

Geostatistical assessment of solid–liquid distribution coefficients (K_d) for Cd, Cu, Pb and Zn in surface soils of Hamedan, Iran

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Abstract This study has applied a geostatistical approach to analyzing and interpreting the distribution coefficient (K_d) in soils collected around Hamedan, west of Iran. The samples collected from the agricultural area (about 100 ha) affected by waste water from Shahid Mofatteh power plant. Sorption experiments were carried out using solution of desired concentration of cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) (10 and 100 mg l⁻¹). Desorption experiments with CaCl₂ 0.01 M, were performed immediately following the completion of sorption experiments. Results showed that in all treatments K_{d100} values is lower than K_{d10} values. The range of K_{d10} (l kg⁻¹) were as follows: Cd (253–1656), Cu (545–100000), Pb (1841–100000) and Zn (198–3115). Median K_d values showed the following order of decreasing affinity in both 10 and 100 mg l⁻¹ metal concentrations: Pb > Cu > Zn > Cd. Desorption analysis indicated that only trace amounts of heavy metal adsorbed was released. Irreversibility was highest for Pb and Cu, which the K_d values were greatest. The resulting variograms of log-transformed K_{d10} data for Cu indicated the existence of strong spatial dependence. The variograms for K_{d10} Cd revealed moderate spatial structure and variograms for K_{d10} Pb and Zn show weak spatial dependence. For K_{d100} , the variogram of Cd show weak spatial dependence and variograms of Cu, Pb and Zn indicate moderate spatial structure.

Keywords Distribution coefficient · Geostatistical assessment · Heavy metal

Introduction

In recent years, increasing deposition of heavy metals on land [e.g. in fertilizers, pesticides, manure, sewage sludge or industrial emissions (Sparks 1995)] has given rise to considerable concern about its impact on the environment in general and human health in particular (Qin et al. 2004), particularly as regards groundwater contamination (Alloway 1995).

The sorption of deposited heavy metals by soil particles can minimize their passage into surface and subterranean waters, but at the same time creates the possibility that alteration of soil conditions may result in release of the accumulated load into the soil solution, thereby causing pollution of groundwater and/or contamination of plants (Karathanasis 1999). Thus the fate of heavy metals, and the toxic risk they pose, depend crucially on their sorption–desorption equilibria and dynamics in the soils on which they are deposited, and on how these equilibria change in response to changing environmental conditions. As sorption and its reversibility are the main processes that control the fate of heavy metals, it is necessary to examine both processes with routine laboratory tests, which need to be robust and capable of providing information on heavy metal interaction in soils without the high cost associated with field experiments and soil monitoring campaigns.

The solid–solution distribution or partition coefficient (K_d) expresses the ratio of the concentrations of adsorbate adsorbed by the mass of solids to the concentrations of adsorbate remaining in the equilibrium solution, and plays a key role in many models used to define guideline values

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of these metals in soils and to assess related environmental risks. Distribution coefficient is often used to characterize the mobility of heavy metals in environments (Anderson and Christensen 1988).

The numerical value of K_d is dependent on the specific characteristics of each soil and on the physicochemical characteristics of the sorbents investigated. Adsorbents with high K_d are more strongly adsorbed to soils and are less likely to leach due to lower availability for transport in the soil solution. In contrast, adsorbents with low K_d are only weakly adsorbed to soils and are more likely to leach as they are more water soluble and hence exhibit greater mobility in the soil solution. While it has been recognized that laboratory studies may give different estimates of partitioning in comparison with field conditions (Walker et al. 2001), standard batch sorption procedures are still of value for initial estimations of sorption behaviour, and in some cases have been shown to provide values comparable to field studies (Wauchope et al. 2002). Furthermore, batch studies are simple and easy to carry out and thus provide a useful means of inter-laboratory comparison for quality control purposes (Ronnefahrat et al. 1997).

Geostatistics is extensively used to assess the level of soil pollution and calculate the risk in polluted areas, by preserving the spatial distribution and uncertainty of estimates and facilitates quantification of the spatial pattern and distribution of pollutants and enables spatial interpolation and mapping (Komnitsas and Modis 2006).

In this study we determined the sorption and desorption of cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) by samples of soils collected in Hamedan (west of Iran). For each soil, and for both sorption and desorption, we ordered the metals by the K_d values obtained with 10 and 100 mg l⁻¹ concentration of each metal in single solution. Then geostatistical methods for spatial interpolation were used to assess the heavy metals pollution in unsampled area by creating kriging map showing the K_d of Cd, Cu, Pb and Zn in the study area. Finally, sorption–desorption data were used to assess the risk derived from a contamination event in the soils considered here.

Materials and methods

Studied area and sampling

The research focused on the agricultural area located about 45 km from Hamedan (west of Iran). This area covers about 100 ha. This area is affected by waste water from Shahid Mofatteh power plant. An area of 1000 × 1000 m was marked, and a grid of 100 × 100 m was established within this area. Thus, the site had 100 grid cells, 10 cells in both the *x*- and *y*-directions. The sampling sites were at

the cell centres of the regular 100-m grid. In addition, 18 samples were taken at random in between the grid points. Figure 1 shows locations of the soil sampling sites. At each sampling point, four cores of soil were taken at a depth of 0–30 cm. Then, samples stored in plastic bags prior to chemical analysis. The soil samples were air-dried and passed through a 2-mm sieve for laboratory analyses.

Soil pH (soil:H₂O ratio 1:5) was measured using a pH-meter with a glass electrode. Electrical conductivity (EC; soil:H₂O ratio 1:5) was measured using an EC-meter. Textural fractions (sand, silt, clay) were determined using hydrometer method (Gee and Bauder 1986). Calcium carbonate equivalent was determined by neutralization with HCl (Rowell 1994).

Batch sorption–desorption studies

Sorption experiments were carried out using 50 ml of metal ions (Cd, Cu, Pb and Zn) solution of desired concentration (10 and 100 mg l⁻¹). In each experiment, 2.5 g of soil sample was suspended in 25 ml of sorption solution, and after equilibration by shaking for 24 h at 25 °C in an orbital shaker this suspension was centrifuged at 4000 g for 10 min. Metal concentrations in the supernatants were determined by atomic absorption spectrophotometer and the amount of each metal sorbed by the soil was calculated by difference.

Desorption experiments were performed immediately following the completion of sorption experiments. After removal of the supernatant, 0.01 M CaCl₂ solutions were added to the centrifuge tubes. The centrifuge tubes were vortexed to disperse the absorbent pellets, and the suspensions were shaken for 24 h. The suspensions were then centrifuged for 10 min at 4000 g. The Cd, Cu, Pb and Zn

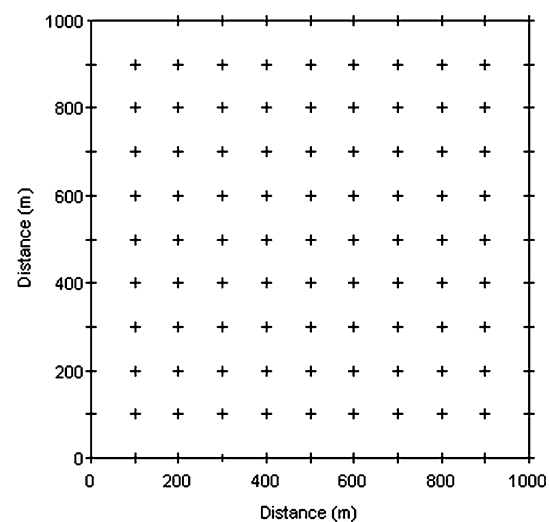


Fig. 1 Scatter diagram of sampled points

Table 1 Summary statistics of soil properties

	N		Mean	SE mean	SD	Variance	Skewness	Kurtosis	Minimum	Maximum
	Valid	Missing								
%										
Clay	113	8	18.00	0.44	4.43	19.74	0.32	-0.98	8.00	28.00
Silt	113	8	15.01	0.62	6.30	39.70	-0.04	0.60	1.50	36.50
Sand	113	8	67.01	0.82	8.24	68.14	0.72	0.004	49.5	82.00
CaCO ₃	120	1	7.64	0.29	3.17	10.05	1.96	6.01	3.00	24.00
pH*	120	1	7.20	0.02	0.18	0.02	-0.002	-0.13	6.80	7.60
dS m ⁻¹										
EC*	120	1	1.51	0.07	0.81	0.66	1.62	1.91	0.59	4.11

* Measured in L/S = 5

concentrations in the supernatant solutions were measured after desorption process and the quantities of metals retained by each soil were calculated by difference with respect to the amounts sorbed in the sorption stage.

The distribution of each metal *i* between soil and solution was calculated with the equation:

$$K_{d_i} = \frac{C_{i,soil}}{C_{i,solu}} \tag{1}$$

where $C_{i,soil}$ is the concentration of metal *i* on the soil (mg kg⁻¹) and $C_{i,solu}$ is the concentration of metal *i* in solution (mg l⁻¹) (Covelo et al. 2007).

Geostatistical methods

Geostatistics uses the technique of variography, i.e., calculating variogram or semi-variogram, to measure the spatial variability and dependency of a regionalized variable. Variography provides the input parameters for the spatial interpolation of kriging. The variogram function is expressed as:

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(x_i) - Z(x_i + h)]^2 \tag{2}$$

where $\gamma(h)$ is the semivariance (variogram), $Z(x_i)$ is the value of the variable *Z* at location of x_i , and $N(h)$ is the number of pairs of sample points separated by the lag distance of *h*.

In order to evaluate the possible anisotropic spatial variability, surface variogram was calculated in accordance with the symmetrical property of variogram function for all variables (Pannatier 1996). Variogram plots (experimental variograms) were acquired by calculating variogram at different lags. Spherical, exponential and Gaussian models were selected in order to model experimental variograms and acquire information about the spatial structure as well as the input parameters for kriging estimation. Information

generated through variography step was used to calculate sample weighting factors for spatial interpolation by an ordinary block kriging procedure.

Result and discussion

Sorption and desorption of Cd, Cu, Pb and Zn

Summary statistics of selected chemical and physical properties of the soil from the field studied are given in Table 1. The soil is neutral to slightly alkaline and has a high EC. The equivalent calcium carbonate contents varied from 3.0 to 24.0 %. The average clay content is 18 %.

Relation between heavy metals K_d and soil properties was analyzed (Table 2). Close correlation existed between some soil properties and the K_d . The negative correlations were observed between K_d and sand content. Significant positive correlations were also found between the K_d and clay content.

The dependence of K_d and CaCO₃ content was observed in Table 2. According to negative correlation, the K_d value decreased with increasing CaCO₃ content. Maybe it was due to competitive adsorption between heavy metals and Ca (Bowman et al. 1981; O'Connor et al. 1983). There may also be some effect of ionic strength on exchange selectivities. It is not possible to explain the different sensitivities of the soils to salt concentration, but they must arise from the initial soluble salt concentration and composition and the nature of the exchange phase.

Table 3 show the value of K_d measured for studied soils. Median K_d values showed the following order of decreasing affinity in both 10 and 100 mg l⁻¹ metal concentrations: Pb > Cu > Zn > Cd.

Gomes et al. (2001) and Fontes and Gomes (2003) observed that Cu and Pb were more strongly adsorbed than Cd and Zn in Brazilian soils. In Spanish soils, Vega et al.

Table 2 The correlation coefficients between heavy metals K_d and some soil properties

	%				pH	dS m ⁻¹ EC
	Clay	Silt	Sand	CaCO ₃		
K_{d10} Cd	0.351*	0.185	-0.121	-0.113**	0.073	-0.291**
K_{d10} Cu	0.452**	-0.071	-0.351	-0.145	0.054	0.133
K_{d10} Pb	0.231*	-0.142	0.314	-0.181*	0.118	-0.273
K_{d10} Zn	0.197	-0.053	-0.263	-0.086	0.284	-0.077
K_{d100} Cd	0.210*	-0.061	-0.068	0.078	0.104	0.093
K_{d100} Cu	0.361	0.190	-0.093	0.089	-0.083	-0.160
K_{d100} Pb	0.322**	-0.030	0.261	-0.189	0.090	-0.033
K_{d100} Zn	0.160*	0.253*	-0.280**	-0.493*	-0.181	-0.230*

* ** Significant at $p < 0.05$ and $p < 0.01$, respectively

Table 3 Summary statistics of K_d (1 kg⁻¹) in adsorption experiment of metals

	N		Mean	SE mean	Median	SD	Variance	Skewness	Kurtosis	Minimum	Maximum
	Valid	Missing									
K_{d10}											
Cd: adsorb	118	3	549.17	20.551	203.16	223.24	49840	2.49	9.40	253.16	1656.67
Cu: adsorb	118	3	28829	3304.8	9080.9	35899	1.289E9	1.27	-0.028	545.56	1.00E5
Pb: adsorb	118	3	37691	3000.5	33323	32593	1.062E9	1.01	-0.25	1841.85	1.00E5
Zn: adsorb	118	3	906.01	42.90	796.45	465.68	216900	2.81	9.28	198.77	3115.00
K_{d100}											
Cd: adsorb	118	3	244.05	16.23	180.32	176.26	31072.10	2.205	4.851	94.34	886.86
Cu: adsorb	118	3	1474.78	74.80	1234.43	812.68	660472.74	1.384	2.425	357	4951.49
Pb: adsorb	118	3	2853.44	205.54	1941.75	2232.8	4985677.6	1.539	1.562	87.66	9793.92
Zn: adsorb	118	3	340.91	13.73	280	149.13	22244.15	1.278	1.011	188.16	866.72

(2006) studied the adsorption and desorption of Cd, Cr, Cu, Ni, Pb and Zn and concluded that Pb, Cu and Cr had the greatest affinity in both cases. The selectivity sequences based on the K_d were in line with the values of the first hydrolysis constant of the elements. Low value of K_d for Cd and Zn indicate that most of the metals present in the system remain in the solution and are available for transport, chemical processes and plant uptake; on the other hand, large value of K_d for Pb and Cu reflect a large affinity of solid soil components for the metals.

In all treatments K_{d100} values is lower than K_{d10} values (Table 3). The range of K_{d10} (1 kg⁻¹) were as follows: Cd (253–1656), Cu (545–100000), Pb (1841–100000) and Zn (198–3115).

The K_d quantification was extremely dependent on the initial metal concentration, with decreases of various orders of magnitude in the K_d values, especially for Pb and Zn, when the initial metal concentration was increased (Mesquita and Vieira e Silva 1996). This indicates that heavy metal sorption at low metal load is controlled by high selectivity sorption sites, in which adsorption is the main process governing sorption, and that when the metal load increases sorption sites become saturated and metal

sorption takes place in low selectivity cation exchange sites. For high initial metal concentrations, accumulation in the solid phases by precipitation should not be disregarded either, especially for metals with low solubility, such as Cu (Sastre et al. 2002).

Extraction of adsorbed heavy metals with CaCl₂ allowed consideration of the reversibility of heavy metal soil adsorption. Analysis indicated that only trace amounts (0.01–1.9 %) of heavy metal adsorbed was released by the 0.01 M CaCl₂ solution, reflecting the highly irreversible nature of heavy metal adsorption to soils, in agreement with the high soil K_d estimated in the batch experiments (Table 3). Irreversibility was highest for Pb and Cu, which the K_d values were greatest, demonstrating the strong nature of the chemical binding.

Descriptive statistics

According to statistical summary of the K_d for heavy metals is given in Table 3, almost the medians of all treatments were much lower than means, which is consistent with the high skewness, showing there were some very high values. Also Figs. 2 and 3 revealed that K_d data was

Fig. 2 Histograms of the K_{d10} and the log-transformed K_{d10} values of Zn (**a-a***), Pb (**b-b***), Cu (**c-c***) and Cd (**d-d***)

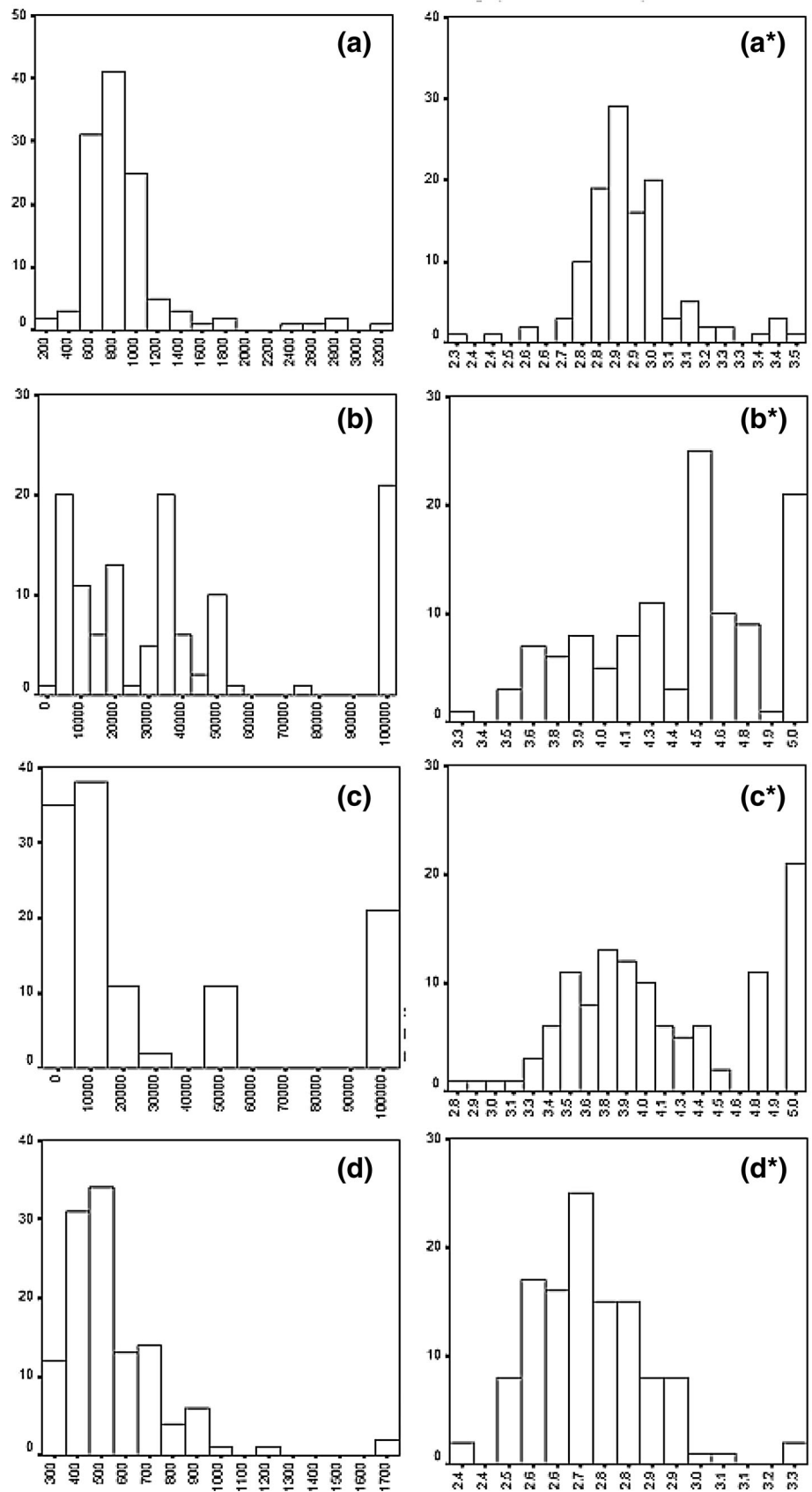


Fig. 3 Histograms of the K_{d100} and the log-transformed K_{d100} values of Zn (**a–a***), Pb (**b–b***), Cu (**c–c***) and Cd (**d–d***)

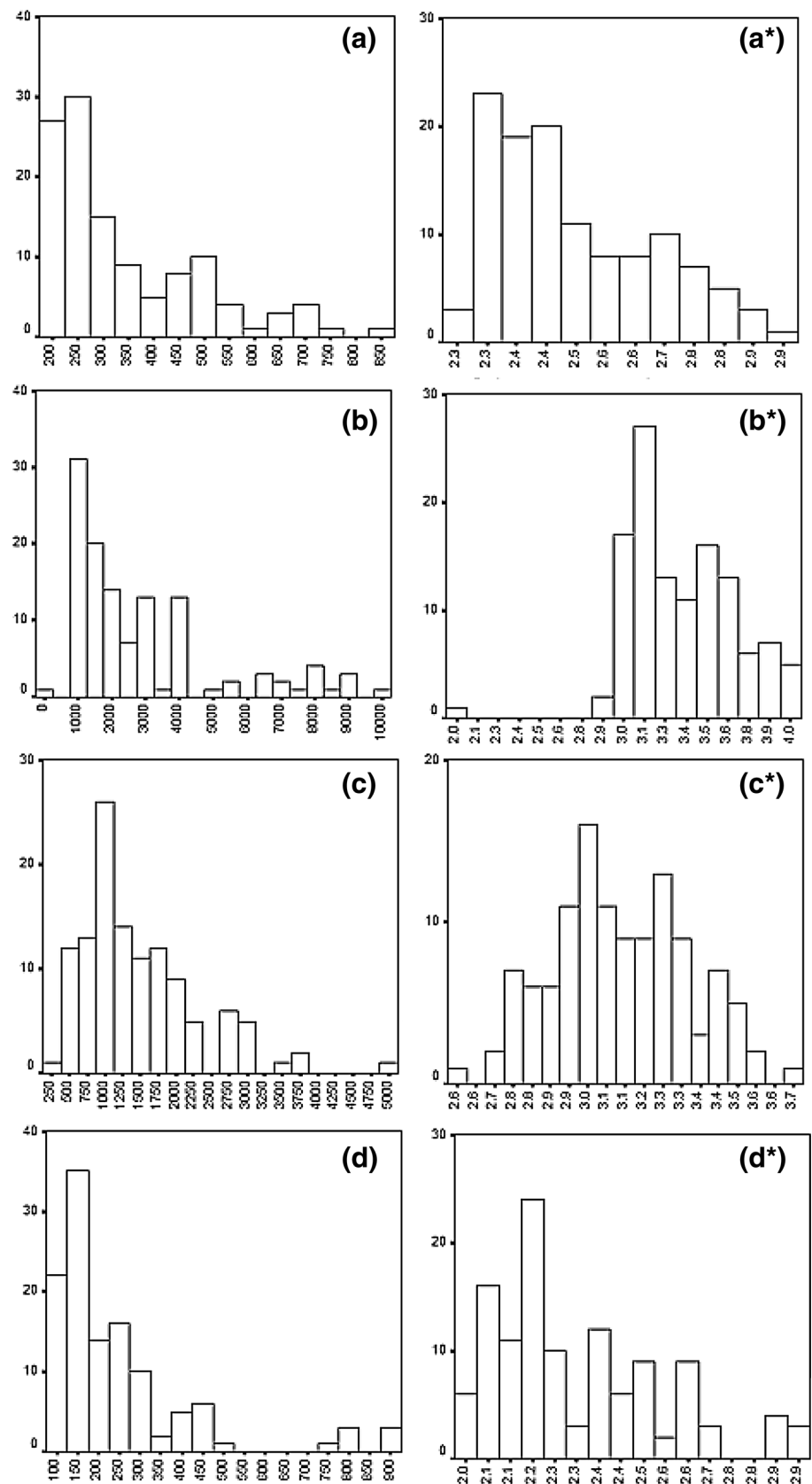


Table 4 Parameters of isotropic variogram models (K_{d10} and K_{d100})

Variable	Best-fitting model	Nugget (C_0)	Sill ($C_0 + C$)	Range (A_0)	$C:(C + C_0)$ Ratio (%)	r^2	RSS
K_{d10}							
Cd: adsorb	Exponential	0.05990	0.14250	465.0000	58.0	0.848	5.033E-4
Cu: adsorb	Linear	1.5787	1.5787	1034.2087	0.00	0.293	0.0550
Pb: adsorb	Gaussian	0.6630	3.4360	1560.0000	80.7	0.981	0.0208
Zn: adsorb	Gaussian	0.08700	1.22400	2301.0000	92.9	0.980	9.230E-4
K_{d100}							
Cd: adsorb	Exponential	0.12900	0.98100	2460.0000	86.9	0.970	2.051E-3
Cu: adsorb	Gaussian	528000.0	1464200.0	1578.0000	63.9	0.915	1.053E10
Pb: adsorb	Spherical	0.24600	0.75300	1381.0000	67.3	0.982	2.994E-3
Zn: adsorb	Gaussian	0.13590	0.38480	2171.0000	64.7	0.323	2.286E-3

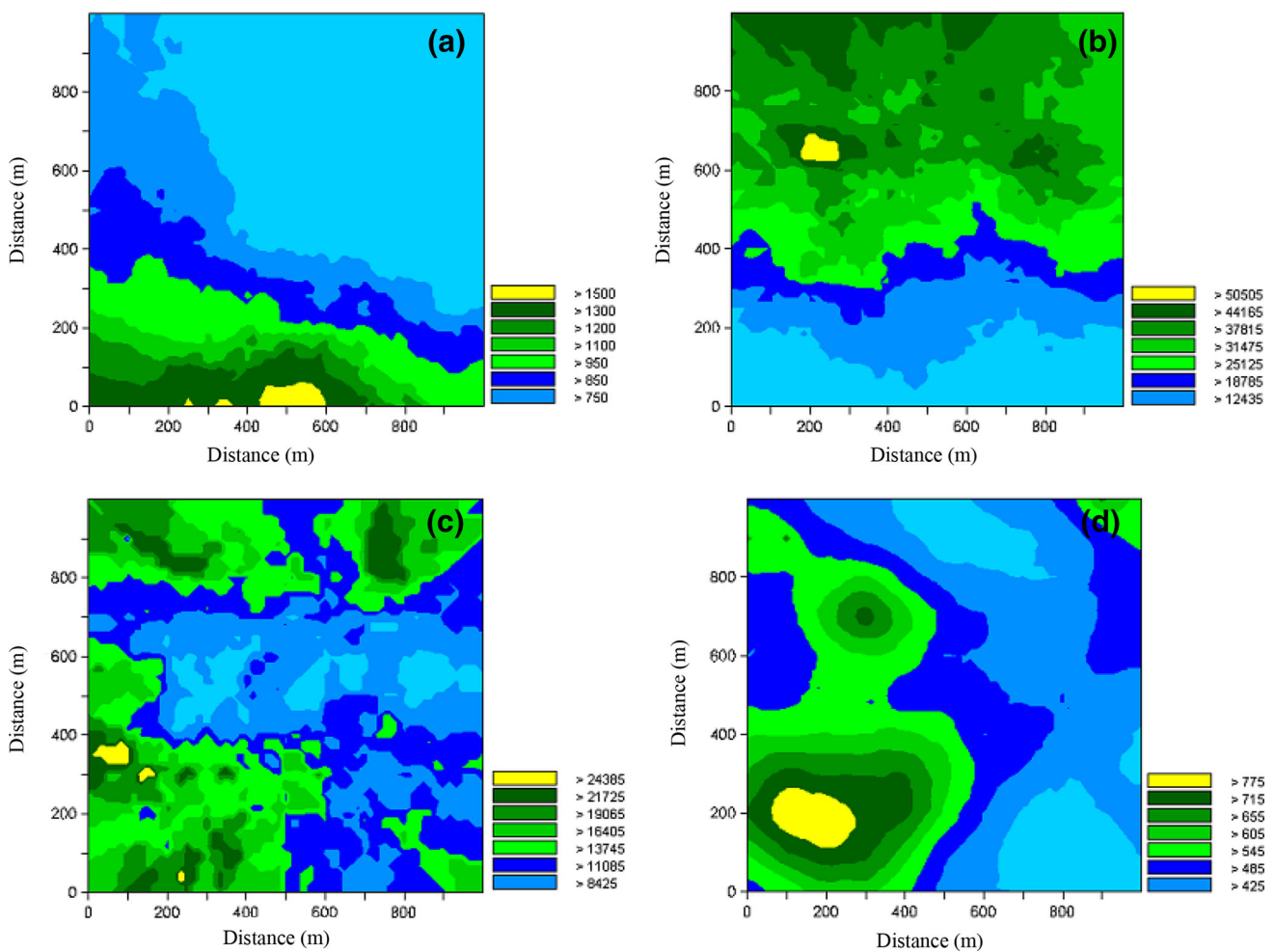


Fig. 4 Kriged maps of the K_{d10} values of Zn (a), Pb (b), Cu (c) and Cd (d)

highly skewed. A distribution is considered highly positively skewed when the coefficient of skewness is much higher than 1 (Webster and Oliver 2001). A Kolmogorov–Smirnov test was computed and indicated that all K_d data

were significantly lognormal ($p < 0.001$). As in conventional statistics, a normal distribution for a variable under study is desirable in linear geostatistics (McGrath et al. 2004). Serious violation of normality, such as too high

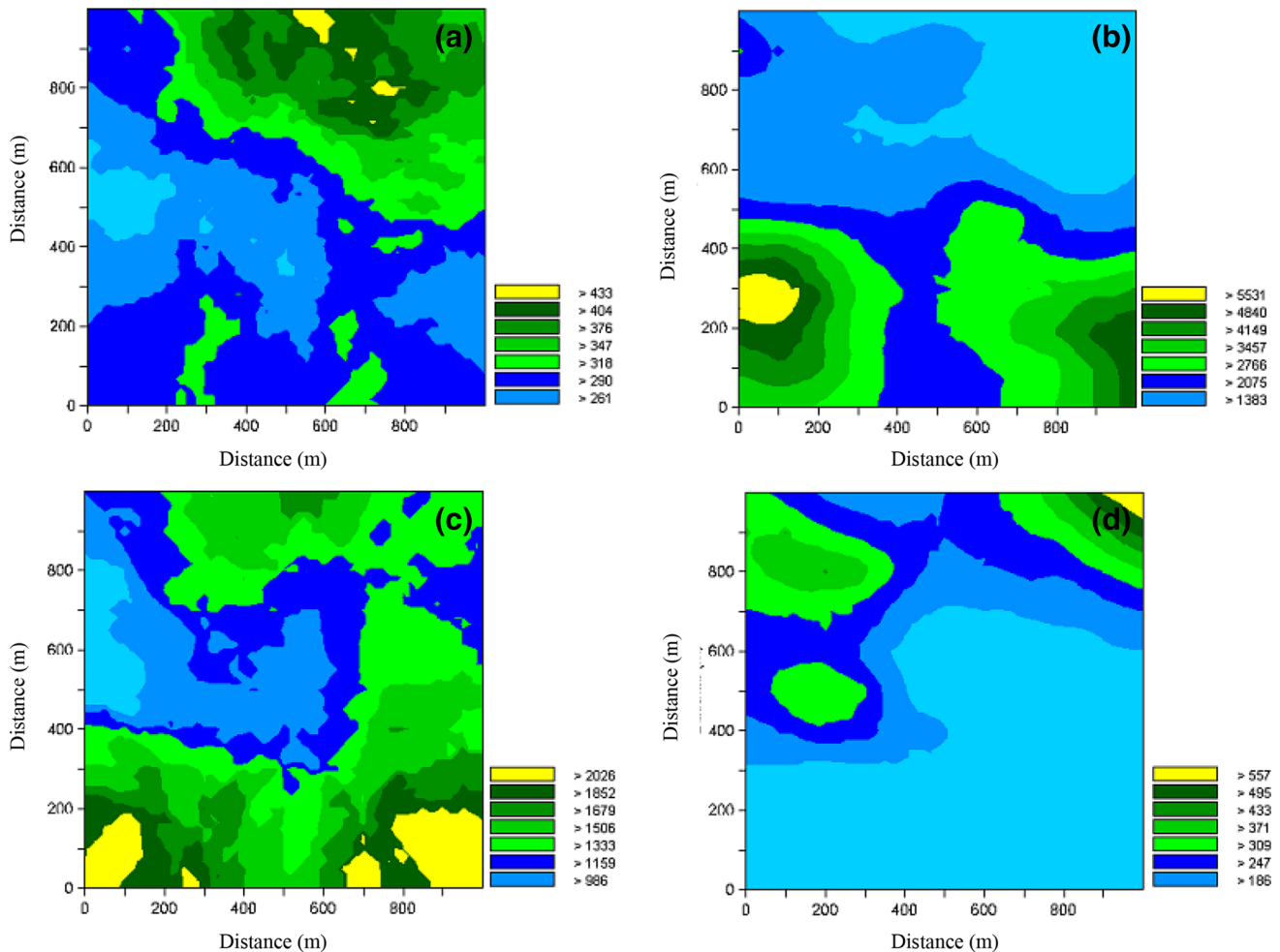


Fig. 5 Kriged maps of the K_{d100} values of Zn (a), Pb (b), Cu (c) and Cd (d)

skewness, can impair the variogram structure and the kriging results. It is often observed that environmental variables are lognormal or positively skewed, and data transformation is necessary to normalize such data sets. Taking logarithms of the K_d data removed most of the skewness (Figs. 2, 3).

Geostatistical analysis

Experimental variograms were computed on the log-transformed data. The directional variograms suggest a fairly isotropic spatial distribution of the log-adsorption heavy metals values, so that the omnidirectional variograms with the fitted models were considered. Linear, Gaussian, spherical and exponential functions were fitted to the experimental variograms.

The selection of appropriate model was based on qualitative interpretation of which model best represented the overall behavior of the experimental variogram. The numerical results are given in Table 4. To define the degree

of spatial dependency, spatial class ratios similar to those presented by Cambardella et al. (1994) were adopted. That is the ratio of nugget variance (noise) to total variance (sill) multiplied by 100. If the ratio of spatial class was $< 25\%$ then the variable would be considered to be strongly spatially dependent; if the ratio was between 25 and 75 %, the variable was regarded as moderately spatially dependent; and if the ratio was more than 75 %, the variable was considered weakly spatially dependent.

The resulting variograms of log-transformed K_{d10} data for Cu indicated the existence of strong spatial dependence. The variograms for K_{d10} Cd revealed moderate spatial structure and variograms for K_{d10} Pb and Zn show weak spatial dependence. For K_{d100} , the variogram of Cd show weak spatial dependence and variograms of Cu, Pb and Zn indicate moderate spatial structure.

For mapping the K_d data, ordinary kriging system was used along with isotropic variograms to estimate K_d values at unobserved locations. For all treatments, log-transformed data used for kriging interpolation and then the

estimated kriged values were back-transformed. Optimal kriging parameters were found based on the results from the cross validation procedure.

Figures 4 and 5, respectively, presents the spatial patterns of the K_{d10} and K_{d100} of heavy metals adsorption values generated from their variograms and corresponding kriging systems. The kriged maps show the spatial variation of soil K_d for heavy metal adsorption estimates.

Conclusion

Laboratory measurements of Cd, Cu, Pb and Zn K_d values for 109 soil samples revealed a large range of values: from a few to several thousand l kg^{-1} . The soil distribution coefficient of Cd, Cu, Pb and Zn was found to be related to the some soil properties. The negative correlations were observed between K_d and sand content, also negative correlation were between K_d and CaCO_3 content. Significant positive correlations were found between the K_d and clay content.

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