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RESEARCH ARTICLE

Spatial distribution of soil heavy metals in the Zaida mine (Morocco) based on Geostatistical Methods

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Abstract

Geostatistical methods were applied to investigate spatial distribution of heavy metals in the soils around the Zaida mining district in Morocco. Soil samples from 51 locations were collected at various distances and directions from tailings. Concentrations of seven heavy metals (Co, Cr, Cu, Cd, Ni, Zn and Pb) were measured using Inductive Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES). Results show that heavy metal contents in investigated soils are significantly higher than those in uncontaminated soils reported by many other authors. The average abundance order of heavy metal levels are Pb>Zn>Cr>Cu>Ni>Co>Cd. Kriged maps of all studied heavy metals showed a strong gradient of contamination around mine tailings. The degree of contamination decreases when the distance from the tailings pounds increases. In addition, soils located in the prevailing wind directions from the mine tailings were enriched in heavy metals. In conclusion, the tailings of Zaida can be considered as a potential source of contamination with heavy metals for surrounding soils, mainly attributed to dispersion tailings particles under wind action.

INTRODUCTION

In recent decades, problems associated with increasing levels of heavy metals and their persistence in the environment have attracted the attention of researchers **(Parizanganeh et *al.*, 2012; Soffianian et *al.*, 2014)**. Although low content of these metals are naturally found in soils and stones, human activities have elevated their release and propagation in the environment **(Conesa et *al.*, 2006)**. Mining and associated activities are the primary source of heavy metals and can be responsible for significant negative impacts on the surrounding environments **(Navas and Machin, 2002; Ferreira da Silva et *al.*, 2004; Ungaro et *al.*, 2008; Chaoyang et *al.*, 2009; Dayani and Mohammadi, 2010),** both during the mining operations and for years after mine closure **(Mileusnic et *al.*, 2014)**. The negative impact of these mining activities is mainly due to the presence of high volumes of tailings **(Dudka and Adriano, 1997)**, which are often left without proper management **(Muhammad et *al.*, 2011).** Thus, tailings and wastes are dispersed by wind and erosion on soils, plants and water in the vicinity of the mining site (**Meza-Figueroa et *al.*, 2009; Martínez-Martinez et *al.*, 2010; Babbou-Abdelmalek et *al.*, 2011; Amune et *al.*, 2012; Su et *al.*, 2014**). This dispersion is highly dependent on the local meteorological conditions, mainly on the prevailing wind direction **(Kribek et *al.*, 2010; Sharma and Siddiqui, 2010; Ettler et *al.*, 2011).** The metal contamination can extend several kilometers away from the mine sites **(Escarre et *al.*, 2011)**.

The basin of the Moulouya River is a region where mining industry has been developed early in the 20th century. Consequently, residues generated from past mining activities over the years have been dumped as piles of tailings. Zaida is one of the most affected region in this basin because of lead mine exploitation for long time. While the potential environmental risks posed by these tailing have been previously documented (**Saidi et *al.* 2002; Bouabdli et *al.* 2004, 2005; El Hachimi et *al.* 2005, 2006, 2007; Baghdad et *al.* 2006, 2009; El Himer et *al.*, 2012**).The spatial distribution of soil heavy metals contamination and the effects of aeolian processes on the soil enrichment by trace metals have been less well studied.

Study of spatial distribution to recognize the extremely contaminated areas and determine the potential of contamination source is very important (**Mahmoudabadi et *al.*, 2012)**. Previous researches has shown that geostatistics can be successfully applied in studying and mapping the distribution of heavy metals in soil (**Simasuwannarong et *al.*, 2012; Sollitto et *al.*, 2010; Xie et *al.*, 2011; Hani and Pazira, 2011; Karanlık et *al.*, 2011; Marchant et *al.*, 2011; Hofer et *al.*, 2012).** Geostatistics is able to prepare the data processing and their spatial description. In addition, geostatistical methods can describe and feature the pattern of spatial data and provide an estimate and quantitative map of the distribution of pollution with a minimum variance **(McGrath et *al.* 2004; Carlon et *al.*, 2001; Komnitsas and Modis, 2006). Dayani and Mohammadi (2010)** highlighted the usefulness of applying geostatistics to address spatial patterns of soil heavy metals at mining sites.

Several geostatistical methods have been used to estimate the spatial distribution of a variable **(Gunal et *al.*, 2012; Mahmoudabadi et *al.*, 2012)**. Kriging is the most popular estimation method used **(Liu et *al.* 2007; Gunal et *al.*, 2012).** This is a technique of making optimal, unbiased estimates of regionalized variables at unsampled locations using the structural properties of the semi-variogram and the initial set of data values **(David, 1977; Simasuwannarong et *al.*, 2012)**. Kriging provides estimation variance at every estimated point, which is an indicator of the accuracy of the estimated value. This is considered as the major advantage of kriging over other estimation techniques **(Gandhimathi and Meenambal, 2011).**

The objective of the present study is to characterizethe spatial distribution of heavy metals (Cd, Co, Cr, Cu, Ni, Zn, and Pb) in soils in the vicinity of the abandoned mine of Zaida. Geostatistical approach was used to identify their spatial patterns by creating kriging maps.

Material and methods

Description of the studied area

The mining area of Zaida was the largest Pb-mines in Morocco. It is located at about 30 Km North East of Midelt in Upper Moulouya (Morocco), with a total area of 300 km^2 (Figure 1). This area is affected by Pb mining activities, which commenced in 1972 and continued until 1985, due to large amounts of mine wastes that were abandoned without implementing any protection system. Zaida has an arid climate, characterized by hot summers, and generally cold, vigorous and long winters. Annual precipitation is about 300 mm. The temperature ranged from – 6 to 36°C. The dominant wind comes from the North-East and the South-West. The dominant soil types are mineral soil regosoil and calcisoil (**Baghdad, 2008)**. The geology of the mine is mainly hornblende granite and Chunyang granite.

Soil sampling and analyses

Surface soil (0 - 20 cm in depth) samples were collected randomly around the mining district. A total of 51 soil samples representing all directions were collected and located by means of a GPS (figure 1). Soils were air-dried and ground through 2 mm sieve for analyses. Samples were then digested by concentrated acid solutions (1 ml nitric acid 70% + 10 ml fluorhydric acid) at about 120°C. After drying, perchloric acid was added (5 ml for plant tissues and 10 ml for soil) and evaporated at 160°C. After drying, minerals were dissolved in nitric acid 70% (1 ml) and hydrochloric acid 38% (3 ml). Solutions were filtered and volume was completed with deionised water (H_2O MQ). In order to determine total heavy metal content, solutions were analyzed by inductively coupled plasma–atomic emission spectrometry (ICP–AES), in the laboratory of the National Centre for Scientific and Technical Research (Rabat, Morocco). Each sample was analysed in triplicates.

Exploratory analysis and data transformation

Descriptive statistics including maximum, minimum, mean, median, standard deviation (SD), variation coefficient (CV), skewness and kurtosis were carried out for the seven studied heavy metals. Skewness and kurtosis characterize the degree of symmetry of a distribution around its mean and give information about the normality of a variable **(Cisar and Cisar, 2010; Webster, 2001).** Geostatistical methods are optimal when data are normally distributed **(Clark and Harper, 2000).** However, **Reimann and Filzmoser (2000)** showed that geochemical data never follow normal distribution. Prior to geostatistical analyses, data transformation is necessary to make it more normal and less asymmetric **(McGrath et *al.*, 2004)**. The log-transformation is widely applied to approach symmetry **(Webster and Olivier, 2001; Skrbic and Durisic-Mladenovic, 2010)**. In the case of environmental data analyses, **Templ et *al.* (2008)** and **Zhang and McGrath (2004)** showed that the Box-Cox transformation **(Box and Cox, 1964)** is more suitable because the data sets in environmental sciences do not always follow the lognormal distribution **(Zhang and Zhang, 1996; Zhang and Selinus, 1998).** In the present study, the Box-Cox transformation was used to normalize data sets.

The Box-Cox transformation is given by:

$$y = \begin{cases} \frac{x^{\lambda} - 1}{\lambda} \lambda \neq 0 \\ \ln(x)\, \lambda = 0 \end{cases}$$

where y is the transformed value and x is the value to be transformed. For a given data set ($x_1,x_2,...,x_n$), the parameter λ is estimated based on the assumption that the transformed values ($y_1,y_2,...,y_n$) are normally distributed. When λ=0, the transformation becomes the logarithmic transformation **(McGrath et *al.*, 2004)**.

Geostatistical analysis

The main application of geostatistics to soil science is to estimate and map soil attributes at unsampled areas (**Goovaerts, 1999; Liu et *al.*, 2007**). In the present study, ordinary kriging was used to assess the spatial distribution of seven heavy metals. This method uses the semi-variogram to quantify the spatial variation of a regionalized variable **(Huo et *al.*, 2012**). For discrete sampling sites, such as soil samples, the semi-variogram function is expressed as (**McGrath et *al.*, 2004):**

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

where γ (h) is the semi-variance (variogram), Z (xi) is the value of the variable Z at location xi, and N(h) is the number of pairs of sample points separated by the lag distance h.

A variogram plot is obtained by calculating values of the variogram at different lag distances (**Webster and Oliver, 2001)**. For the sake of kriging, the empirical semi-variogram has to be replaced with an acceptable semi-variogram model **(Bohling, 2005)**. Several theoretical models are used to fit the experimental semi-variogram, such as spherical, exponential, Gaussian, linear and power models. Based on the fitted semi-variogram models, which provides information about the spatial structure (**Fu et *al.*, 2013),** the ordinary kriging was used to map the spatial distribution of studied heavy metals.

Data treatment with computer software

The descriptive parameters were calculated with the SPSS software. Box–Cox transformation was performed by the SAS software. The kriging interpolation and maps were produced using the Geostatistical Analyst extension of the ArcGIS software.

Results and discussion

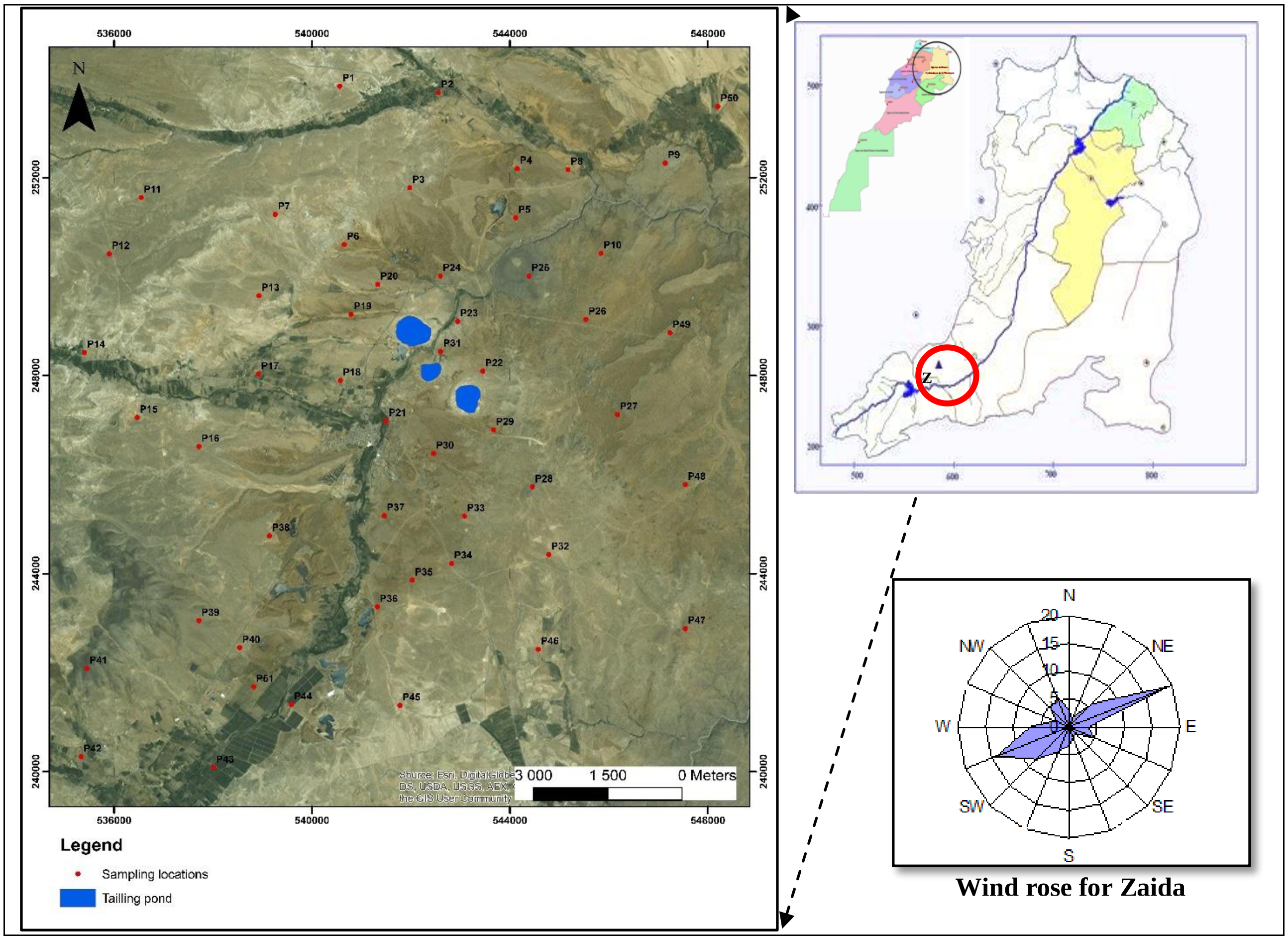


Figure 1. Location of the study area and sampling points around tailings in the Zaida mine.

Basic statistics of heavy metal contents in soils

Table 1 summarizes descriptive statistics, including mean, maximum, minimum, median, standard deviation (SD), skewness and kurtosisof the seven heavy metals investigated in 51 soil samples collected in the vicinity of the abandoned mine of Zaida. The results were compared with some reference values and concentrations observed in earlier works conducted in this area (table 2). The mean concentrations of Cd, Co, Cr, Cu, Ni, Zn, and Pb were 0.99, 5.42, 36.38, 15.31, 13.12, 48.50 and 94.49 mg/kg, respectively. Approximately 57.5 % of the samples for Cd, 58.8 % for Cu, 49 % for Zn, and 47 % for Pb exceeded WHO standards. For Co and Ni, 41.4 % and 33.3 % of samples exceeded the limits in the ordinary soils, respectively **(Baize, 1997).** The concentration of the studied metals are in the order of Pb>Zn>Cr>Cu>Ni>Co>Cd. The comparison of results issued from the present study and other previous works revealed that the heavy metal contents observed varied greatly. This may be attributed to the number of studied soil samples, the sample collection and preparation techniques and methods of heavy metal analysis.

Table 1. Summary statistics of heavy metal contents in soils at the Zaida mine.

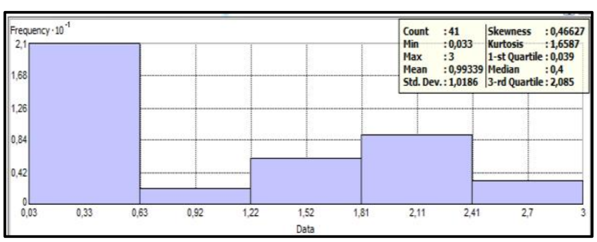
Variable	Mean	Min	Max	Median	SD	Raw Data		Box-Cox	
						Skewness	Kurtosis	Skewness	Kurtosis
Cd	0.99	0.03	3.00	0.4	1.01	0.47	1.66	-0.14	1.21
Co	5.97	0.72	20.40	1.27	6.54	0.80	2.13	0.24	1.25
Cr	36.38	0.01	190.0	26.3	43.77	1.69	6.11	-0.23	1.48
Cu	14.93	0.11	77.2	8.98	20.04	1.65	4.69	-0.29	1.53
Ni	12.87	0.03	48.90	7.47	14.73	0.97	2.83	-0.09	1.41
Zn	47.60	0.13	206.00	49.97	45.76	1.46	5.94	-0.53	1.86
Pb	89.81	0.36	830.95	17.82	162.87	2.82	11.30	-0.30	2.48

Table 2. Comparison of heavy metal contents with some background values (mg/kg).

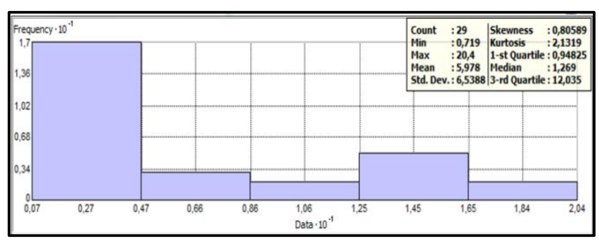
Variable	Reference values				Present study	Previous studies	
	1	2	3	4		Saidi (2004)	Baghdad (2008)
Cd	0.05-0.45	-	0.3	-	0.03 - 3	0.2 - 2	0.05 - 0.4
Co	2-23	6.9	19	8	0.72 - 20.4		6 - 16.9
Cr	10-90	-			0.01 - 190	-	37.3 - 100.2
Cu	2-20	14	4	30	0.11 – 77.2	38 - 56	11.4 - 53.2
Ni	2-60	18	68	40	0.03 – 48.9		14.1 - 34.5
Zn	10-100	62	50	-	0.13 - 206	113 - 236	34.7 - 84.6
Pb	9-50	25	0.2 - 2	10	0.36 – 830.9	51 - 3061	3 - 63.2

[1] Ordinary soils (Baize, 1997)
[2] Worldwide data (Kabata-Pendias and Pendias, 1999)
[3] WHO (cited by Parizanganeh et *al.*, 2012)
[4] United States Environmental Protection Agency (cited by Parizanganeh et *al.*, 2012)

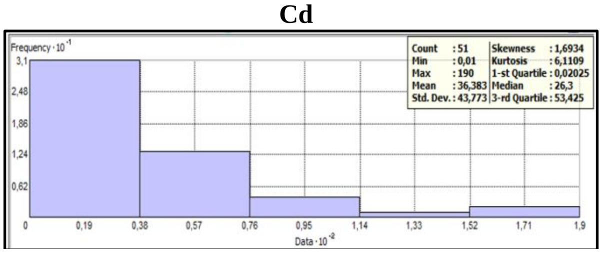
The investigation of histograms of soil heavy metal contents (figure 2) and coefficients of skewness (table 1) revealed that all variables were characterized by large variability, with positively skewed frequency distributions. This is common for heavy metals because they usually have low concentrations in the environment, so that the presence of a point source of contamination may cause a sharp increase of local concentration, so exceeding the thresholds **(Zovko and Romic, 2011)**.



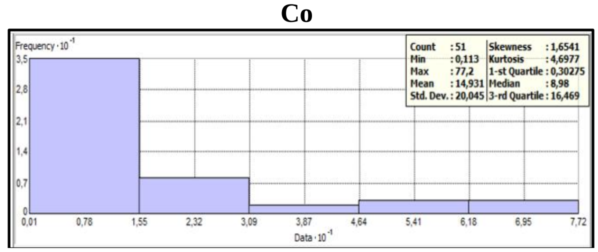
Cd



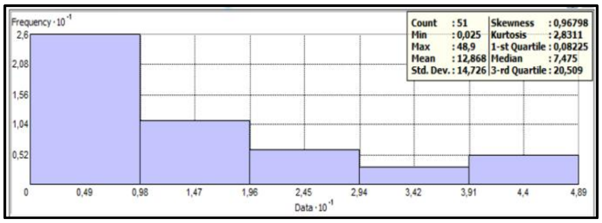
Co



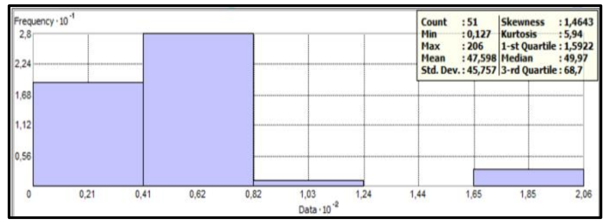
Cr



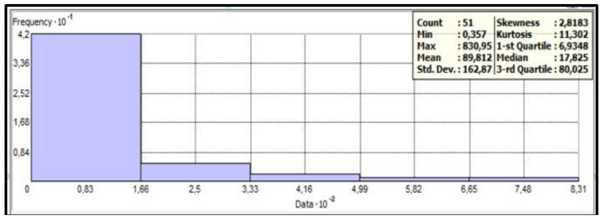
Cu



Ni



Zn



Pb

Figure 2.Histograms of the original concentration values of heavy metals (Cd, Co, Cr, Cu, Ni, Zn, and Pb).

Analysis of spatial structure of heavy metals

Semi-variograms were used to establish the degree of spatial continuity and the range of spatial dependence **(Yang et *al.*, 2009)**. Table 3 summarizes parameters of the fitted semi-variogram models of heavy metals. The nugget represents the undetectable experimental error and field variation within the minimum sampling spacing **(Guoet*al.*, 2001),** whereas the partial sill represents the spatial variation **(Martin et *al.*, 2009)**. The range of influence is the maximum separation distance betweendata pairs with spatial autocorrelation **(Li et *al*., 2007).** The nugget/total sill ratios were used to classify the degree of spatial dependency of soil heavy metal contents **(Robertson et *al.*, 1997; Sun et *al.*, 2003; Wang et *al.*, 2003).** In the present work, spatial classes developed by **Cambardella et *al.* (1994)** were adopted. The variable is considered to have a strong spatial dependence if the ratio is less than 25%, amoderate spatial dependence if the ratio is between 25% and 75%, and a weak spatial dependence if the ratio was higher than 75%, or the slope of the semi-variogram was 0 (pure nugget) **(Ozgoz et *al.*, 2012; Sun et *al.*, 2003)**. Many authors concluded that the spatial variability of soil heavy metal contents may be affected by intrinsic (soil parent materials) and extrinsic factors that can be attributed to human activities **(Facchinelli et *al.*, 2001; Huang et *al.*, 2007; Zhao et *al.*, 2015).** Usually, strong spatial dependence of soil properties can be attributed to intrinsic properties, and weak spatial dependence can be attributed to extrinsic aspects **(Liu et *al.*, 2007; Wei et *al.*, 2009)**.

Soil heavy metals Cd, Co, Cu, Cr, and Pb were fitted by Gaussian model, whereas the Ni and Zn data were best fitted by the spherical model.The semi-variogram models are described in Figure 3. For Co, Ni, Pb and Zn, the nugget value of less than 0.005 and the low ratio of nugget to sill (less than 25 %) indicated the existence of a strong spatial auto-correlation for these elements **(Armah et *al.*, 2011; Chaoyang et *al.*, 2009).** This ratio ranged from 48 to 64 % for Cd, Cr, and Co, which revealed moderate spatial structure. The spatial variability of Cd, Cr, and Co may be affected by intrinsic (parent materials) and extrinsic factors (mining activities). The range values of heavy metals were in the order: Zn>Ni> Pb>Cu>Cd>Co>Cr. A close similarity between range values of Cd (4670 m), Co (4515 m), Cr (4430), Cu (4775 m), and Pb (4795m) was observed. This confirmed the hypothesis of a possible spatial correlation between these elements.

Table 3. Parameters of the best-fitted semi-variogram models of heavy metals.

Heavy metal	Model	Nugget (mg/kg)²	Partial sill (mg/kg)²	Range (m)	Spatial dependency (%)
Cd	Gaussian	1.78	1.92	4670	48
Co	Gaussian	0	0.61	4515	0
Cr	Gaussian	12.56	8.33	4430	60
Cu	Gaussian	3.18	1.78	4775	64
Ni	Exponential	0	11.20	5925	0
Zn	Exponential	0	15.79	8540	0
Pb	Gaussian	0.005	5.07	4795	0

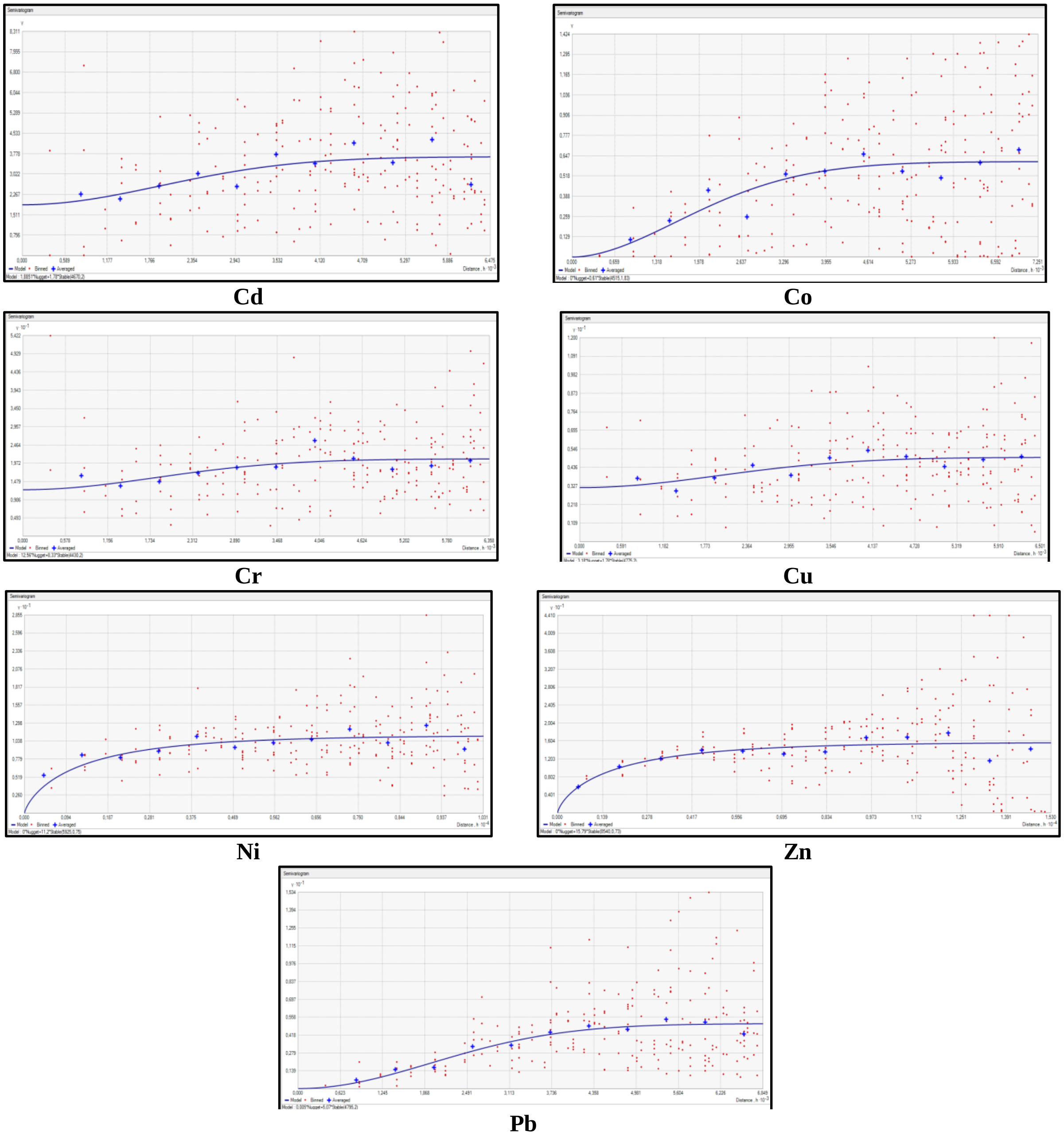


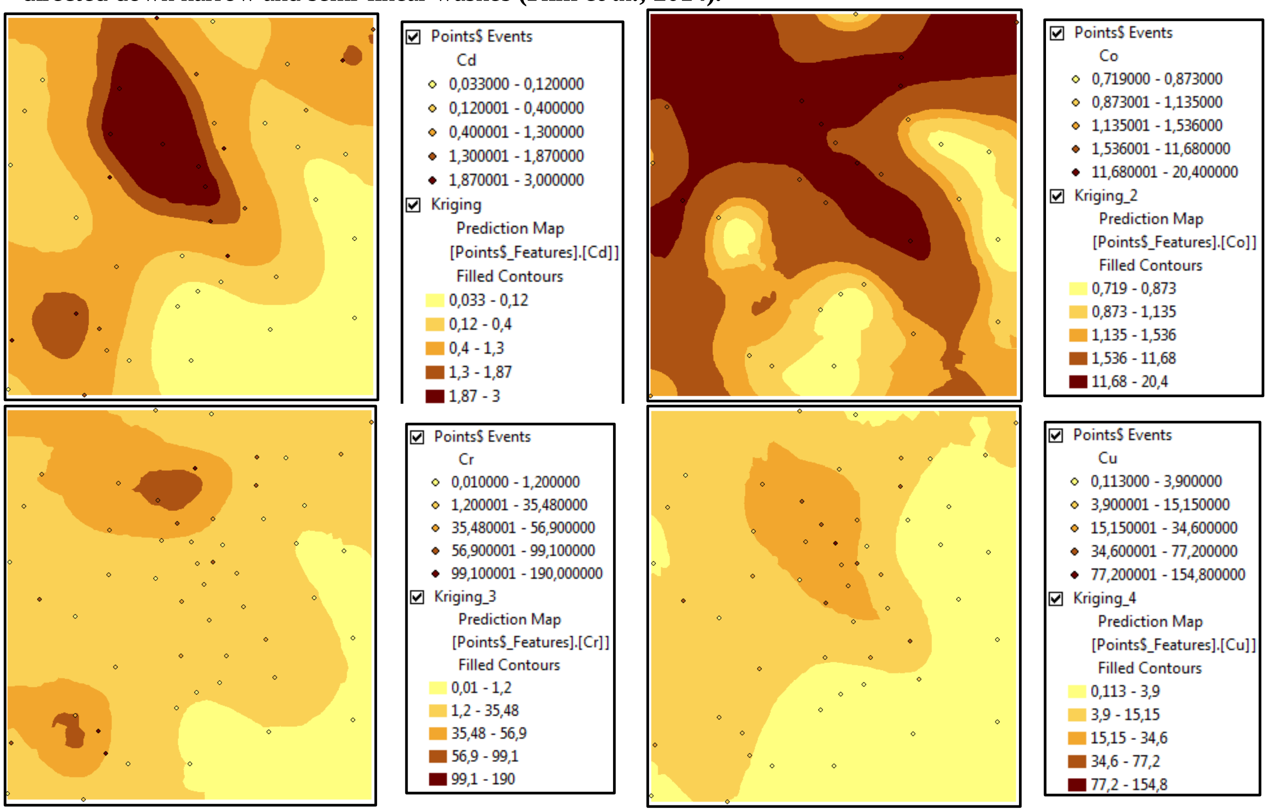
Figure 3. Experimental semi-variograms (+) and fitted theoretical models (line) forthe soil heavy metals.

Spatial distribution

The ordinary kriging interpolation was used for mapping heavy metals (Cd, Co, Cr, Cu, Ni, Zn, and Pb) distribution in soils (Figure 4). For the seven studied heavy metals, Box-Cox transformed data were used for kriging interpolation. Spatial distribution of all heavy metals showed similarity. The kriged maps showed that the greatest concentrations occur near mine tailing areas and that the degree of contamination decreases when the distance from the tailings pounds increases. In addition, according to figure 4, there is a relationship between prevalent wind directions (North-East, South-West and North-West) and distribution pattern of heavy metals. Soils located in the prevailing wind directions from the mine tailings were enriched by heavy metals. In the abandoned mine of Zaida, the tailings are not covered by vegetation or any other material. As a result, the sandy particles may be transported by wind to the soils and areas near the mine. The study conducted by **El hachimi et *al.* (2007)** showed that the Zaida mine is subject to very strong winds in summer as well as in winter.

Tailing dams in Zaida are suspected to be a source of soil contamination by heavy metals. This enrichment can be attributed to dispersion of fine particles from mine tailings to surrounding soils under wind action. Previous studies conducted in different mining areas concluded that mining activities contributed to the enrichment of surrounding soil by trace metals **(Sadhu et *al.*, 2005; Karczewska et *al.*, 2006; Matini et *al.*, 2011; Ameh, 2013; Das and Chakrapani, 2011).** Other authors confirmed this finding and proved that aeolian transport plays an important role in the dispersion of fine particles when released around former mine sites **(Lee et *al.*, 2001; Boussen et *al.*, 2010; Babbou-Abdelmalek et *al.*, 2011; Kim et *al.*, 2014).** This dispersion is a major source of soil contamination by heavy metals **(Yang et *al.*, 2003; Schippera et *al.*, 2008; Jimenez et *al.*, 2009; Wang et *al.*, 2009, Wei et *al.*, 2009; Damian et *al.*, 2010; Ghorbel et *al.*, 2010). Simon et *al.* (2001)** and **Dayani and Mohammadi (2010)** showed that the soil contamination is related to the distance from the storage site of tailings.

In arid and semi-arid areas and in carbonate context, many authors have concluded that the environmental risks associated with mining activities are mainly related to the dispersion of fine particles that were emitted under the action of wind **(Meza-Figueroa et *al.*, 2009; Csavina et *al.*, 2012; García-Lorenzo et *al.*, 2012; Boussen et *al.*, 2013).** They have all reported that soils located in the prevalent wind direction from the studied mine tailings were enriched in heavy metals due to the aeolian deposition of heavy metal-rich particles. The aeolian transport is local or regional, diffuse, and covers much larger spatial areas than fluvial transport, which is highly localized and typically directed down narrow and semi-linear washes **(Kim et *al.*, 2014).**



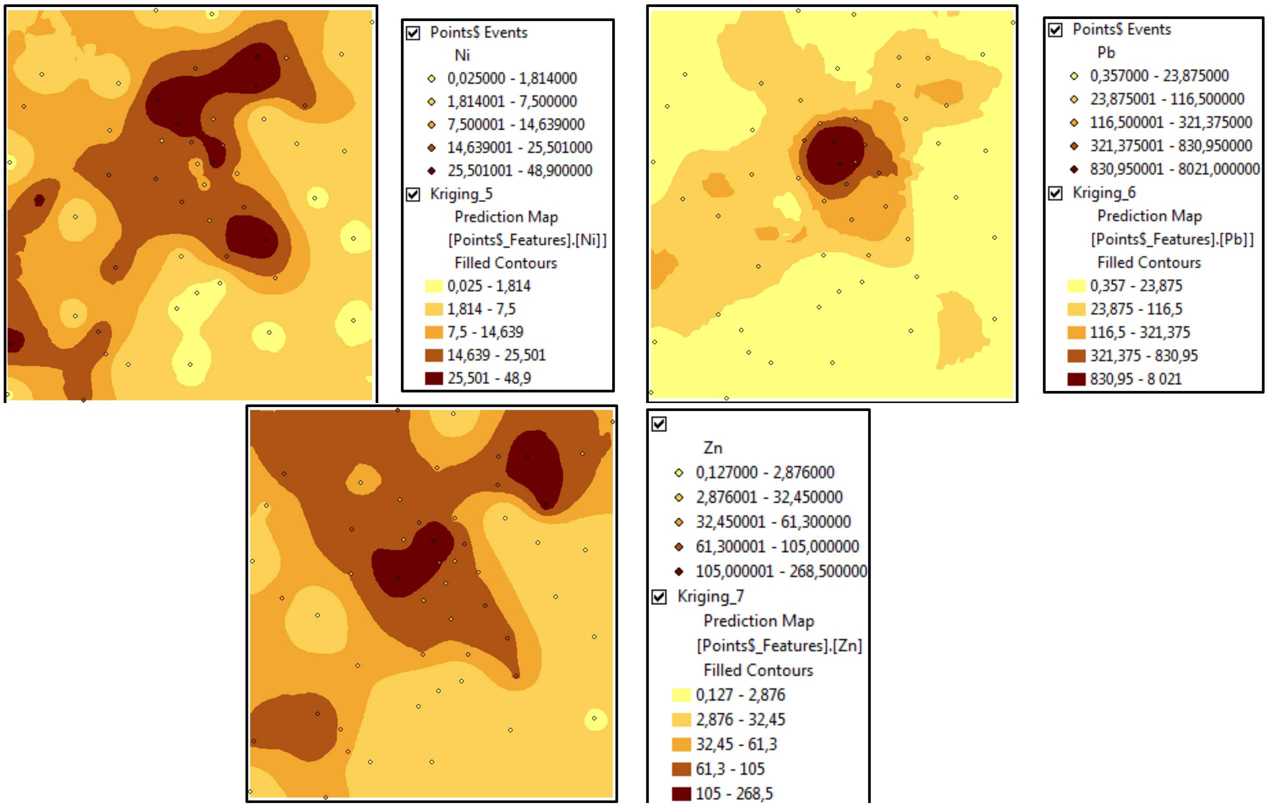


Figure 4. Spatial distribution maps of Cd, Co, Cr, Cu, Ni, Pb, and Zn concentrations in soils surrounding the tailing pits in the Zaida mine.

Conclusion

Geostatistical approach was applied to study the spatial distribution of seven heavy metals in soils surrounding tailing in the abandoned mine of Zaida. Descriptive parameters showed that soil samples are enriched by heavy metals since the determined values exceeded the maximum levels given by many authors.The kriged maps showed that the tailing pounds constitute a potential source of soil contamination by heavy metals. In the abandoned mine of Zaida, the strong wind seem to be the principal factor controlling the spatial distribution of heavy metals. The spatial distribution of heavy metals showed that the degree of contamination decreases when the distance from the tailings pounds increases and soils located in the prevailing wind directions from the mine tailings were enriched by heavy metals.This result suggested the effect of wind on the dispersion of fine particles from tailings to surroundings soils.

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