium element zoning map and land use in the studied area.



**Figure 4b:** Overlaying of the zoning map of the lead element and land use in the studied area



**Figure 5a:** Zoning map of cadmium in the studied area by kriging method



**Figure 5b:** Overlaying of the zoning map of the cadmium element and land use in the studied area

The zoning map shows that cadmium contamination is higher than the standard level in most regions of the studied area except the western regions in which it is less than the standard (Figure 5b).

This figure shows that there is no relation between land use and intensity of pollution, but when the distance from the Karoon River increases, the pollution levels decrease substantially.

### Discussion

The results of correlation analysis between elements show that the correlation between these two elements is due to presence of heavy large industrial sources of contaminants in the city of Ahvaz.

In study carried out by Sollitto and colleague a certain correlation was observed between the spread of heavy metals in soil. This study was conducted in different areas in terms of land use.

Guo et al. conducted a study near the mining and metal industries in China and found that concentrations of heavy metals in the soil near to these industries are very high. They also reported that there is a very high correlation between the metals<sup>17</sup>.

The results of the study carried out by Maas et al, on the heavy metals in urban, suburban, and agricultural areas in the Mediterranean areas showed that two elements of Pb and Cd are not correlated with each other because of the correct usage of chemical pesticides and appropriate control of the industries' pollutions in the region<sup>18</sup> but in this study, correlation results showed that Pb and Cd are correlated and effect of spatial variations on the concentration changes is almost similar in the lead and cadmium models.

Finally, further studies are recommended in the areas with high pollution, to determine the source of contamination and also to examine the amount of pollution generated from industries.

Due to population growth, urban areas have become extremely close to industrial plants, so it is proposed to transfer factories and industrial units to other sites remote from urban areas.

### Conclusion

The results showed that concentration of heavy metals is low in the western part of the studied area, i.e., the moorlands and new farmlands, while in the northern and southern regions heavy metals pollution are observed, that is likely to be due to steel and other metal industries.

Correlation analysis showed that there is a significant correlation between Pb and Cd elements, which is according to the semi-variance model.

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### Conflict of interest

The authors declare that they have no competing interests.

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