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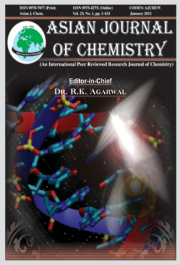

Application of Geostatistical Methods to Heavy Metals Status in Çarsamba Plain Soils

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The understanding of the spatial variability of soil heavy metals is an important precondition for potential contamination risk and evaluating eco-environment quality in a primary arable soil. To date, little research on soil pollution in Çarsamba delta plain has been conducted. To identify the concentrations and sources of heavy metals, 174 soil samples (0-20 cm) were collected from the study area. Subsequently, the concentrations of Cd, Co, Cu, Ni, Pb and Zn in the samples were analyzed. In order to evaluate natural or anthropogenic sources of heavy metal content and their spatial distribution in agricultural fields of Çarsamba delta plain and near district soil, statistics, geostatistics and geographic information system (GIS) were used. GIS technology was employed to produce spatial distribution maps of the 6 elements. The results showed that the concentration of Ni exceeded its threshold level. The local pollution from Ni was attributed to the natural and anthropogenic influences. The concentrations of the other heavy metals are relatively lower than the critical values. The mean values of the heavy metal contents arranged in the following decreasing order: Ni > Zn > Cu > Co > Pb > Cd in the study area. In some regions of the study area, the Cd, Cu and Zn contents were also slightly raised, possibly due to excessive P fertilization and field traffic.

Key Words: Soil pollution, Spatial distribution, Çarsamba delta plain.

INTRODUCTION

Accumulation of heavy metals in arable soils is important because of the potential transfer of heavy metals through crops to animals (feed crops) and humans (food crops and vegetables)[1]. To this respect Cd, Cu, Co, Ni and Pb are important elements, not only because of the long term accumulation in humans but also because of the high potential for root uptake and accumulation in above ground plant parts. Some soil physico-chemical conditions such as pH, organic matter and lime content, texture play a very important role in toxicity of heavy metal in the soil[2]. Physical and chemical soil properties may depend on several factors, both natural and anthropogenic ones, jointly acting over different spatial and temporal scales. Natural pedological processes (*e.g.*, rock weathering and organic matter decomposition) are related to parent material, geomorphology of the area, presence of vegetation, the climate conditions and other interactions with the environment[3]. In addition, anthropogenic sources of heavy metal contamination are mainly combustion processes in industry, transportation and waste water from industrial processes. Moreover, mining activities for extraction and manufacturing of metal products and long-term and extensive use of agricultural land with frequent application of pesticides may result in a large amount of pollutants to be released into the atmosphere and, secondly, in the adjoining soils and waters[4]. Therefore, natural factor and human activity are both important in determining the complex spatial variability of heavy metal concentrations in soil[5]. A soil pollution assessment becomes very difficult when different sources of contamination are present and their products are variably distributed. In these cases, geostatistical application of the heavy metal concentrations in soils has vital role for risk assessment, soil remediation, as well as effective management recommendations and widely applied in soil since 1980. Prediction methods to reliably estimate heavy metal distribution in space and time should be based on spatial variability of soil properties. Geostatistical methods that are based on the theory of regionalized variables[6-8] can provide reliable estimates at the unsampled locations provided that the sampling interval resolves the variation at the level of interest[9]. Recently, the kriging interpolation method has been used increasingly in spatial distribution of heavy metals by many researchers[10-12].

The spatial variability of soil heavy metals is an important part of environmental supervision and ecosystem evaluation[13]. The main objective of this study is to determine contents of heavy metal status and physico-chemical properties of soil using statistics, geostatistics and geographical information system (GIS) techniques, in order to find out heavy metal scale variability and spatial distribution maps and provide valuable information for the regional soil quality management.

EXPERIMENTAL

Field description of the study area: This study was carried out in Samsun-Çarsamba delta plain and near district. The Çarsamba plain found in the Yesilirmak delta and located in the central Black Sea region of Turkey (Fig. 1). The study area is far 30 km from west of the Samsun province (4560-4580 km N-780-840 km E UTM), it covers 210987.5 ha and its lies at an elevation from sea level 0-650 m. The current climate in the region is semi-humid. The summers are warmer than winters (the average temperature in July is 23.5 and in January is 6.2 ºC). The mean annual temperature, rainfall and evaporation are 14.3 ºC, 1045.2 and 739.1 mm, respectively. According to soil survey staff[14], the study site has mesic soil temperature regime and ustic moisture regime. These areas are mainly flat, slightly sloped (0.0-2.0 %) and hilly. The majority of soils on alluvial lands were vertisol, inceptisol and entisol in soil taxonomy. In their soil properties, top soil texture is heavy (13-65 % clay), while sub soil texture is different due to alluvial deposit in the study area. Soil organic matter content ranges from 0.90 % to 4.12. electrical conductivity and pH values of soils are changing 0.24-0.91 dS m^{-1} and 7.80-8.16. Flat land of the study area has been under intensive agricultural activities. Rice, maize, pepper, watermelon, cucumber and tomato with sprinkler and furrow irrigations in the summer and cabbage and leek in the winter have been produced in the study area.

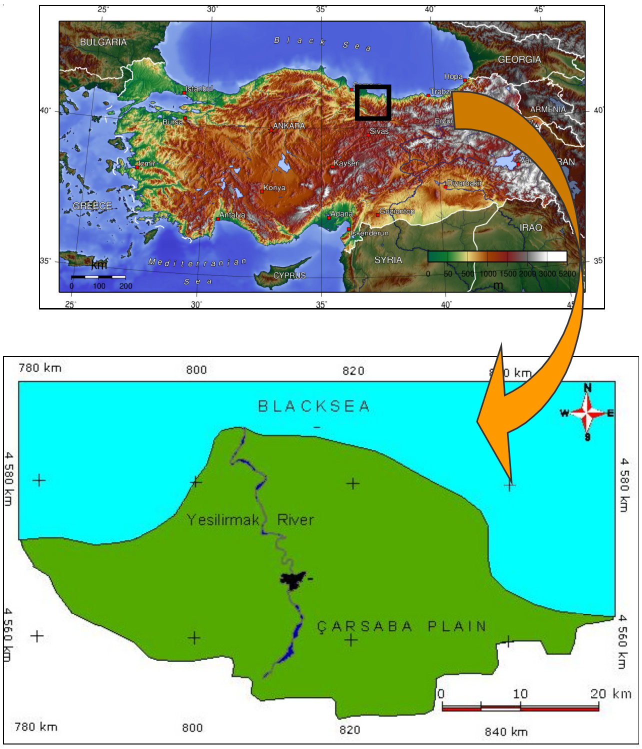


Fig. 1. Location of the study area

Soil sampling: Soil samples were obtained in the July of 2009. The sites divided into 2000 m × 2000 m grid squares (Fig. 2). The total of 174 grid points was obtained and soil samples were collected at 0-20 cm depths of each grid center. The samples were transported to the laboratory. The soil samples were crumbled gently by hand without root material. These samples were used to determine physico-chemical and heavy metal concentrations of soils.

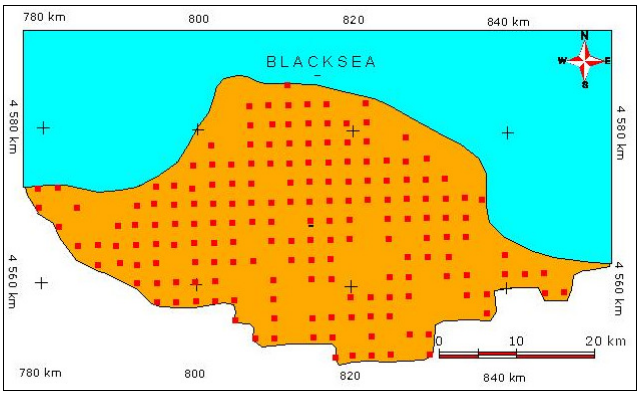


Fig. 2. Soil sampling design on the study area

Physico-chemical analyses of soil: Physico-chemical analyses were conducted on air-dried samples stored at room temperature and from which crop residues, root fragments and rock larger than 2 mm in diameter had been removed. Selected physico-chemical properties of soil were determined by the following methods: soil particle size distribution by the hydrometer method, pH and electrical conductivity (EC) in 1:2.5 (w/v) in soil:water suspension by pH-meter and electrical conductivity-meter and $CaCO_3$ content by the volumetric method, total nitrogen (N) by the Kjeldal method, available phosphorus (P) by 0.5M $NaHCO_3$ extraction method, exchangeable potassium (K) by the 1N ammonium acetate extraction method[15]. All soil samples were sieved through a 150 mm mesh before determining the total organic matter content by the wet oxidation method (Walkley-Black) with $K_2Cr_2O_7$[16].

Heavy metal concentrations in soil: The soil samples were dried in the oven at 110 ºC for 24 h. For the sake of homogeneity, samples were sieved using 0.074 mm sieves. Weighted soil samples were transferred into acid baths. The acids and their spent volumes used for this study were 15 mL HCl (12 M) and 5 mL HNO_3 (14 M) for each sample (10:1 extractant to soil ratio). On a hot plate, the samples were heated at 120 ºC. After observing reddish gas exit from the heated samples and making sure that the prepared samples are almost dry, the samples were removed from the hot plate. A 10 mL HCl (12 M) and HNO_3 (14 M) mixture (both were 1 % v/v) was added to each sample. Whatman filter papers were used to filter the prepared samples into the test tubes. For quality control/quality assurance purpose, the same steps were taken without using any soil samples. For each heavy metal of concern, three standards were used for completing the analyses using a Perkin Elmer A400 model atomic absorption spectrophotometer[17].

Statistical analysis

Statistical and geostatistical analyses: Data analyses for each grid were done in three steps: (i) normality tests were applied (Shapiro-Wilks); (ii) distributions were described with classical statistics (arithmetic mean, standard deviation, arithmetic maximum and minimum mean and coefficient of variation, CV) and heavy metal concentrations of soil were compared with *t*-test; (iii) for each variables, range, nugget and sill variance values were determined using semi-variograms. Maps of variables were produced by kriging technique[7]. Normality tests were performed by SPSS 11.0.

Geostatistical software (GS+ 7.0, 2001) was used to construct semivariograms and spatial structure analysis for variables. The hypothesis and parities by Burgess and Webster[18]. Semivariance is defined as the half of estimated square difference between sample values in a given distance (lag)[19].

The degree of spatial dependence of a random variable $Z(x_i)$ over a certain distance can be described by the following semivariogram function:

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

where $\gamma(h)$ is the semivariance for the interval distance class h, N(h) is the number of pairs of the lag interval, $Z(x_i)$ is the measured sample value at point i and $Z(x_i + h)$ is the measured sample value at position (i + h). All geostatistical analyses were performed with the GS^+ package program. GS^+ has several models that can be fitted to estimate semivariograms, but in this study, we used the isotropic spherical model:

$$\gamma(h) = C_0 + C\cdot\left[1.5\cdot\left(\frac{h}{A_0}\right) - 0.5\cdot\left(\frac{h}{A_0}\right)^3\right] \qquad h \le A_0$$

$$y(h) = C \quad + C \qquad h > A_0$$

we used the isotropic exponential model:

$$\gamma(h) = C_0 + C.\left[1 - \exp\left(\frac{-h}{A_0}\right)\right]$$

Also, we used the isotropic Gaussian model:

$$\gamma(h) = C_0 + C\left[1 - \exp\left(\frac{-h^2}{A_0^2}\right)\right]$$

where; C_0 is the nugget variance ≥ 0, C is the structural variance ≥ C_0, $(C_0 + C)$ is the sill variance and A_0 is the range of spatial correlation.

Correlation analysis: Pearson correlation analyses were performed using SPSS 11.0 statistical software (SPSS Inc.). The asterisks, *, ** and *** indicate significant at $p < 0.05$, 0.01 and 0.001, respectively.

RESULTS AND DISCUSSION

Physico-chemical properties of soil: Some physico-chemical properties of soil such as pH, salinity, electrical conductance and soil texture and other important factors have vital role on heavy metal accumulation in soil. As Loganathan[20] and Loganathan and Hedley[21] stated a long term application of superphosphate fertilizer onto soils impacts total cadmium and extractable cadmium concentrations in soil depending on amount of organic and inorganic matters especially types and availability of clay minerals. Table-1 shows the minimum, maximum, mean and coefficients of variation of chemical and physical properties of soil samples. The values of pH in soil samples ranged between 4.48 and 7.92, whereas electrical conductivity had a minimum value of 0.13 dS m^{-1} and a maximum value of 1.86 dS m^{-1}. All sampling points have low $CaCO_3$, with the exception of 33, 69, 92 and 136 samples which have more than 10 % $CaCO_3$. The mean value of organic matter and $CaCO_3$ content (%) were 2.88 and 2.42. The percentage of clay, silt and sand content ranged between 2.90-69.54, 4.14-54.84 and 3.02-91.98, respectively. Available P and exchangeable K showed high variation between minimum and maximum values. Total N varied between 0.05 and 0.45 and the average value of total N was 0.16.

Heavy metal concentrations in soils: Data indicate that not only the basic soil properties show great variation but also the heavy metal content in soils. Table-2 shows maxima, minima, means, variance, standard deviations and coefficient of variation of the total and available heavy metal (cadmium, cobalt, copper, nickel, lead and zinc) contents. Total concentrations of heavy metals ranged as follows: Cd (0.22-11.7), Co (7.19-65.12), Cu (9.51-176.54), Ni (8.63-240.90), Pb (5.72-45.0) and Zn (16.16-104.37) mg kg^{-1}. In Table-3, maximum permitted values of heavy metal concentration in agricultural soils that have been evaluated by Kloke[17] are shown. In all cases, soil samples from the area studied had higher maxima values of heavy metal concentrations than those permitted from the Kloke[17], except for Pb and Zn concentrations. Ni concentration is higher than maximum permitted values in 60 % of soil samples whereas, only less than 3 % of soil sample has high Cd, Co and Cu concentration.

Spatial variability: Geostatistics provides a set of statistical tools for incorporating spatial coordinates of observations

TABLE-1
MAXIMA, MINIMA, MEANS, VARIANCE, STANDARD DEVIATIONS (SD), COEFFICIENT OF VARIATION (CV), SKEWNESS AND KOURTOSIS OF THE SOIL PHYSICO-CHEMICAL PROPERTIES STUDIED (n = 174)

	Mean	Variance	SD	CV	Max.	Min.	Skewness	Kourtosis
Clay	40.75	193.86	13.92	34.16	69.54	2.90	0.00	0.00
Silt	33.86	88.59	9.41	27.79	54.84	4.14	-0.14	-0.49
Sand	25.37	255.40	15.98	62.98	91.98	3.02	1.27	1.82
pH	6.60	0.67	0.82	12.44	7.92	4.48	-0.58	-0.72
EC	0.45	0.05	0.22	48.33	1.86	0.13	2.72	13.42
$CaCO_3$	2.42	12.15	3.49	144.20	14.70	0.08	1.77	2.16
Organic matter	2.88	2.00	1.41	49.08	13.96	0.48	3.54	23.69
Total N	0.16	0.00	0.06	39.19	0.45	0.05	1.44	3.40
Available P	8.09	148.54	12.19	150.71	79.24	0.22	3.58	15.13
Exchangeable K	63.57	2303.33	47.99	75.50	255.00	8.00	2.18	5.14

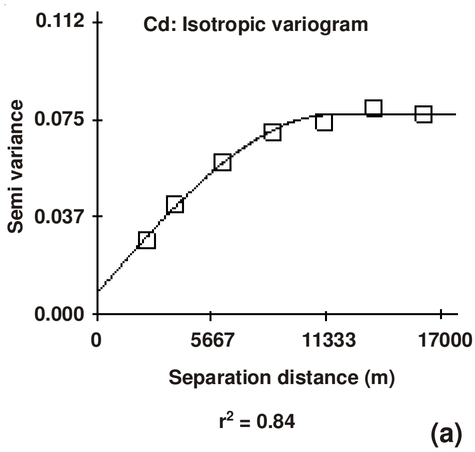
TABLE-2
MAXIMA, MINIMA, MEANS, VARIANCE, STANDARD DEVIATIONS (SD), COEFFICIENT OF VARIATION (CV), SKEWNESS AND KOURTOSIS OF THE HEAVY METALS STUDIED (n = 174)

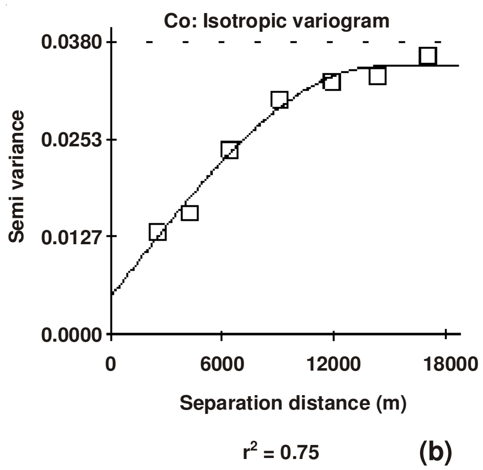
	Mean	Variance	SD	CV	Max.	Min.	Skewness	Kourtosis
Cd	1.32	0.72	0.85	64.06	11.07	0.22	8.91	102.14
Co	25.09	91.89	9.59	38.20	65.12	7.19	1.60	3.15
Cu	47.85	682.10	26.12	54.58	176.54	9.51	2.44	8.21
Ni	87.14	3643.69	60.36	69.27	240.90	8.63	0.52	-0.92
Pb	22.47	26.77	5.17	23.03	45.00	5.72	0.74	3.44
Zn	62.58	257.84	16.06	25.66	104.37	16.16	-0.28	0.04

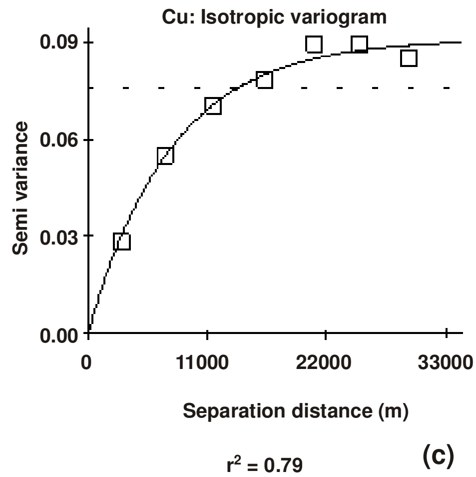
TABLE-3
MAXIMUM PERMITTED VALUES OF HEAVY METAL CONCENTRATION IN AGRICULTURAL SOILS THAT HAVE BEEN EVALUATED FROM KLOKE[17]

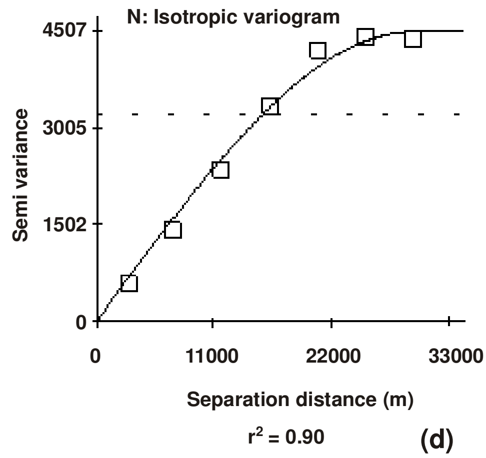
Heavy metals	Maximum permitted values (mg kg^{-1})	Heavy metals	Maximum permitted values (mg kg^{-1})
Cd	3	Ni	50
Co	50	Pb	100
Cu	100	Zn	300

in data processing[22]. Geostatistics provides a tool for the optimum sampling design and interpolation on unsampled locations, taking into account the spatial correlation of adjacent pixels based on the semi-variance. This procedure is optimal in the sense that estimates are unbiased and the estimation variance is minimum[23]. Four models were tested to fit the semi-variogram models in this study. While, the isotropic spherical model showed the best fitting value for the computed semi-variance points for Cd, Co, Ni, Pb and Zn, isotropic exponential model showed suitable for Cu (Fig. 3 and Table-4).









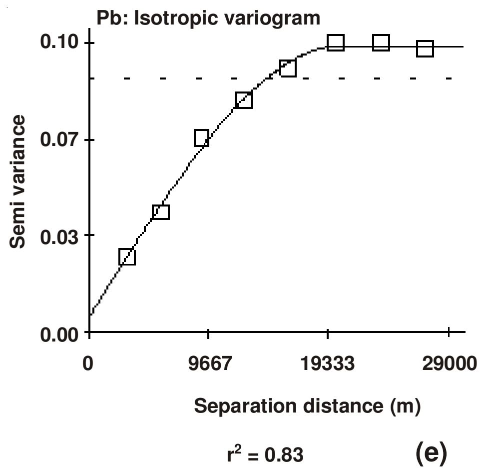


TABLE-4
PARAMETERS OF ISOTROPIC MODELS FOR BEST FITTED SEMI-VARIOGRAM MODELS OF HEAVY METAL CONCENTRATION IN SOILS

	Nugget (C_0)	Sill ($C_0 + C$)	Range (m)	r^2	RSS	Model	$C_0/(C_0 + C)$	
Cd	0.0083	0.0772	11570	0.993	1.60E-05	Spherical	0.11	Strong
Co	0.00489	0.03488	14430	0.984	8.22E-06	Spherical	0.14	Strong
Cu	0.0001	0.086	23250	0.984	4.50E-05	Exponential	0.00	Strong
Ni	10	4507	29740	0.993	143476	Spherical	0.00	Strong
Pb	0.0051	0.097	20480	0.995	2.77E-05	Spherical	0.05	Strong
Zn	26.3	230	18170	1	11.3	Spherical	0.11	Strong

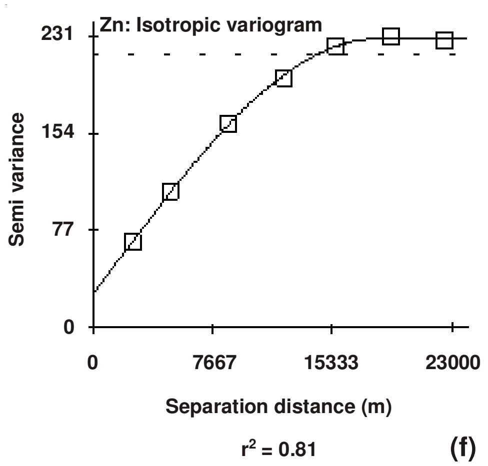
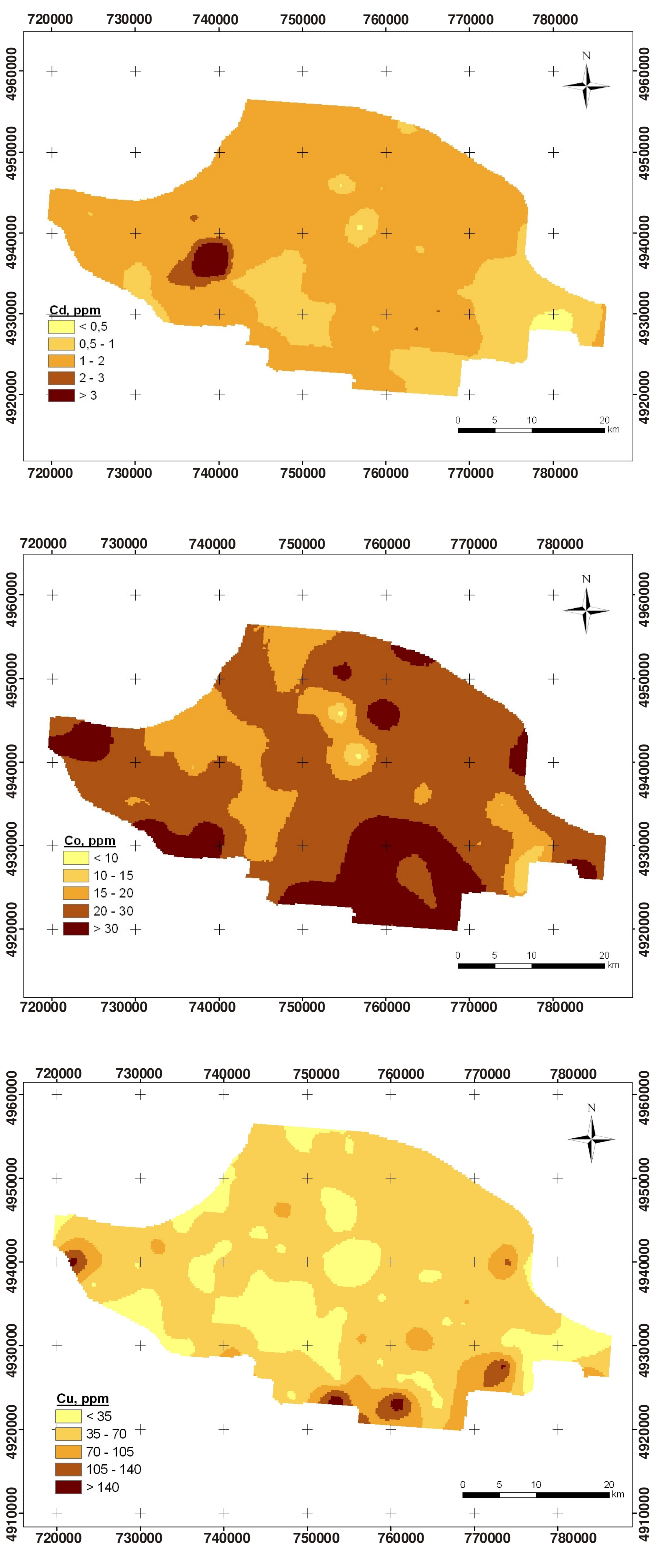


Fig. 3. Experimental semi-variograms for each heavy metals: (a) Cd; (b) Co; (c) Cu; (d) Ni; (e) Pb and (f) Zn



The experiment semi-variogram depicts the variance of the sample values at various separation distances[24]. 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 %) plays an important role in spatial heterogeneity of soil properties. In this study, the nugget value of less than 26.3 and the low ratio of nugget to sill (less than 25 %) for Co, Cu, Cd, Pb, Ni and Zn indicated the existence of a strong spatial auto-correlation for these elements (Table-4).

The distribution maps of risk elements including Cd, Co, Cu, Ni, Pb and Zn concentrations are illustrated in Fig. 4 and distribution of heavy metals in the study area is given in Table-5. As seen from the maps and Table-4, almost all heavy metal element concentration was found as low level except for Ni concentration (Table-3). On the other hand, to evaluate sensitively accumulation of heavy metals in the study area, all elements were classified as five levels. Results show that only nickel concentration exceeded limited level in soils taken from middle and north parts of the delta plain; 77.6 % of the study area has more than 50 mg kg^{-1}. It was thought that this result is related with parent material (volcanic) of soils that were formed from alluvial deposit which include high amount of nickel and industrial effect on some part of the study area. As Brohi[25] and Chen[26] noted nickel concentrations are found 20-40 fold higher in volcanic-based soils than that in normal soils.

However, all the others element concentration was found under line the threshold level. The highest total cadmium concentration (2-3 mg kg^{-1}) was found in southwestern part of the

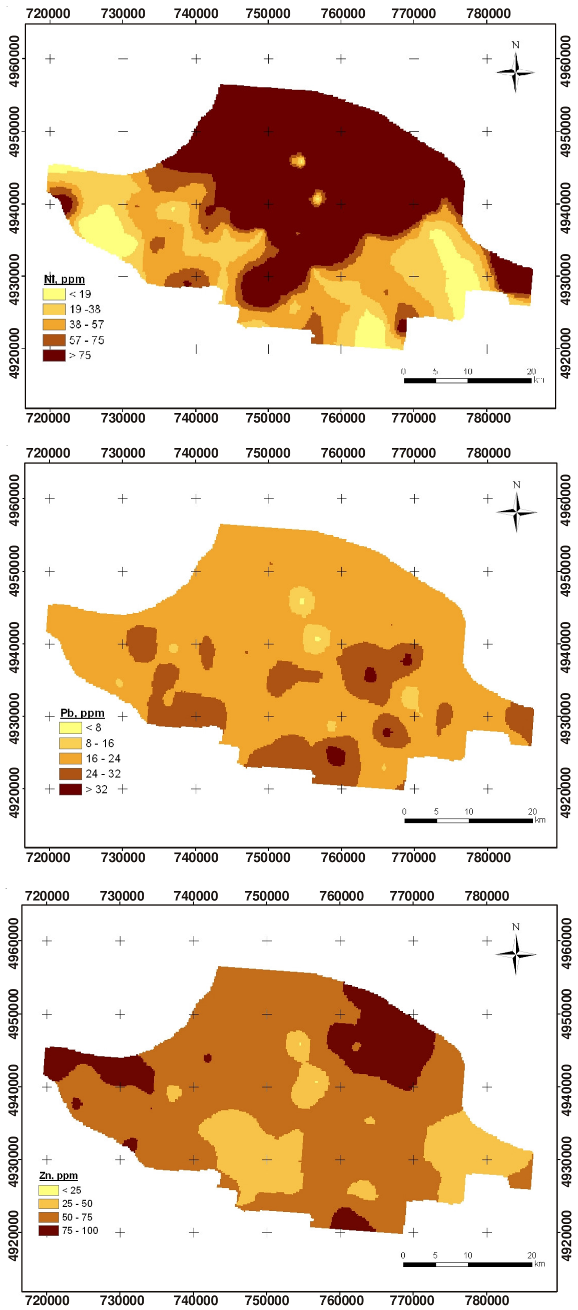


Fig. 4. Interpolation mapping of heavy metal enrichment factor in Çarsamba delta plain

study area that covers 2.5 % of the total area. In addition, the natural concentration of heavy metals in arable soil depends primarily on the geological parent material composition[1,27]. It has been shown that the application of P fertilizer to soils can be an important source of Cd[28,29]. Therefore, the long term application of P fertilizer can probably cause the accumulation of Cd in the topsoil of arable lands. However, exceed threshold level (> 3 mg kg^{-1}) area of Cd accumulation is very small (1.1 %) in the total study area. Accumulation of Cu concentration (more than 100 mg kg^{-1}) is located on sought parts of the study area that covers 2.1 % of total area. This is most probably caused by extensive use of pesticides that contain copper. Secondarily, traffic might be responsible for higher amounts of copper accumulated in soil, especially closer locations to the roads (Çarsamba-Samsun highway). The highest accumulation lead (16-24 mg kg^{-1}) that is very lower than threshold level located on middle and south parts of the study area (77.1 % ha). This area is also closer to the Çarsamba-Samsun highway. It is clear that others sampling locations have almost negligible amount of lead. Distribution of the highest accumulation place for cobalt is located of south parts of the study area and that covers 19 % of the total area. In addition, the highest accumulation (more than 75 mg kg^{-1}) place for zinc covers 13.8 % of the study area.

Correlation analysis: The correlation analysis was carried out to determine relationships between soil physico-chemical properties and enrichment factor in soils and given in Table-6. Soil conditions such as pH and texture play a very important role in the availability of cadmium in the soil[30-33]. Mico[32] stated that the levels of organic matter, high percentages of clay and the presence of carbonate seem to suggest an important retention of heavy metals by these components. In addition, some soil properties such as salinity[34] could facilitate the mobility of some trace elements (*e.g.*, Cd, Cu). Significantly negative relationships between sandy, silty and clay texture and Cu, Zn and Pb were found whereas, significantly positive relationships were determined between silty texture Cd. Heavy metal accumulation in sandy soils is generally low due to leaching process. pH, electrical conductivity and $CaCO_3$ are important factors for heavy metal accumulation in soil. There are liner positive relations between Cd and electrical conductivity, whereas it was found negative relation between Cu, Zn and these factors.

Conclusion

These results present the spatial pattern of Cd, Cu, Pb, Co, Zn and Ni in Çarsamba delta plain using statistics, geostatistical analysis and geographic information system to attain the natural and anthropogenic effects such as industrial effluents, agricultural activities, *etc*. on heavy metal pollution in arable soils. Especially, geostatistical analysis has been successfully applied in investigating and mapping soil pollution by heavy metals, in recent years[35]. At any rate, human activities may increase the content of heavy metals in the soil to reach levels that are considered to be hazardous. Although the geological conditions of the region (carbonated lithologies which give rise to a high pH) favour the fulfillment for agricultural on soils with pH > 7, mainly for metals like Cu, Pb and Zn, their concentration in soil can increase due to an intensification of farming practices and may locally reach contaminating levels under other edaphic conditions[36]. Therefore for most of the elements there was some slight increase above the background values and in a very few cases the soils can be considered as slightly contaminated. Risk assessments based upon[17] limits prove that the soil is a serious health risk to humans. In this study, the mean values of the heavy metal contents arranged in the following decreasing order: Ni > Zn > Cu > Co > Pb > Cd. In some regions of the study area, the Cd, Cu and Zn contents were slightly raised, possibly due to excessive P fertilization and field traffic. Such studies could help validate procedures of spatial predictions that have limited measured data. This may be suitable for many problems in soil monitoring where heavy metal changes are relatively small and slow.

TABLE-5
DISTRIBUTION OF ENRICHMENT FACTOR OF HEAVY METALS IN THE STUDY AREA

Heavy metals	Class (mg kg^{-1})	Area (ha)	Ratio (%)	Heavy metals	Class (mg kg^{-1})	Area (ha)	Ratio (%)
Cd	< 0.5	1581.2	0.7	Ni	< 19	13875	6.6
	0.5-1.0	42125	20.0		19-38	33468.7	15.9
	1.0-2.0	162050	76.8		38-57	40918.7	19.4
	2.0-3.0	2900	1.4		57-75	18256.25	8.7
	> 3.0	2331.3	1.1		> 75	104468.8	49.5
Co	< 10	93.7	0.0	Pb	< 8	137.5	0.1
	10-15	2912.5	1.4		8-16	5187.5	2.5
	15-20	39350	18.7		16-24	162606.3	77.1
	20-30	128512.5	60.9		24-32	41293.7	19.6
	> 30	40118.7	19.0		> 32	1762.5	0.8
Cu	< 35	42537.5	20.2	Zn	< 25	25	0.0
	35-70	148862.5	70.6		25-50	38637,5	18.3
	70-105	15231.2	7.2		50-75	143243.8	67.9
	105-140	3931,2	1,9		> 75	29081,2	13,8
	> 140	425	0,2		–	–	–

TABLE-6
RELATIONSHIPS BETWEEN SOIL PHYSICO-CHEMICAL PROPERTIES AND ENRICHMENT FACTOR IN SOILS

Soil properties	Cd	Co	Cu	Ni	Pb	Zn
Clay	0.113^{ns}	-0.058^{ns}	-0.151^{ns}*	0.317^{ns}	0.264^{ns}	0.164^{ns}
Silt	0.024*	-0.077^{ns}	-0.099$^{ns\ ns}$	0.088^{ns}	-0.015*	-0.208^{ns}
Sand	-0.113^{ns}	0.097^{ns}	0.190$^{ns\ ns}$	-0.328^{ns}	-0.221^{ns}	-0.020*
pH	0.145^{ns}	-0.211^{ns}	-0.263^{ns}*	0.464^{ns}	-0.139^{ns}	0.148^{ns}
EC	0.018*	-0.236^{ns}	-0.264$^{ns\ ns}$	0.326^{ns}	-0.064^{ns}	-0.029*
$CaCO_3$	0.168^{ns}	-0.274^{ns}	-0.184^{ns}*	0.203^{ns}	-0.073^{ns}	-0.065^{ns}
Organic matter	-0.039*	-0.004**	0.116^{ns}*	-0.048*	0.148^{ns}	-0.030*
Total N	-0.008**	-0.095^{ns}	0.023***	0.007**	0.120^{ns}	0.109^{ns}
Available P	-0.090^{ns}	-0.165^{ns}	-0.068^{ns}*	-0.010**	-0.127^{ns}	0.152^{ns}
Exchangeable K	-0.019*	0.024*	0.098^{ns}*	0.102^{ns}	-0.060^{ns}	0.295^{ns}

ns: not significant, *$p < 0.05$, **$p < 0.01$.

Finally, this paper contributes to the knowledge of the content and potential source of heavy metals in agricultural soils of the Çarsamba delta plain, which is a representative area of the middile part of the Black Sea region

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