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Spatial Distribution and Risk Assessment of As, Hg, Co and Cr in Kaveh Industrial City, using Geostatistic and GIS

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Abstract**—**The concentrations of As, Hg, Co, Cr and Cd were tested for each soil sample, and their spatial patterns were analyzed by the semivariogram approach of geostatistics and geographical information system technology. Multivariate statistic approaches (principal component analysis and cluster analysis) were used to identify heavy metal sources and their spatial pattern. Principal component analysis coupled with correlation between heavy metals showed that primary inputs of As, Hg and Cd were due to anthropogenic while, Co, and Cr were associated with pedogenic factors. Ordinary kriging was carried out to map the spatial patters of heavy metals. The high pollution sources evaluated was related with usage of urban and industrial wastewater. The results of this study helpful for risk assessment of environmental pollution for decision making for industrial adjustment and remedy soil pollution.

Keywords**—**Geographic Information system, Geostatistics, Kaveh, Multivariate Statistical Analysis.

I. Introduction

ACCUMULATION of heavy metals in topsoil may be affected by parent materials and anthropogenic sources. Soil contamination by heavy metals due to non-decay by time and long biological half-lives has been severely considered. Various activities are usually the main sources of heavy metal in agricultural soils, such as irrigation by means of using wastewater, agricultural fertilizers, pesticides, organic manures, disposal of urban, industrial wastes, mining, smelting process, atmospheric pollution resulted from motor vehicles and combustion of fossil fuels [9]-[13]. Over the past century, heavy metals have been discharged into the World Rivers and estuaries as a result of the rapid industrialization. People living in industrial cities are particularly exposed to this decline in environment quality leading to human health concerns. Heavy metal contents in the urban soil tend to increase with vehicular emissions, industrial residues the atmospheric deposition of dust and aerosols and other industrial sources such as acid rain, metallurgical industries, and thermoelectric centers. The high concentrations of heavy metals in urban soils become a potential threat to human health and safety because they can be easily transferred in to human bodies from suspended dust and direct contact [2]. Heavy metals pollution in soil is commonly estimated by interpolating concentrations of heavy metals sampled at point locations, so that each heavy metal is represented in a separate map [17]. The methods of geostatistics use the stochastic theory of spatial correlation both for interpolation and for apportioning uncertainty [7]. Particularly, geostatistics has been popularly applied in investigating and mapping soil pollution by heavy metals, in recent years [10]. Geostatistics provides a set of statistical tools for incorporating spatial coordinates of observations in data processing [8]. Recent studies have attempted to apply both multivariate analyses and GIS techniques in industrial soil studies [12]. Solid and liquid wastes proceeding from the industrial activities are the unavoidable via products of manufacturing process. These wastes contain toxic chemicals such as chromium salts, sulfides and other substances including heavy metals [16].

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II. Materials and methods

A. Study area

The study area is located in a industrial city Kaveh (35°02′55″~35°08′45″N, 50°02′07″~ 50°28′11″E) situated in center of Markazi province with an area of 420 Km. Kaveh industrial development area, has been established in 1973 (Fig.1). It is also identified as the largest industrial city in Iran. This zone is characterized by mild-cold winters and arid continental climate with an average annual rainfall of 216 mm with a minimum and a maximum average annual temperature of 0 and 22.6°C. Industrial effluents contain appreciable amounts of inorganic and organic chemicals and their by-products. Most of the industries are small to medium-scale sector and are not having any sewer lines. Many of them do not have proper wastewater treatment plants and they discharge industrial effluents in unlined channels, thereby causing contamination of air, water and soil. As a result the highly toxic chemical effluents have been pollution surface water and groundwater.

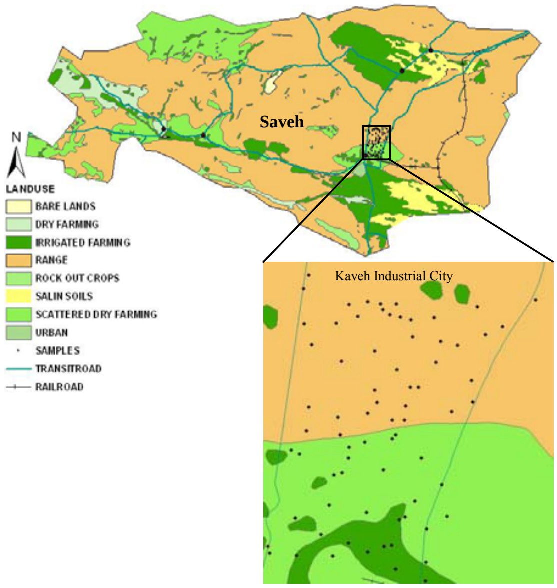

Fig. 1 Land use map and sampling sites of the study area

B. Sampling and Chemical Analysis

Soil samples were taken from soil and effluents channels of different industries corresponding to land use map at 1:100.000. Other samples of soil were also collected from in surroundings of industries. Heavy metals from anthropogenic sources are mainly accumulated at surface and most of the roots of vegetable crops are located down at this depth [14]. Sampling sites were selected randomly around the factories. A composite soil sample consisted of 5-sub samples obtained using stainless steel hand auger at regular distances from each other. Sub-samples were mixed into one composite sample for each soil and analyzed in triplicate. The coordination of the sample locations were recorded with a global positioning system (GPS) receiver. About one Kg of each sample was stored in polyethylene packages and transported to the laboratory. All the samples were air-dried in room temperature (20-22 ºC), and then these dried samples were sieved 2 mm for analysis of their properties. 0.1 g of the sieved dust samples were digested with a mixture 5:2:1 of HNO3–H2SO4–HF and left over night. Then, the solution was heated at 120 °C for 30 min, at 150 °C for 30 min, at 200 °C for 30 min, and at 260–270 °C for 60 min in turn. Finally, the digested samples were diluted to 50 ml with deionized water [10]. The heavy metals concentration of of As, Hg, Co, Cr and Cd were determined using inductively coupled plasma atomic emission spectroscopy (ICP-ES; 138 Ultrace; Jobin Yvon).

B. Geostatistic and Multivariate Statistics

The spatial interpolation methods, including geostatistics, have been developed for and applied to various disciplines. Geostatistics uses the technique of variogram to measure the spatial variability of the recognized variable and provides the input parameters for the spatial interpolation of kriging [17]. Kriging has been widely used as an important interpolation method at different scales, especially in soil pollution [5]. The semivariogram γ (h), measures the mean variability between two points x and x+h, as a function of their distance h, for data location at discrete sampling locations. The semivariogram is an autocorrelation statistic defined as the equation (1) [17]:

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

Where n is the number of pairs of sample points separated by distance h, $z(xi)$ is the value of the variable z at point i , $z(x_i+h)$ is the value of the variable z at point $i+h$. The assumptions of kriging are stationary of difference between x and $x+h$ and variance of differences, which define the requirements for the intrinsic hypothesis [3]. This means that semivariance does not depend on the location of samples and only depends on the distance between samples, thus the semivariance is isotropic. The variogram model is chosen from a set of mathematical functions that describe spatial relationship and fitted usually by weighted lost squares and range, nugget and sill are then used in the kriging procedure. In this study, we used Ordinary kriging as a spatial interpolation technique to make distribution maps because it is very flexible and allows users to investigate graphs of spatial autocorrelation and allow prediction, prediction standard error, and probability maps and at the same time minimize the error of predicted values. The statistics of the differences between the measured and predicted values at sampled points are often used as an indicator of the performance of an inexact method [3]. For the evaluation of the degree simulation quality and the model-experiment comparison of different model approaches, a cross validation indicators and additional model parameters can be used. In this paper for comparing these models, cross validation was used by statistical parameters of mean error (ME), root mean square error (RMSE), average standard error (ASE), mean standard error (MSE), and root mean squared standardized error (RMSSE) [15]. The principal component analysis (PCA), were employed for identification of heavy metal sources. The PCA converts the variables under investigation into factors or principal components and correlation among the original variables can be minimized and measured elements into fewer groups. In addition, Varimax and Kaiser Normalization rotation was applied to maximize the variance of the factor loading across variances for each factor. Multivariate statistical analyses and descriptive statistical parameters of the data were performed by SPSS (V.13) software packages (SPSS Inc., Chicago, USA) for Windows. Geostatistical analysis, semivariogram model fitting and spatial distribution using ordinary kriging were performed with GIS software ArcGIS V.9.2 (ESRI Co, Redlands, USA)

III. RESULT

A. Basic Statistics

The descriptive statistics of heavy metals in topsoil is summarized in Table1. Mean concentrations of As, Hg, Co, Cr and Cd were 4.65 mg kg $^{-1}$, 0.55 mg kg $^{-1}$, 12.73 mg kg $^{-1}$, 54.05 mg kg $^{-1}$ and 0.54 mg kg $^{-1}$ respectively. Skewness values (-0.32-0.47) indicate that the levels of heavy metal concentrations have a normal distribution. The coefficient of variation of As and Hg were 0.62, and 0.0.57% respectively, was relatively higher than the other heavy metals, suggesting that As and Hg has the greatest variation among the soil sample and thus would have the highest possibility of being influenced by anthropogenic activities. The lowest C.V. of Co, Cr and Cd exhibit a weak variation, and their content was almost constant in local and their values may be probably caused by lithogenic process. The mean concentrations of As and Hg in analyzed samples were higher than background level values, while mean concentrations of Co, Co and Cd were lover than their background levels provided by Ministry of Industries and Mines Geological Survey of Iran [1]. High concentrations (i.e. above background levels) coupled with a high coefficient of variation suggest anthropogenic inputs for metal elements [11].

TABLE I SUMMERY STATISTICS FOR HEAVY METALS CONCENTRATIONS ($mgkg^{-1}$) IN TOP SOIL

	As	Hg	Co	Cr	Cd
Mean	4.65	0.55	12.73	54.05	0.54
Minimum	0.12	0.04	5.62	10.25	0.11
Maximum	12.45	1.23	18.52	102.35	1.20
Kurtosis	-0.56	-0.87	-0.67	-0.65	0.16
Skewness	0.22	0.27	-0.32	0.21	0.47
Range	12.33	1.19	12.90	92.10	1.09
Std. Deviation	2.89	0.32	3.30	25.05	0.21
CV%	0.62	0.57	0.26	0.46	0.39
Guide value	12	0.3	40	350	0.6

B. Principal Component Analysis

To better describe the relationship among heavy metals, principal component analysis was performed. The results of PCA for heavy metal concentration in soil are illustrated in Table 2. The rotation of the matrix contributes to clarify ambiguities in component matrix. Based on eigenvalue (eigenvalue>0.75), four main PCs explained 87.25% of the total variance (Table 2). The first PC (PC1) explains 25.89% of total variance and consists of Hg. The initial component matrix (PC1) indicates that Hg is associated, displaying high value in the first component. PC2 explains 47.17% of the total variance and contain Co while PC3 contain Cr. Where as the fourth principal component (PC4) includes As and Cd.

C. Geostatistical Analysis

The experiment semivariogram depicts the variance of the sample values at various separation distances. The ratio of nugget to sill (nugget/sill) can be used to express the extent of spatial autocorrelations of environmental factors. If the ratio is low (< 25%), the variable has strong spatial autocorrelations at a regional scale. A high ratio of nugget effect (> 75%) play an important role in spatial heterogeneity of soil properties. To some extent, the spatial variability of heavy metals may be affected by intrinsic factors (pedogenic factors such as soil parent material) and extrinsic factors (anthropogenic factors such as agricultural practices). In general, strong spatial dependence of soil properties can be affected by intrinsic factors and weak spatial dependence can be affected by extrinsic factors [4]. The attribute of the semivariograms model and best-fit model parameters that are used as input to kriging interpolation are summarized in Table 3.

The results show that soil As, Cr and Cd were fitted with Exponential model and Hg and Co were fitted with Gaussian model. The ratio of nugget to sill of Co and Cr was more than 0.75 showing week spatial dependence due to the effects of extrinsic factors such as industrial production, soil practice management. The ratio of As, Hg and Cd were between 0.25 and 0.75, have moderate spatial dependence, indicating that intrinsic and extrinsic factors such as industrial production, agricultural practice, parent material and topography, changed their spatial correlations.

D. Trend analysis

Trend analysis was apply to diagnostic anisotropic parameters of heavy metals and their characteristic trends, which is helpful for removing a trend from the dataset before using kriging. The result of trend analysis are illustrated if Fig 2. In general, the spatial variation of most of the observed metals in soils demonstrates an inverted-U-shape curve.

IV. SPATIAL DISTRIBUTION

In order to understand the distribution patterns of heavy metals including As, Hg, Co, Cr and Cd, ordinary kriging interpolation was used to obtain filled contour maps (Fig. 3). This show that the spatial variation of heavy metals concentrations generate from their semivariograms. The distribution of As and Hg had a clear boundary in the center of the area. Their spatial distribution maps show similar geographical trends.

V.CONCLUSION

These results present the spatial pattern of As, Hg, Co, Cr and Cd in Kaveh industrial city using multivariate and geostatistical analysis, to attain the industrialization effect on heavy metal pollution in soils. The results of the principal component analysis indicate that Co and Cr were likely affected by pedogenic factors, while, the concentration of As, Hg and Cd were related to the anthropogenic factors (e.g., the discharge of industrial waste such as industrial effluents and wastes and had high risks for environmental pollution and human health.

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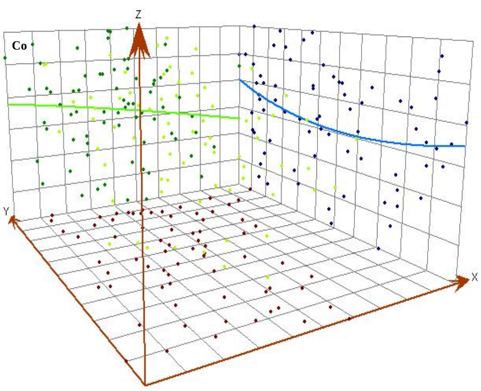
TABLE II TOTAL VARIANCE EXPLAINED AND COMPONENT MATRIXES FOR ELEMENTS

Total variance explain									
Component	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	1.466	29.317	29.317	1.466	29.317	29.317	1.295	25.891	25.891
2	1.067	21.345	50.661	1.067	21.345	50.661	1.064	21.279	47.171
3	.979	19.577	70.238	.979	19.577	70.238	1.003	20.053	67.224
4	.851	17.015	87.253	.851	17.015	87.253	1.001	20.029	87.253
5	.637	12.747	100.000						

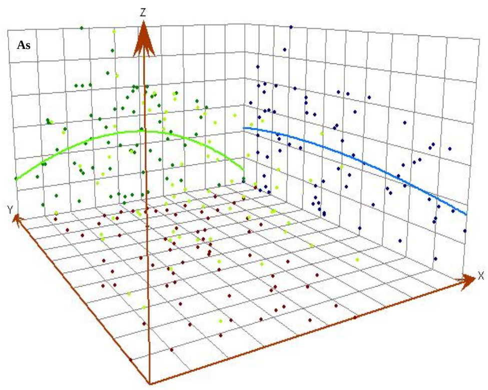
Component matrix								
Element	Component matrix				Rotate component matrix			
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
As	0.57	-0.13	-0.31	0.75	0.11	0.02	0.99	0.010
Hg	0.71	-0.36	0.01	-0.30	0.80	-0.27	0.14	0.001
Co	0.12	0.90	-0.28	0.01	0.01	0.95	0.02	0.005
Cr	0.277	0.25	0.90	0.24	0.05	0.01	0.01	0.998

TABLE III SEMIVARIOGRAMS MODELS AND PARAMETERS OF HEAVY METALS

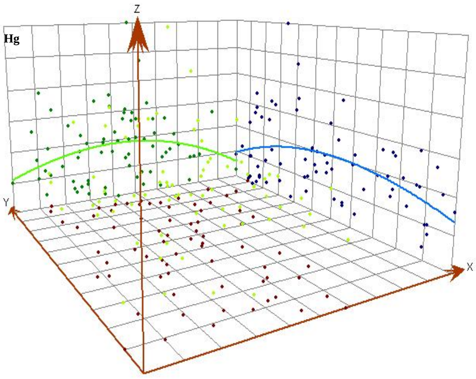
Metal	Semivariogram	Trend	Nugget/Sill	Isotropy/ Anisotropy	MAE	RMSE	RMSSR
As	Exponential	Second	0.28	Anisotropy	0.02967	3.173	0.9916
Hg	Gaussian	Second	0.32	Anisotropy	0.01728	0.3623	1.066
Co	Gaussian	None	0.77	Anisotropy	-0.09147	3.318	0.9849
Cr	Exponential	None	0.82	Isotropic	0.2516	25.13	1.035
Cd	Exponential	Second	0.37	Isotropic	0.003	0.21	1.02



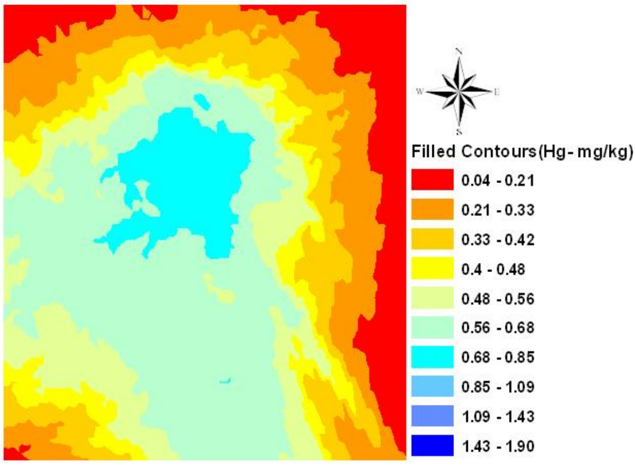
Co

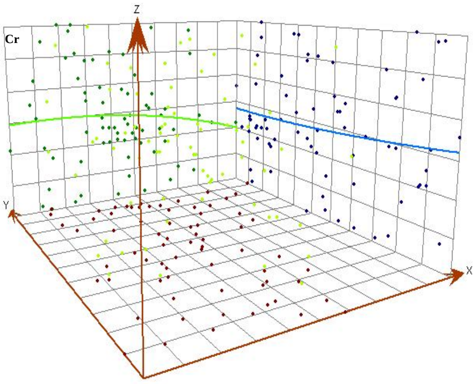


As

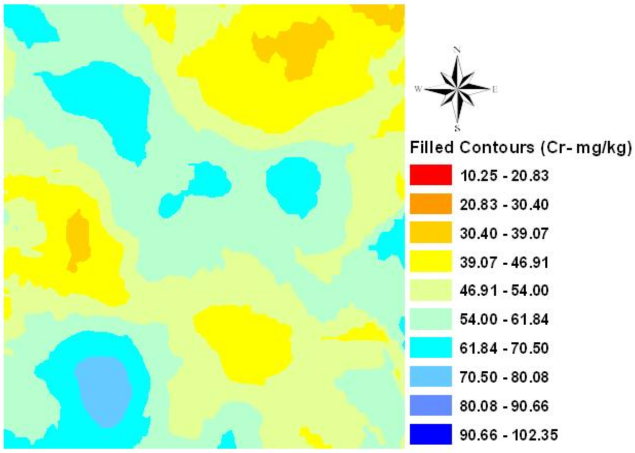


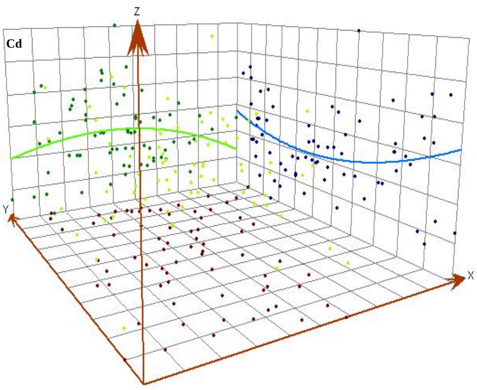
Hg





Cr





Cd

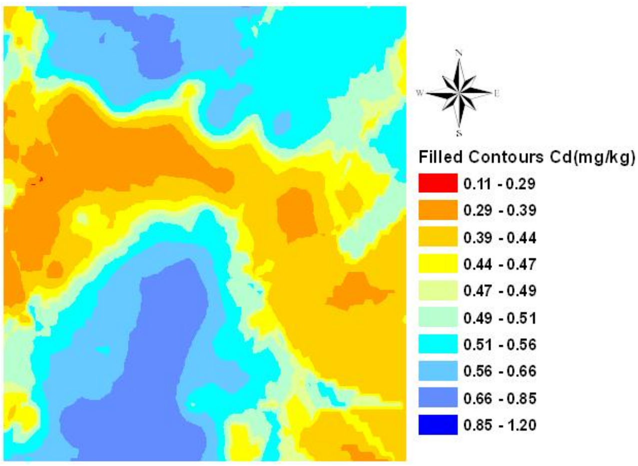
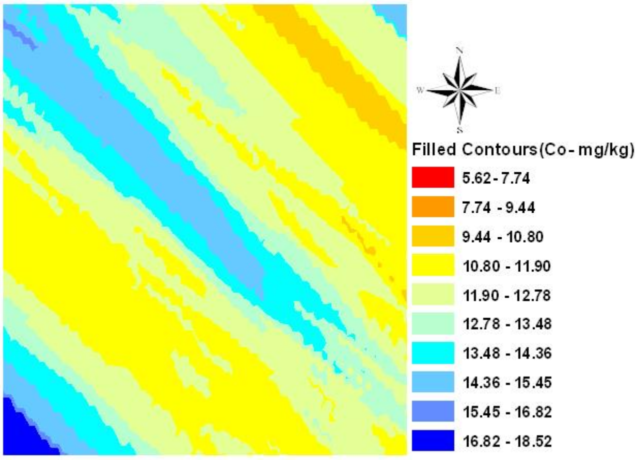


Fig. 2 The spatial variation patterns of Co, As, Hg, Cr and Cd. X axes represent east-west direction; Y axes represent south north direction; Z axes represent metal content



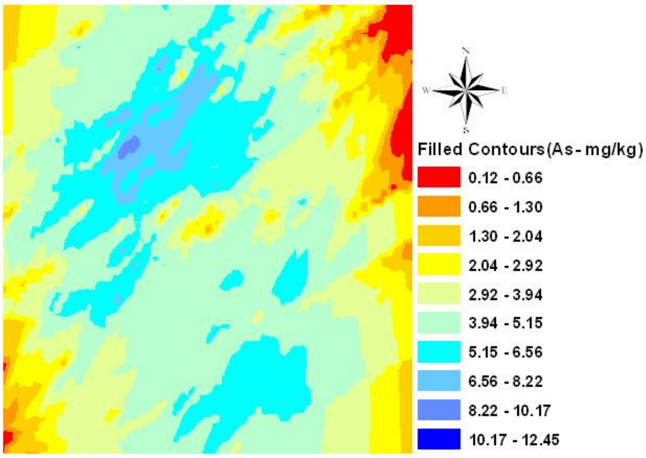


Fig. 3 Filled contours maps of Hg,Cr, Cd. Co and As in soils

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