

HEAVY METAL VARIABILITY OF A NATIVE SALINE PASTURE IN ARID REGIONS OF CENTRAL ANATOLIA

Hikmet GUNAL¹, Nurullah ACIR¹ & Mesut BUDAK²

¹*Gaziosmanpasa University, Faculty of Agriculture, Soil Science and Plant Nutrition Department, Tokat/Turkey:
e-mail: hikmet.gunal@gop.edu.tr, e-mail: nurullah.acir@gop.edu.tr*

²*Hakkari University, Hakkari/Turkey e-mail: m_budak1981@hotmail.com*

Abstract: Spatial distribution of heavy metals can be used for planning, risk assessment, and decision making in the environmental management of a region. In this context, the present research has three specific objectives: to characterize spatial distribution of heavy metals in a saline environment, to determine the relationship between some of soil properties and heavy metal distributions, and to assess the controlling factors for the spatial variability of heavy metals prior to reclamation and intensive irrigated agricultural activities. The field was 2650 ha, and divided into square sub-blocks, with 400 m spacing in x and y directions, for sampling procedure. One hundred fifty one soil samples were collected from 0-30 cm of soil surface. Heavy metal (nickel (Ni), cadmium (Cd), lead (Pb), cobalt (Co) and chromium (Cr)) concentrations of soils along with some of physical and chemical characteristics were determined. Geostatistical techniques were employed to determine the spatial variability of heavy metals. Topsoil salinity was highly variable at short distances and terrain attributes were the most influential factors. Mean concentrations of metals were lower than that of allowable level in European Union. The nugget variance to sill ratio ranged from 0.2 for Cr to 28.02% for Cd suggesting strong to moderate spatial dependency that might be attributed to the effect of intrinsic factors (such as parent material) in the distribution of metals. Low levels of heavy metals in this arid region indicate that the main factor in distribution of metals was lithology, and contributions from agricultural activities and atmospheric deposition are negligible at the moment. However, the levels of metals need to be monitored with the introduction of fertilizers, pesticides and other agricultural inputs to the region.

Keywords: salinity, spatial distribution, heavy metal, lead, chromium, nickel, cobalt, cadmium.

1. INTRODUCTION

Spatial interpolation techniques are used in estimating values of a variable at locations that have not been sampled. In this study, spatial distribution of six micro elements found in a large saline environment prior to intensive agricultural production and reclamation was investigated for input to further agricultural and environmental activities. Maps produced after spatial interpolations are useful in decision making during the establishment of agricultural management strategies (Uygan & Cetin, 2012).

Several methods have been used to estimate the spatial distribution of a variable. Kriging is the most popular estimation method used, because it is a collection of generalized linear regression techniques for minimizing and estimating variance defined from a prior model for a covariance. The kriging estimates can be used to map the distribution of a particular

variable. These maps provide a helpful visual display of the spatial variability in the field and representation of soil properties where natural hazards can be identified (Burgos et al., 2006).

Heavy metals may be beneficial to some species at trace level, and they are usually considered to be toxic at higher concentrations (Xu & Tao, 2004). Heavy metals accumulated in soil are made bioavailable to biological communities (e.g. plants) and thereby enter the human food chain (Bevacqua & Mellano, 1993; Lacatusu et al., 1995; Church et al., 1997). Cadmium is one of the heavy metals that is well known for its high availability and toxicity to biota (Das et al., 1997). Increased heavy metal concentrations may arise from both natural processes and anthropogenic pollution sources (Doelsch et al., 2006). Soil may be the first recipient of heavy metals released from both processes. Irrespective of the origin, accumulation of heavy metals in soils is

environmentally significant, especially if the soil is used for agricultural purposes (Qishlaqi et al., 2010).

Studies conducted on heavy metal distributions have mainly conducted to give a snapshot of heavy metal distributions in soils (White et al., 1997; Vrana et al., 1997; Xu & Tao, 2004). Variability of soil properties from a spatial resolution of centimeters to meters (Webster & Nortcliff, 1984) and to regional scale (Lado et al., 2008) are commonly analyzed by geostatistical methods. Yu et al. (2008) stated that the main factor of accumulation of Cu, Pb, Cr, Hg and As was lithological factor in arid agricultural areas. They reported striking dissimilarity of heavy metals sources in agricultural soils between the irrigated agriculture and arid agriculture. The processes or factors affecting heavy metal variability in soils pointed mainly to the parent material and topography (natural) and anthropogenic factors such as fertilizer application. Since these factors vary over space, existence of heavy metals is also space dependent (Xu & Tao, 2004). Webster et al., (1994) reported that heavy metals such as Co and Ni, with longer spatial structures were under geological effect and Cd, Cr, Cu and Pb with relatively shorter spatial structures were under the effects of human activities.

Identification of relationship between heavy metals and other soil properties could provide valuable information for further environmental risk assessment (Xu & Tao, 2004). The characterization of the spatial variability of soil attributes is essential to achieve a better understanding of the complex relations between soil properties, environmental factors and land use (Yemefack et al., 2005).

Primary objective of this research was to examine the spatial distribution and evaluation of Ni, Cd, Co, Cr and Pb in the saline arable land in this potentially agriculturally important region using geostatistics. Soil properties influencing the spatial distribution of heavy metals and their phyto available content should be taken into account in an effective environmental assessment. Thus, evaluating the relations between heavy metals and some of soil physical and chemical properties was the secondary purpose of the study. The results of this study are particularly important to monitor the changes in heavy metal concentrations of soils used only for grassland following the reclamation and intensive use in agriculture.

2. MATERIALS AND METHODS

2.1. Study area

The study area is located in Emen plain which is a part of the great Konya Basin. The basin is situated in the Central Anatolian Plateau at latitude of 37° and between longitudes 33° and 35° East. Study area covers 2650 ha land and has been used for pasture up to 2008

when soil samples were collected. A private company started a reclamation project to clean up soils from salts. Following the reclamation of fields, wheat, alfalfa, and barley will be the dominant crops of the study area. Manure brought surrounding farms will be applied to soils in order to increase the aggregation and improve the soil quality. Altitude of the study area ranges from 1044 m to 1058 m and average slope of the land is around 0.6%.

Emen Plain is known as arid agricultural area for the majority of its agricultural lands are dry land in the region. The annual long term (1971-2000) average of precipitation is 322.4 mm, mean air temperature is 11.7 °C. Soil temperature regime is mesic with 13.5 °C mean annual soil temperature at 50 cm depth, and soil moisture regime is aridic (Soil Survey Manual 1999). The dominant plant species were halophytes. Spatial variation in soil salinity resulted in differences at plant species throughout the study area.

2.2. Geology of Study Area

The Konya Basin covers about 1 million hectares (or 2 million acres) and is enclosed by uplands and mountains which prevent any superficial drainage to the sea. The area is surrounded by Neogene aged volcanic units of Mid-Toros Mountains in the south and Erciyes Mountains in the north. The basin formed mainly over tertiary aged units and salinity formed due to saline nature of upper Eocene aged volcanisms (Fig. 1) (Ozguner et al., 1999). Evaporative environments were dominated during upper Eocene-Oligocene periods (Atabey & Ayhan, 1986). As Jordan et al., (2004) also stated possible sources of salts in study area are ancient drainage basin. Emen Plain which used to be an ancient drainage basin evaporated during arid periods and in addition, artificially drainage constructed by government left behind huge salt deposits. The salts in the Great Konya Basin are of different origins. The major groups are those from marine sediments, from volcanic deposits, and from weathering of rocks. High salt content is probably due to the accumulation of salts leached out of the surrounding volcanic ash and pumice soils (De Meester 1970).

2.3. Soil Sampling

The total area sampled was 2650 ha covering and used as pasture at the time of sampling. Spatial locations of all sampling points were acquired using portable GPS (global positioning system) equipment.

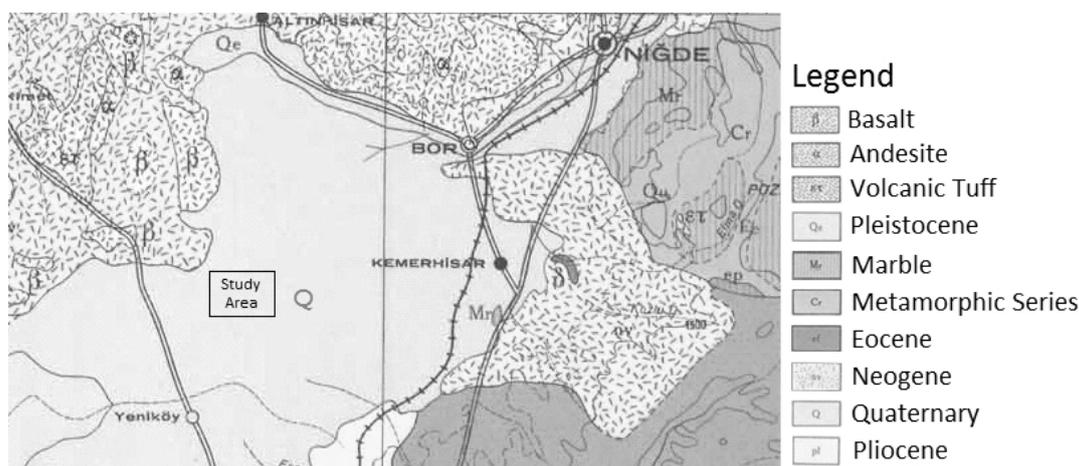


Figure 1. Geology of the study area (Ulu, 2002)

Seven soil series were identified which had been named Kizilica (Xeric Petrocalcids), Leben (Xeric Petrocalcids), Karadeli (Calcic Petrocalcids), Acir (Vertic Natrargids), Kizilkuyu (Vertic Natrargids), Cobul (Xeric Petrocalcids) and Tektome (Xeric Torrifuvents). Considering the uniformity of soil sample distribution in the study area, 151 topsoil (0-30 cm) samples were collected from different locations at an approximate grid interval of 400 m (Fig. 2).

2.4. Soil characterization

Samples were air dried at room temperature and sieved with a 2 mm sieve. The contents of Ni, Cd, Pb, Co and Cr were determined by the extraction with DTPA using a soil:extractant ratio of 1:2. This method is commonly used by agronomists to evaluate the plant available fraction of metals found in soils. Metals extracted were measured with an ICP-AES (Varian-Vista Model) (Lindsay & Norvell 1978). Extractable B of soils was determined by the method of Cartwright et al. (1983). Boron was extracted with 0.01 M CaCl_2 plus 0.01 M Mannitol using 1:5 (soil:extractant) ratio, and measured with an ICP-AES.

Retention and release characteristics of micro nutrients are highly affected by soil properties, thus electrical conductivity and pH of soils were measured 1:2.5 soil water suspension (Hendershot et al., 1993), organic matter was measured by the Walkey Black method (Nelson & Sommers, 1982), and calcium carbonate content was determined with a pressure calcimeter (Nelson, 1982). Hydrometer method was employed to measure the particle size distribution of < 2 mm fraction of each sample (Gee & Bauder 1986). Exchangeable cations (Na, K, Ca and Mg) were extracted using 1 mol L^{-1} NH_4OAc and then measured by flame emission spectrometry (Thomas 1982). Plant available boron content was determined by mannitol CaCl_2 method (Cartwright et al., 1983).

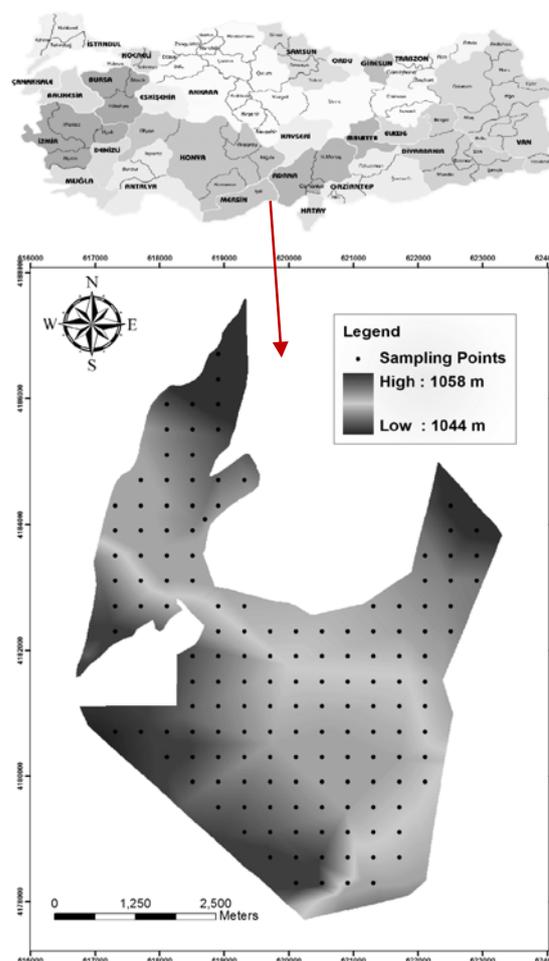


Figure 2. Digital elevation map of study area and distributions of sampling locations.

2.5. Statistical Analyses

Mean, standard deviation, and coefficients of variation which are generally accepted as indicators of the central trend and of the data spread, were analyzed.

Table 1. Descriptive statistics for physical and chemical characteristics of soils studied at 0-30 cm depth.

		Minimum	Maximum	Mean	Std. Deviation	CV	Skew	Kurt
Clay	%	22.0	81.1	52.4	16.29	31.09	-0.12	-1.27
Sand		3.9	61.6	26.1	14.24	54.58	0.43	-0.83
Silt		8.8	55.1	21.5	6.45	29.97	0.67	2.56
pH		7.37	9.66	8.55	0.34	3.98	0.22	0.74
EC	dS/m	0.40	18.38	3.91	3.64	92.91	1.30	1.38
CaCO ₃	%	3.99	49.47	31.43	10.81	34.40	-0.70	-0.60
Na	meq 100g ⁻¹	0.55	76.18	14.74	14.41	97.77	1.37	1.60
K		1.63	11.98	4.16	1.87	44.83	1.61	3.31
Ca		14.98	185.72	35.87	22.76	63.46	2.96	12.77
Mg		1.12	17.58	6.85	2.98	43.54	0.63	0.24
B	mg kg ⁻¹	1.41	97.84	47.76	31.80	66.58	0.23	-1.46
OM	%	0.32	4.50	1.87	0.70	37.19	0.52	0.60

Webster (2001) indicated that examining the skewness of soil data may be sufficient to decide whether or not data follow the normal frequency distribution. All heavy metals and some other soil properties were positively skewed, thus data were log transformed to sufficiently reduce the skewness. The statistical analyses were performed using SPSS for Windows (version 13).

Statistical and geostatistical methods were applied to determine the spatial distribution of the heavy metals and quantifying the relationship between spatial variability of heavy metals and other soil properties. The spatial structure of variables was characterized using experimental semivariogram, expressed as;

$$\lambda(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [z(x_i) - z(x_{i+h})]^2, \quad (1)$$

where, $z(x_i)$ and $z(x_{i+h})$ are the variables of interest at locations x_i and x_{i+h} respectively, and $N(h)$ is the number of pairs on the locations separated by a distance h (Isaaks & Srivastava 1989). Theoretical semivariogram (covariance) models are used to predict the values of heavy metals at unsampled locations. The geostatistical analyses were carried out with GS+ (Version 7.0) and maps were produced with ArcGIS 9.2 software.

Since asymmetric distributions and outliers can cause problems leading to biased conclusions in geostatistical analysis, it is necessary to carry out data transformation prior to further analyses. In this study, log-transformation was applied to total and available to heavy metal concentrations. The lognormal kriging estimator provides an approximately unbiased estimate. Logarithmic transformation resulted in smaller skewness and kurtosis of the variables. It should be noted that back transformation to the original data is necessary to provide approximate estimates (McGrath et al., 2004).

Nugget to sill ratio ($Co/(Co+C)$) is calculated to define the spatial dependence for a given variable (Cambardella et al., 1994). If the ratio is less than 25%,

the variable was considered having strong spatial dependence; between 25% and 75%, the variable was considered having moderate spatial dependence; greater than 75%, the variable was considered having a weak spatial dependence. The spatial variability of soil variables may be influenced by intrinsic (soil formation factors, such as soil parent materials) and extrinsic factors (soil management practices, such as fertilization). Usually, strong spatial dependence of soil variables is attributed to intrinsic factors, while weak spatial dependence is attributed to extrinsic factors (Cambardella et al., 1994).

3. RESULTS AND DISCUSSION

Soils in study area have developed on nearly level sloping lacustrine environment. Soil texture is mainly clayey with the mean clay content of 52.4%, and soil consistency is generally friable. Since the natural drainage of the land had never been established, water ponds in the soil surface for a long period of time. Such water can only leave the field either by percolating soil profile or evaporation. In both cases, evaporation of stagnant waters left considerable amounts of salts on the soil surface and somewhere in soil profile. Therefore, the main restrictions for agricultural production in the farmland (at this moment) are salinity, alkalinity, boron toxicity, impermeable layer between 60 to 120 cm and inadequate drainage system (Erdem et al., 2012). Driessen (1970) reported that major source of boron present at toxic levels is the volcanic deposits found at the surrounding areas.

Summary statistics for some of physical and chemical characteristics and heavy metal contents for the soil samples were presented at table 1 and 2. High pH values and low organic matter contents are the two typical characteristics which define the general makeup of Anatolian soils.

Table 2. Descriptive statistics for heavy metals of soils studied

		Minimum	Maximum	Mean	Std. Deviation	CV	Skew	Kurt
Ni	mg kg ⁻¹	2.84	41.35	14.84	8.87	59.90	1.24	0.64
Pb		11.4	165.8	48.5	33.9	70.06	1.87	2.65
Cd		0.38	1.98	0.68	0.28	41.00	1.91	4.35
Co		0.85	10.4	3.03	1.95	64.40	1.75	2.96
Cr		0.12	3.16	0.64	0.33	51.13	3.69	24.00

Soils of the area are predominately basic (the pH of 50% of samples is >8.2), due to the high percentage of carbonates (mean CaCO₃ is 31.43%) in the parent materials (Table 1). The mobility and retention of metals are strongly affected by soil pH, and cations tend to be more mobile with decreasing pH levels (Martinez & Motto, 2000; Kashem & Singh 2001), and many of the micro elements are adsorbed as pH levels increased. Plant available boron content was at toxic level to the plants (Table 1). The skewness of EC, exchangeable Na, K and Ca are rather high in comparison with the coefficients of normal distribution (Table 1).

These soils were predominately used for pasture. The soils are low in organic matter due to the prevailing arid climate conditions and high intensity of grazing. The average organic matter content was 1.87%, with values ranging between 0.32% and 4.50% (Table 1). Although organic matter is known as the primary constituent of soils which specifically adsorbs metals, due to the high cation exchange capacity of organic material (Tichy et al., 1997, Martin & Kaplan, 1998). Contribution of organic matter to available metals pools is limited in study area due to the low organic matter content of soils. Thus, excessive metals can seriously cause problems to plants. Concentrations of heavy metals range over several orders of magnitude: nickel (Ni) and lead (Pb) had the lowest concentrations, and the most enriched metal was cobalt (Co) in study area (Table 2).

Total heavy metal values were several orders of magnitude lower than the threshold soil concentration. Acosta et al. (2011) evaluated the enrichment of metals in soils subjected to different land uses and indicated that cadmium (Cd), chromium (Cr) and Ni contents of natural sites were lower as compared to that of the urban, industrial and agricultural areas. Relatively low concentration of metals in natural sites is probably due to the lack of anthropogenic influence on land and low metal contents of the parent materials. The relatively large CVs, indicate that there is a high variability at local scale and that the variables are not distributed evenly over the area (Table 2). The CVs' for the all metals were high to be considered as highly variable according to the classification of Camberdella et al.,

(1994).

Total heavy metal values were several orders of magnitude lower than the threshold soil concentration. Acosta et al. (2011) evaluated the enrichment of metals in soils subjected to different land uses and indicated that cadmium (Cd), chromium (Cr) and Ni contents of natural sites were lower as compared to that of the urban, industrial and agricultural areas. Relatively low concentration of metals in natural sites is probably due to the lack of anthropogenic influence on land and low metal contents of the parent materials.

Table 3. The threshold contents of heavy metals in soils for Turkey and European Economic Community (EEC) (Regulations 2003; Kaptan, 2003)

Heavy metal (mg/kg)	Turkey		EEC
	pH<6	pH>6	
Lead (Pb)	50	300	50-300
Cadmium (Cd)	1	3	1-3
Chromium (Cr)	100	100	100
Nickel (Ni)	30	75	30-75
Cobalt	--	20	--

The relatively large CVs, indicate that there is a high variability at local scale and that the variables are not distributed evenly over the area (Table 2). The CVs' for the all metals were high to be considered as highly variable according to the classification of Camberdella et al. (1994).

Chromium (Cr) in natural soils is mainly indigenous and Cr concentration ranges from nearly zero to several thousands of mg kg⁻¹ in soils developed from ultramafic rocks. The mean Cr concentration in the soils of world is approximately 84 mg kg⁻¹ (Paz-Gonzales et al., 2001). Diethylene triamine pentaacetic acid (DTPA) extractable Cr content of soils investigated ranged from 1.2 mg kg⁻¹ to 31.6 mg kg⁻¹ which is much lower than the allowable threshold values of metals in Turkish Standards and European Union (Table 3).

Cadmium is considered to be one of the most problematic pollutants, due to its high solubility in water and its carcinogenic, mutagenic, and

teratogenic effects in numerous animal species (Das et al., 1997). Mean Cd concentration of soils was only 0.68 mg kg⁻¹, and ranged from 0.38 to 1.98 mg g⁻¹ which is lower than the allowed threshold level in Turkey and Europe (Table 3).

Mean Pb concentration of soils was 48.5 mg kg⁻¹, and ranged from 11.4 to 165.8 mg kg⁻¹. Although Pb in soil might originate from various sources like mining, burning of coal, automobile exhausts, fertilizers, pesticides, and additives in pigments and gasoline (Verma & Dubey 2003), low concentration indicates no contribution of Pb existed in the area.

3.1. Relationship between soil properties and heavy metal contents

The correlation analyses between heavy metals and other soil properties confirmed that clay, sand, silt and organic matter can be used to explain the distribution of heavy metal contents in soils. The heavy metals evaluated were highly intercorrelated and also correlated with organic matter content and soil textural components (Table 4) suggesting that their mutual correlation is due to pedogenic processes and subsequent bedrock influence or

material deposition. Correlation coefficients between heavy metal contents, as shown in table 5, revealed that Pb and Cd are closely related to clay, sand and silt contents while Ni and Co are also closely related to the sand and silt contents of soils (P<0.01 for Ni, Pb and Co, and P<0.05 for Cd). Chromium had only a weak correlation with silt content (P<0.05). Heavy metals other than Cr had a strong negative correlation with organic matter of soils. The correlation coefficients carry little information about the scale dependent relationships of the heavy metal contents. A weak correlation of two variables could be the result of the counteract of different correlation behavior at various spatial scales (Xu & Tao 2004).

3.2. Spatial Variability of Heavy Metals

Spatial distribution maps of metals were prepared to visualize the distribution of metals in soils of the study area (Fig. 3). The attributes of semivariograms for each heavy metal are presented in table 6. Semivariogram results showed that heavy metals studied were best fit to a spherical model. The spatial autocorrelation structure of heavy metals showed that they present distinct spatial autocorrelation patterns (Fig. 4).

Table 4. Correlation coefficients between heavy metals and other soil properties

	Ni	Pb	Cd	Co	Cr
Clay	0.154	0.302**	0.190*	0.148	0.048
Sand	-0.299**	-0.425**	-0.325**	-0.293**	-0.143
Silt	0.259**	0.163*	0.224**	0.260**	0.186*
pH	-0.088	-0.109	-0.095	-0.085	-0.001
EC	-0.132	-0.114	-0.202*	-0.153	-0.143
CaCO ₃	-0.035	-0.022	0.027	-0.095	-0.012
Na	-0.122	-0.141	-0.210*	-0.155	-0.119
K	0.032	-0.033	-0.036	0.078	-0.021
Ca	-0.048	0.032	-0.131	-0.074	-0.076
Mg	0.090	0.172*	0.074	0.033	0.060
B	-0.079	-0.037	-0.130	-0.091	-0.161*
Organic Matter	-0.231**	-0.319**	-0.187*	-0.272**	-0.021

Significant at ** P<0.01 and *P<0.05, respectively

Table 5. Correlation coefficients of heavy metals

	Ni	Pb	Cd	Co	Cr
Ni	1	0.790**	0.788**	0.842**	0.352**
Pb	0.790**	1	0.759**	0.786**	0.358**
Cd	0.788**	0.759**	1	0.811**	0.311**
Co	0.842**	0.786**	0.811**	1	0.377**
Cr	0.352**	0.358**	0.311**	0.377**	1

Significant at ** P<0.01 and *P<0.05, respectively.

Table 6. The attributes of semivariograms for each heavy metal

	Model	Nugget Variance(Co)	Sill (Co+C)	Spatial Dependency (%)	Range (m)	R 2	RSS
Ni	Spherical	0.0484	0.2988	16.20	1698	0.682	0.018
Pb	Spherical	0.0183	0.3196	5.73	1999	0.778	0.0202
Cd	Spherical	0.0325	0.116	28.02	2065	0.676	0.00376
Co	Spherical	0.0442	0.3324	13.30	1794	0.749	0.0285
Cr	Spherical	0.0100	4.953	0.20	1198	0.836	3.46

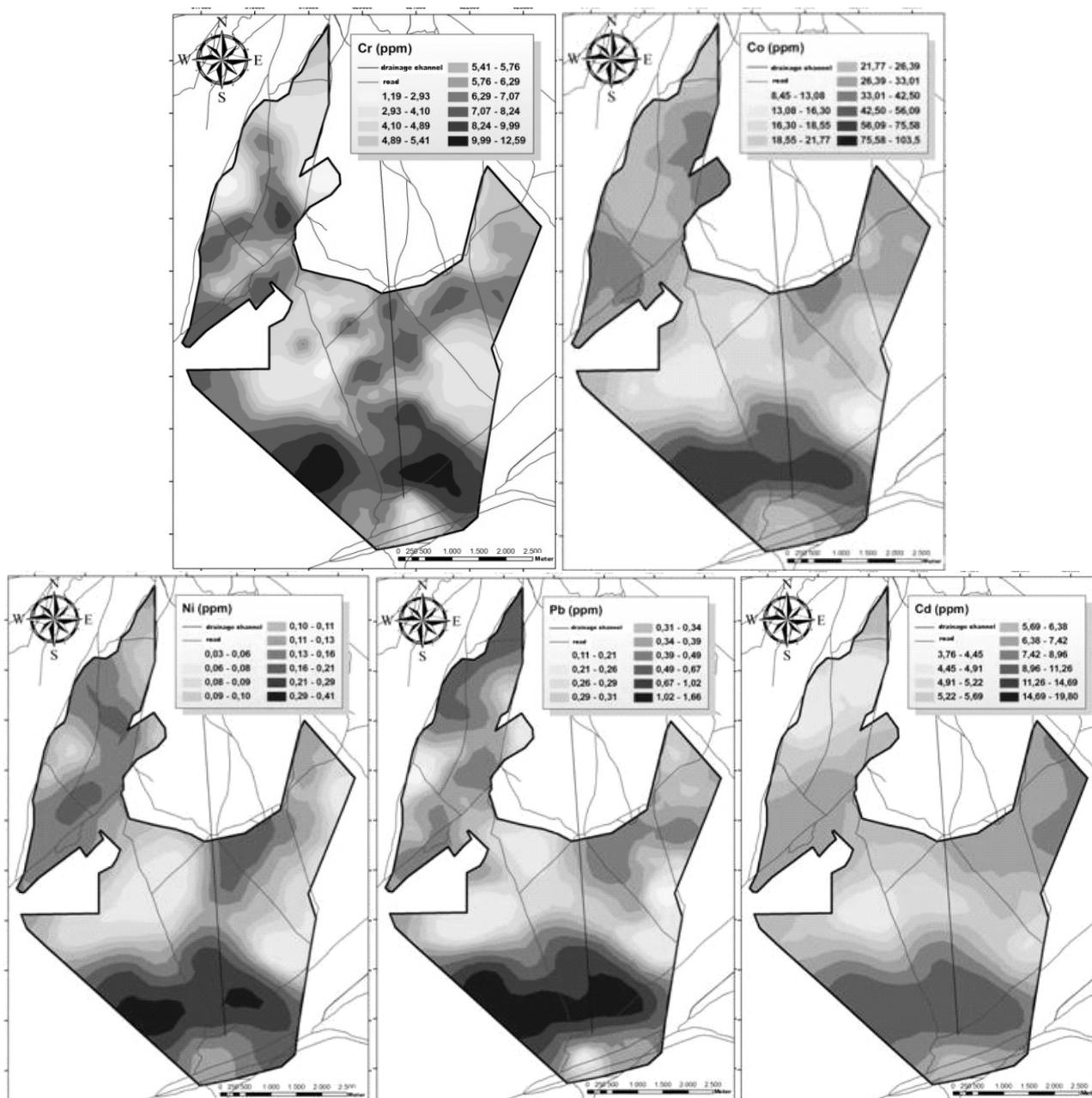


Figure 3. Spatial distributions of heavy metals

The spatial dependency (nugget:sill ratio) ranged from 0.2% for Cr to 28.02% for Cd suggesting strong to moderate spatial dependency.

The intrinsic (soil formation factors such as parent materials) and extrinsic (soil management practices such as fertilization) factors affect the spatial

variability of soil properties (Mulla & McBratney 2000), and strong spatial dependencies were attributed to intrinsic factors and weak spatial dependencies were attributed to extrinsic factors (Camberdella et al., 1994). Strong spatial dependency of heavy metals also indicates the parent material influence on heavy metal distribution in study area.

Assuming that the heavy metals have been measured with a relatively high precision; most of the nugget variance can be attributable to the short-range variability of the heavy metals (Lado et al., 2008). The maps created can be used to identify the metal enriched spots and monitor the metal enrichment within the study area. Although none of the metal concentrations exceeded the threshold values in study area, the maps will give us opportunity to follow the distributions with the ongoing reclamation and agricultural processes. The highest concentrations of metals were located in the south west part of the study area where the highest EC values (not presented in this paper) were also observed.

The geostatistical range called the largest spatial correlation distance reflected the autocorrelation range of variables and was related to the interaction between various processes of soil properties, which are affected at both observing and sampling scale. The soil properties have spatial autocorrelation within the range; otherwise it was not exist (Wang et al., 2008).

The largest range was obtained for Cd and the shortest range was for Cr content. The range values of Pb, Cd and Co were close to each other and were determined as 1999, 2065 and 1794 m, respectively. The smaller range suggests smaller sampling intervals for Cr content. Lead (Pb), cobalt (Co) and chromium (Cr) concentrations have a greater spatial dependency (nugget effect) in comparison with nickel (Ni) and cadmium (Cd) concentrations of soils. The existence of a larger nugget effect for the latter variables may be attributed to the small-scale variation in the data. However, sampling error or analytical variability (measurement error) could not be ruled out.

The problems associated with the characterization of heavy metals in the majority of sites are often due to multiple sources of pollution which can act on different scales (Rodriguez et al., 2008). The strong spatial dependence for available Pb, Co and Cr concentrations indicates that the available Pb, Co and Cr contents of the soils depend mainly upon the parent materials from which soil parent materials were derived. Single source of heavy metals in study area contributed to low nugget variance of variograms. De Temmerman et al.

(2003) also indicated that natural concentration of heavy metals in arable soils depends on the geological material composition. However, the moderate spatial dependence for available Cd and Ni contents in formerly grassland suggests that extrinsic factors other than fertilization or other soil management practices may be reduced their spatial distributions at a large scale.

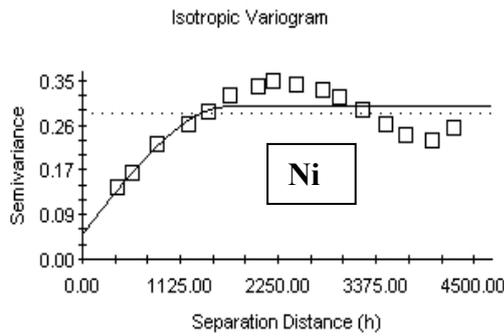
Semivariograms of metals show similar patterns (Fig. 4). Parent materials differ widely in heavy metals, modes of deposition and transport may vary, and weathering regimes can be different (Jeffrey & Robert 1999). Similarity in heavy metal distributions in the area is probably resulted from the mode of sediment deposition within the lacustrine environment and is shown in the correlations between textural components and heavy metal contents (Table 4). Similar results for micronutrient concentration of saline soils were reported by Erdem et al., (2012).

Chromium concentrations of soils were lower than that of the tolerable levels (Table 3). The spatial distribution of Cr in the study area had a patchy structure with high concentrations were distributed to the field (Fig. 3). The highest Cr concentration was found in the southern part of the study area. Similar to the distribution of Cr, all heavy metal distributions were more or less resemble to each other and the highest concentrations were found in the south side of the study area (Fig. 3). Beside the increasing soil salinity in the south area, clay content of soils apparently led to increase in heavy metal concentrations (salinity and clay distributions are not presented in this paper).

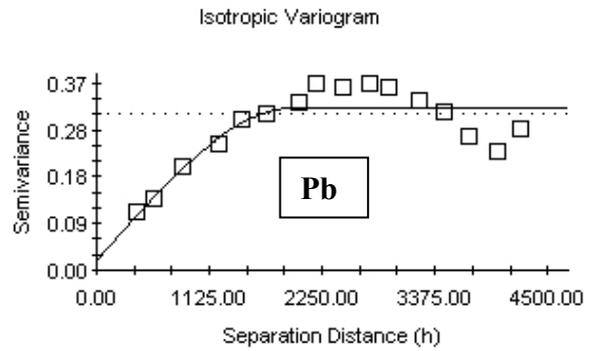
4. CONCLUSIONS

Soils in study area have never been used in agriculture and used only for pasture. The soils are saline ($EC > 4 \text{ dS m}^{-1}$) and some cases saline and alkaline ($EC > 4 \text{ dS m}^{-1}$ and $ESP > 15\%$). Metal (Pb, Co, Cr, Ni and Cd) concentrations were below the threshold values determined for European countries. Low concentrations of metals in soils can be attributed to the low metal contents of parent materials and lack of anthropogenic influence on study area.

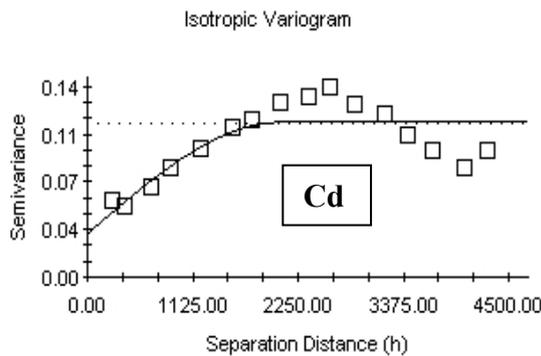
Although the concentrations are low at this moment, the heavy metal contents of soils should be monitored with the implementation of intensive agricultural practices. Since organic matter content is quite low in the area, increased levels of heavy metals can cause serious problems in plants. The plants grown in the area will be mostly forage crops; therefore, high metal concentration in plant materials can be transferred to animals and human.



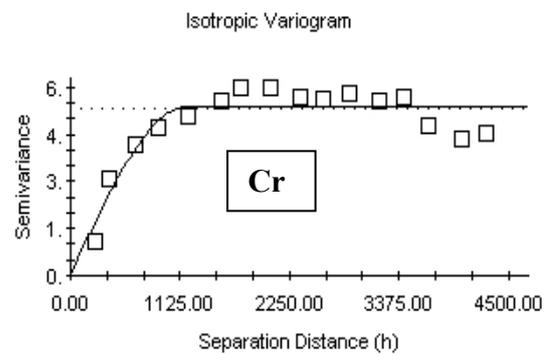
Spherical model (Co = 0.0484; Co + C = 0.2988; Ao = 1698.00; r2 = 0.682; RSS = 0.0180)



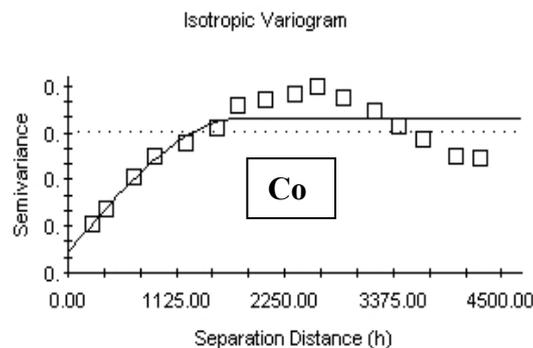
Spherical model (Co = 0.0183; Co + C = 0.3196; Ao = 1999.00; r2 = 0.778; RSS = 0.0202)



Spherical model (Co = 0.0325; Co + C = 0.1160; Ao = 2065.00; r2 = 0.676; RSS = 3.764E-03)



Spherical model (Co = 0.0100; Co + C = 4.9530; Ao = 1198.00; r2 = 0.836; RSS = 3.46)



Spherical model (Co = 0.0442; Co + C = 0.3324; Ao = 1794.00; r2 = 0.749; RSS = 0.0285)

Figure 4. Semivariograms of heavy metals with fitted models

ACKNOWLEDGEMENT

The authors would like to thank the Cingilli Organic Farming Company for the logistic and financial support in field and laboratory studies. The authors would like to thank Dr Huseyin ONEN for his valuable contributions to the manuscript.

REFERENCES

Acosta, J.A., Faz, A., Martínez-Martínez, S. & Arocena J.M., 2011. *Enrichment of metals in soils subjected to different land uses in a typical Mediterranean environment (Murcia City, southeast Spain)*. Applied Geochemistry, 26, 405-414.

- Atabey, E. & Ayhan, A., 1986. *Geology of Niğde-Ulukışla-Çamardı-Çiftehyan Region*. M.T.A. Review Report. No: 8064. p.60. (in Turkish).
- Bevacqua R F & Mellano V J., 1993. *Crop response to sewage sludge compost: a preliminary report*. California Agriculture, 47, 22–24.
- Burgos, P., Madejón, E., Pérez-de-Mora, A. & Cabrera, F., 2006. *Spatial variability of the chemical characteristics of a trace-element-contaminated soil before and after remediation*. Geoderma, 130, 157–175.
- Cambardella, C.A., Moorman, T.B., Novak, J.M., Parkin, T.B., Karlen, D.L., Turco, R.F. & Konopka, A.E., 1994. *Field–Scale Variability Soil Properties in Central Iowa Soils*. Soil Science Society of America, Journal, 58, 1501–1511.
- Cartwright, B., Tiler, K.G., Zarcinas, B.A. & Spouncer, L.R., 1983. *The chemical assessment of boron status of soils*. Australian Journal of Soil Research, 21, 321–332.
- Church, S.E., Kimball, B.A., Fey, D.L., Ferderer, D.A., Yager, T.J. & Vaughn, R.B., 1997. *Source, transport, and partitioning of metals between water, colloids, and bed sediments of the Animas River, Colorado*. U.S. Geological Survey Open-File Report, 97-151.
- Das, P., Samantaray, S. & Rout, G.R., 1997. *Studies of cadmium toxicity in plants: a review* Environmental Pollution, 98, 29–36.
- De Meester, T. D., 1970. *Soils of the Great Konya Basin, Turkey*. Agricultural Research Reports, N.740, Pudock, Wageningen.
- De Temmerman, L., Vanongeval, L., Boon, W. & Hoenig, M., 2003. *Heavy metal content of arable soil in Northern Belgium*. Water Air Soil Pollution, 148, 61–76.
- Doelsch, E., Macary, H. S. & Van de Kerchove, V., 2006. *Sources of very high heavy metal content in soils of volcanic island (La Réunion)*. Journal of Geochemical Exploration, 88 (1-3.), 194–197.
- Driessen, P., 1970. *Soil salinity and alkalinity in the great Konya Basin, Turkey*. Agricultural research reports 743. Wageningen, the Netherlands. 50 P. GA, 71B-1304.
- Erdem, H., Budak, M., Acir, N. & Gokmen, F., 2012. *Micronutrient Variability in a Lacustrine Environment of Calcic Haplosalids*. Fresenius Environmental Bulletin, 21(3), 1-10.
- Jordán, M.M., Navarro-Pedreño, J., García-Sánchez, E., Mateu, J. & Juan, P., 2004. *Spatial dynamics of soil salinity under arid and semi-arid conditions: geological and environmental implications*. Environmental Geology, 45(4), 448–456.
- Hendershot, W.H., Lalonde, H. & Duquette, M., 1993. *Ion exchange and exchangeable cations*. In: Carter, R. (Ed.), Soil Sampling and Methods of Analysis Edited by Canadian Society of Soil Science. Lewis Publisher, Boca Raton, 167–176.
- Isaaks, E.H. & Srivastava, R.M., 1989. *Applied Geostatistics*. Oxford University Press, New York, 46(39), p 561
- Kaptan, H., 2003. *Harmonization of methods of sampling and analysis of heavy metals in soil and sewage sludge, organic pollutants and pathogens in some of European Union member countries*. Ankara European Studies Journal, 3(1), 45–72. (In Turkish)
- Kashem, M.A. & Singh, B.R., 2001. *Metal availability in contaminated soils: I. Effects of flooding and organic matter on changes in Eh, pH and solubility of Cd, Ni and Zn*. Nutrient Cycling in Agroecosystems. 61, 247–255.
- Lacatusu, R., Rauta, C., Carstea, S. & Ghelase, I., 1995. *Soil–plant–man relationship in heavy metal polluted areas in Romania*. Applied Geochemistry, 11, 105–107.
- Lado, L.R., Hengl, T. & Reuter, H.I., 2008. *Heavy metals in European soils: a geostatistical analysis of the FOREGS geochemical database*. Geoderma, 148, 189–199.
- Lindsay, W.L. & Norvell, W.A., 1978. *Development of a DTPA test for zinc, iron, manganese and copper*. Soil Science Society of America, Journal, 42, 421–428.
- Martin, H.W. & Kaplan, D.I. 1998. *Temporal changes in cadmium, thallium and vanadium mobility in soil and phytoavailability under field conditions*. Water Air Soil Pollution. 101, 399–410.
- Martinez, C.E. & Motto, H.L., 2000. *Solubility of lead, zinc and copper added to mineral soils*. Environmental Pollution. 107, 153–158.
- McGrath, D., Zhang, C. & Carton, O.T., 2004. *Geostatistical Analyses and Hazard Assessment on Soil Lead in Silver mines Area, Ireland*. Environmental Pollution, 127, 239–248.
- Mulla, D.J. & McBratney, A.B., 2000. *Soil Spatial Variability*. In: Handbook of Soil Science, M. E. Sumner (ed.) CRS Press. Baco, Raton. FL, 321–352.
- Nelson, R. E., 1982. *Carbonate and gypsum*. A.L. Pageet al. (ed.) Methods of soil analysis. Part II. 2nd ed. Agronomy Monograph, 9. ASA and SSSA, Madison, WI, 181–197.
- Nelson, D.W. & Sommers, L. E., 1982. *Total carbon, organic carbon and organic matter*. In: Methods of soil analysis. Part 2. Chemical and Microbiological Properties, Page, A. L., Miller, R. H. & Keeney, D. R. (eds) 2nd edition. SSSA Inc. Publisher, Madison, WI, 539–577.
- Qishlaqi, A., Moore, F. & Forghani, G., 2010. *Assessing the Spatial Variability of Total and Available Cadmium in Soils of the Angouran Area, NW Iran*. Soil and Sediment Contamination: An International Journal, 19(6), 707–724.
- Özgüner, A. M., Büyüktemiz, M., Atilla, A., Erdem, F., Mutlu, H., Karatosun, H. & Yumuşak, S., 1989. *Chemical salt possibilities in Konya (Ereğli)-Niğde (Bor) sedminenter basin*. 43th

- Geology Congress of Turkey. Ankara.(in Turkish).
- Paz-Gonzalez, A., Taboada-Castro, M.T. & Vieira, S. R.,** 2001. *Geostatistical analysis of heavy metals in a one-hectare plot under natural vegetation in a serpentine area.* Canadian Journal of Soil Science, 81, 469–479.
- Rodriguez, J.A., Nanos, N., Grau, J.M., Gil, L. & Lopez-Arias, M.,** 2008. *Multiscale analysis of heavy metal contents in Spanish agricultural topsoils.* Chemosphere, 70, 1085–1096.
- Thomas, G.W.,** 1982. *Exchangeable cations.* In A.L. Page, R. H. Miller, and D. R. Keeney (eds.). *Methods of soil analysis. Part 2. Chemical and microbiological properties.* 2nd ed., Agronomy Monograph, 9, ASA and SSSA, Madison, WI, 159-165.
- Tichy, R., Fajtl, J., Kuzel, S. & Kolar, L.,** 1997. *Use of elemental sulphur to enhance a cadmium solubilization and its vegetative removal from contaminated soil.* Nutritional Cycling in Agroecosystems, 46, 249–255.
- Ulu, U.,** 2002. *Geologic Maps (1:500.000 scale) of Turkey, Adana.* General Directorate of Mineral Research and Exploration. No. 15.
- Uygan, D. & Cetin, O.,** 2012. *Mapping boron pollution using GIS for boron-affected soils in western Turkey.* Carpathian Journal of Earth and Environmental Sciences, 7(1), 89-94.
- Verma, S. & Dubey, R. S.,** 2003. *Lead toxicity induces lipid peroxidation and alters the activities of antioxidant enzymes in growing rice plants.* Plant Science, 164, 645–655.
- Vrana, K., Rapant, S., Bodis, D., Marsine, K., Mankovska, B., Curlik, J., Sefcik, P., Daniel, J., Lucivjansky, L., Lexa, J. & Pramuka, S.,** 1997. *Geochemical atlas of the Slovak Republik at a scale of 1: 1,000,000.* Journal of Geochemical Exploration, 60, 7–37.
- Wang, S.Y., Yu, T.Q., Wang, J.L., Yang, L. & Lu, P.,** 2008. *Preliminary Study on spatial Variability and distribution of Available Micronutrients in Pinggu County, Beijing, China.* Agricultural Sciences in China, 7(10), 1235-1244.
- Webster, R. & Nortcliff, S.,** 1984. *Improved estimation of micronutrients in hectare plots of the Sonning Series.* Journal of Soil Science, 35, 667-672.
- Webster, R., Atteia, O. & Dubois, J.,** 1994. *Coregionalization of trace metals in the soil of Swiss Jura.* European Journal of Soil Science, 45, 205–218.
- Webster, R.,** 2001. *Statistics to support soil research and their presentation,* European Journal of Soil Science, 52, 331-340.
- White, J. G., Welch, R. M. & Norvell, W. A.,** 1997. *Soil zinc map of the USA using geostatistics and geographical information systems.* Soil Science Society of America Journal, 61, 185–194.
- Xu, S. & Tao, S.,** 2004. *Coregionalization analysis of heavy metals in the surface soil of Inner Mongolia,* Science of The Total Environment, 320, 73-87.
- Yemefack, M., Rossiter, D. G. & Njomgang, R.,** 2005. *Multi-scale characterization of soil variability within an agricultural landscape mosaic system in southern Cameroon.* Geoderma, 125, 117–143.
- Yu, L., Xin, G., Gang, W., Qiang, Z., Qiang, S. & Guoju, X.,** 2008. *Heavy metal contamination and source in arid agricultural soil in central Gansu Province, China.* Journal of Environmental Science, 20, 607–61.
- *** Ministry of Environment and Urbanism 2003. *Regulations on Soil Pollution Control and Point Source Contaminated Sites.* Available http://www2.cevreorman.gov.tr/yasa/y/27605_ek.doc.

Received at: 21. 11. 2011

Revised at: 04. 02. 2012

Accepted for publication at: 13. 02. 2012

Published online at: 15. 02. 2012

