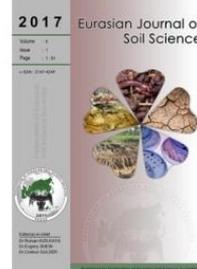




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Spatial distribution of heavy metals density in cultivated soils of Central and East Parts of Black Sea Region in Turkey

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Abstract

Heavy metal contamination has caused serious environmental and health-related problems around the world. To identify the concentrations and sources of heavy metals, 3400 surface soil samples (0-20 cm depth) were collected from the study area. Subsequently, the concentrations of Cd, Co, Cu, Ni, Pb and Zn in the samples were measured. In order to evaluate natural or anthropogenic sources of heavy metal content and their spatial distribution in agricultural fields of Central and East Parts of Black Sea Region soil geostatistic approach were combined with geographic information system (GIS). GIS technology was employed to produce spatial distribution maps of the 6 elements in the study area. The results showed that the concentration of Ni and Co exceeded its threshold level. The local pollution from Ni was attributed to the natural 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 > Pb > Co > Cd in the study area. On the other hand, according to distribution ratio of heavy metals in total soil samples, except for Co and Ni distribution in total soil samples, all other heavy metal element exceeded concentration in samples were determined about less than 10% total soil samples. However, in some regions of the study area, the Cd, Cu and Zn contents were also slightly raised, this case possibly stem from excessive P fertilization and field traffic.

Keywords: Heavy metal contamination, GIS, soil properties.

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Introduction

Metal accumulation in the soil is largely irreversible and may cause serious environmental problems health-related problems around the world if certain concentration levels are exceeded. The aim of sustainable heavy-metal management in agro-ecosystems is to ensure that the soil continues to fulfill its functions: in agricultural production, in environmental processes such as the cycling of elements, and as a habitat of numerous organisms (Moolenaar, 1999). In view of sustainability, a preventive and monitoring approaches based on predicting spatial and temporal soil heavy-metal contents is therefore promising. 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) (De Temmerman et al., 2003). 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 (Saglam et al., 2011; Datsenko and Khimenko, 2016).

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Heavy metal inputs into agricultural soils due to atmospheric deposition and application of commercial fertilizers, animal manure, sewage sludge and pesticides take place at rather slow rate but on large areas (Ali et al., 2017). Hence, it may take decades to detect accumulation trends in soil by repeated sampling. Such contamination may not be of concern in terms of immediate toxicity effects. Yet, it is the ubiquitous character and the increase of heavy metal flows through the soil system that may cause serious problem for soil fertility, ground water quality and food chains. Previous studies indicated that the extent of heavy metal pollution in rural areas varied across time (Pfeiffer et al., 1991) and location (Albasel and Cotteni, 1985), and that increased levels of heavy metals in cultivated soil was related to the intensity of agricultural activities and field traffic (Zheng et al., 2002; Kızılkaya et al., 2004).

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 (Journel and Huijbregts, 1978; Isaaks and Srivastava, 1989; Goovaerts, 1997; Kızılkaya et al., 2011) can provide reliable estimates at the unsampled locations provided that the sampling interval resolves the variation at the level of interest (Kerry and Oliver, 2004).

The objective of this study is determine contents of heavy metal status and physico-chemical properties of soils in agricultural fields of Central and East Parts of Black Sea Region in Turkey 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 about soil heavy metal pollution for this region.

Material and Methods

Field description of the study area

This study was carried out at arable lands of the central and eastern Black Sea Regions including eight provinces (Sinop, Samsun, Ordu, Giresun, Trabzon, Gümüşhane, Rize, Artvin). Total regions' area is about 5.075.413 ha. However, arable lands selected for this study cover about 32.8 % in total area (Figure 1).

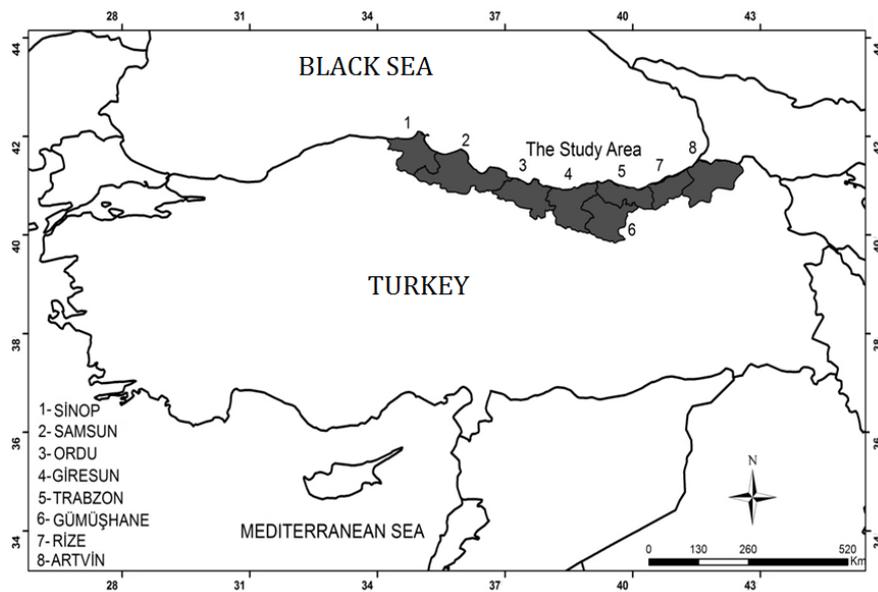


Figure 1. Location map of the study area

The Black Sea Region has a steep, rocky coast with rivers that cascade through the gorges of the coastal ranges. A few larger rivers, those cutting back through the Pontic Mountains, have tributaries that flow in broad, elevated basins. Access inland from the coast is limited to a few narrow valleys because mountain ridges, with elevations of 1525 to 1800 meters in the west and 3000 to 4000 meters in the east in Kaçkar Mountains, form an almost unbroken wall separating the coast from the interior. The higher slopes facing northwest tend to be densely forested. Because of these natural conditions, the Black Sea coast historically has been isolated from Anatolia.

Total heavy metal concentrations

The total heavy metal (HM) concentration for investigated each heavy metal elements was measured using the following procedure. The soil samples were preliminarily dried in a thermostat at 110°C for 34 h. They were sifted using a sieve with a mesh of 0.074 mm. The weighed soil samples were placed into a mixture of 12 M HCl and 14 M HNO₃ (the solution to soil ratio was 10:1). The soils were heated on a hot plate to 120°C. The heating stopped after a reddish gas was removed. The soils were dried. The HCl and HNO₃ mixture (10 ml) was added to each sample; then the samples were filtered through Whatman filters. A blank test was made to check the quality of the reagents. Three standards were used for the determination of each metal. The samples for the HM contents were analysed by the method of atomic absorption on a Perkin Elmer A400 spectrophotometer (Kloke, 1980).

Statistical and geostatistical analyses

The descriptive statistics of soil properties including sample mean, minimum, maximum and coefficients of variation were calculated. Moreover, in order to determine six heavy metal distributions and to produce their maps, inverse distance weighted (IDW) interpolation method that is one of the spatial analysis tools of geographic information systems (GIS-ArcGIS 10.0v) was used.

Results and Discussion

Soil physico-chemical properties

Physical and chemical properties that have been taken into consideration in this study showed variability as a result of dynamic interactions among natural environmental factors (degree of soil development and leaching processing etc.) and human activities such as fertilization management. Soil chemical and physical properties considered in this study are pH, EC, soil organic matter, total CaCO₃ content, total N, available P, exchangeable K, exchangeable Ca, exchangeable Na, exchangeable Mg, available Mn, available Zn, available Fe, available Cu and soil texture. The descriptive statistics as minimum, maximum, mean, and coefficients of variation of physic-chemical properties surface soil samples were presented in Table 1.

Table 1. Descriptive statistics of the soil physico-chemical properties studied.

Properties	Mean	Min.	Max.	S.D.	C.V., %	Skew.	Kurt.	n
Sand,%	41.62	1.61	91.98	16.66	40.04	0.08	-0.71	3400
Clay,%	29.98	2.49	79.23	13.67	45.60	0.33	-0.49	3400
Silt,%	28.39	1.10	65.78	7.96	28.03	0.38	0.97	3400
pH	6.28	3.14	8.50	1.33	21.24	-0.60	-0.98	3400
EC, dS m ⁻¹	0.47	0.05	3.08	0.29	62.67	2.86	14.70	3400
CaCO ₃ ,%	4.48	0.10	58.80	7.76	173.10	2.59	7.82	3400
SOM,%	3.35	0.30	12.91	1.74	52.02	1.41	2.86	3400
AP, mg kg ⁻¹	19.02	0.09	226.47	28.52	149.91	3.12	12.06	3400
TN, %	0.20	0.01	0.88	0.09	47.80	1.45	3.77	3400
K, cmol _c kg ⁻¹	0.57	0.02	4.65	0.45	78.93	2.60	12.04	3400
Ca, cmol _c kg ⁻¹	217.19	1.45	908.50	141.01	64.92	0.68	0.42	3400
Mg, cmol _c kg ⁻¹	29.18	1.66	224.64	28.58	97.94	2.67	9.63	3400
Na, cmol _c kg ⁻¹	5.70	0.47	77.61	5.94	104.12	4.09	25.45	3400
Fe, mg kg ⁻¹	36.56	0.75	278.32	35.16	96.19	1.96	5.43	3400
Cu, mg kg ⁻¹	2.55	0.03	29.31	2.20	86.05	2.89	17.29	3400
Zn, mg kg ⁻¹	1.26	0.03	25.98	1.98	156.75	5.05	36.42	3400
Mn, mg kg ⁻¹	31.12	0.10	227.98	29.47	94.70	2.36	7.24	3400

SOM: Soil organic matter, AP: Available phosphorus, TN: Total nitrogen, S.D: Standard deviation, C.V: Coefficient of variation

The values of pH in soil samples widely ranged between 3.14 and 8.50 that called from strong acid to moderately alkali soil reaction, whereas electrical conductivity had a minimum value of 0.05 dS m⁻¹ and a maximum value of 3.08 dS m⁻¹. Most of the all sampling points have low CaCO₃, with the exception of 5.4% of total soil samples which have more than 20% CaCO₃. The mean values of organic matter and CaCO₃ content (%) were 3.35 and 4.48. As for macronutrient element of samples, available P and exchangeable K showed

high variation between minimum and maximum values. Total N varied between 0.01 and 0.88 and the average value of total N was 0.20. The mean values of Ca, Mg, and Na concentration were found 217.19, 29.18 and 5.70 cmol_c kg⁻¹, respectively. In addition, Table 1 shows statistical distribution of micronutrient elements (Fe, Cu, Zn and Mn) concentration of samples. According to limit values reported by Lindsay and Norvell (1978), Fe and Cu were found in sufficient amounts in all of the soil samples and their mean values are 36.56 and 2.55 mg kg⁻¹, whereas all samples were insufficient in respect to available Zn content and its mean value is 1.26 mg kg⁻¹. Besides, 12% of samples were insufficient in respect to available Mn and it has high variation between minimum and maximum values (0.10-227.98).

Heavy metal concentrations in cultivated soils

The 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 heavy metal (cadmium, cobalt, copper, nickel, lead, and zinc) contents. Total concentrations of heavy metals ranged as follows: Cd (0.04-34.65), Co (1.52-97.50), Cu (2.60-308.13), Ni (2.19-1063.99), Pb (3.65-444.91) and Zn (0.81-552.89) mg kg⁻¹. In Table 3, maximum permitted values of heavy metal concentration in agricultural soils that have been evaluated by Kloke (1980) are shown. In all cases, soil samples from the area studied had higher maxima values of heavy metal concentrations than those permitted from the Anonymous (2001). Ni and Co concentrations are higher than maximum permitted values in 25% and 73% of soil samples, respectively whereas, only less than 3% of soil samples have high Cd, Pb, Zn and Cu concentration.

Table 2. Maxima, minima, means, variance, standard deviations (SD), coefficient of variation (CV), Skewness and Kurtosis of the heavy metals studied (n=3400).

	Cu (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Ni (mg kg ⁻¹)	Cd (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Co (mg kg ⁻¹)
Min.	2.60	0.81	2.19	0.04	3.65	1.52
Max.	308.13	552.89	1063.99	34.65	444.91	97.50
Mean	44.73	57.51	62.15	1.26	29.27	25.57
Kurt.	5.91	42.76	50.91	112.71	116.75	5.61
Skew.	1.94	4.60	5.87	9.13	8.88	1.35
CV	65.58	60.65	133.50	145.22	72.15	38.72
SD	29.33	34.88	82.97	1.84	21.12	9.90
Variance	860.34	1216.5	6884.3	3.37	445.99	98.00

Table 3. Maximum permitted values of heavy metal concentration in agricultural soils that have been evaluated from Anonymous (2001).

Heavy metals	Maximum permitted values (mg kg ⁻¹)
Cd	3
Co	20
Cu	140
Ni	75
Pb	300
Zn	300

Spatial distribution of heavy metals

One of the spatial analysis tools of geographic information systems (GIS) is geostatistical analysis module. In order to determine 6 heavy metal distributions and create their maps in the study area, ArcGIS 10.0v interpolation model called IDW was used. Many researchers indicated that this technique is a suitable interpolation method for general assessment purposes and a potential timesaving alternative to current survey methods for generating distribution maps (Lo and Yeung, 2002; Roberts et al. 2004; Dogan et al. 2013). The interpolated maps of heavy metal elements including Cd, Co, Cu, Ni, Pb and Zn concentrations are illustrated in Figures 3-8. As seen from the maps and Figures, almost all heavy metal element concentration was found as low level except for Ni and Co concentrations in the study area. Almost the same results were detected by Saglam et al. (2011) in Çarşamba Delta Plain in order to evaluate natural or anthropogenic sources of heavy metal content and their spatial distribution in agricultural fields.



Figure 3 - Interpolation mapping of copper in the study area



Figure 4 - Interpolation mapping of zinc in the study area

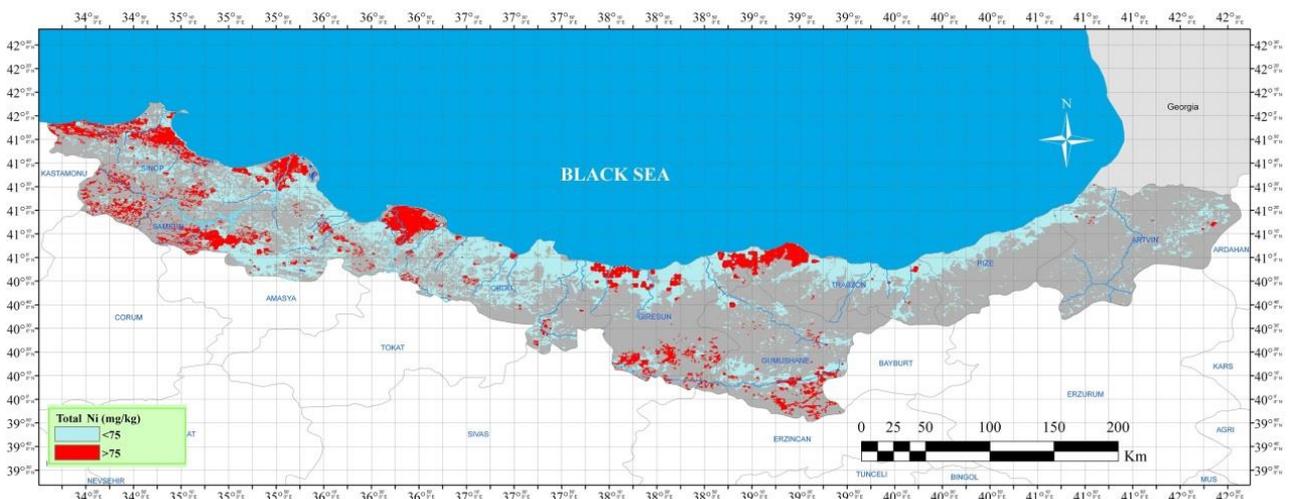


Figure 5. Interpolation mapping of nickel in the study area

Distribution of the total sample numbers for each eight provinces was given Table 4. In order to assess the results for these provinces, the Regulation for the Control of Soil Pollution (Anonymous, 2001) was taken into consideration for threshold level heavy metals presented in Table 3. Results also show that copper

concentrations exceeded the threshold level in soils taken from Samsun, Ordu, Giresun, Gümüşhane, Trabzon and Artvin. However, sample amount and ratio are lower than 2%. In addition to that, it was not found exceeded the threshold level in soils taken from Sinop and Rize provinces. The zinc and lead concentrations of arable land soils in all provinces were found to be under the threshold levels or less than 1%.

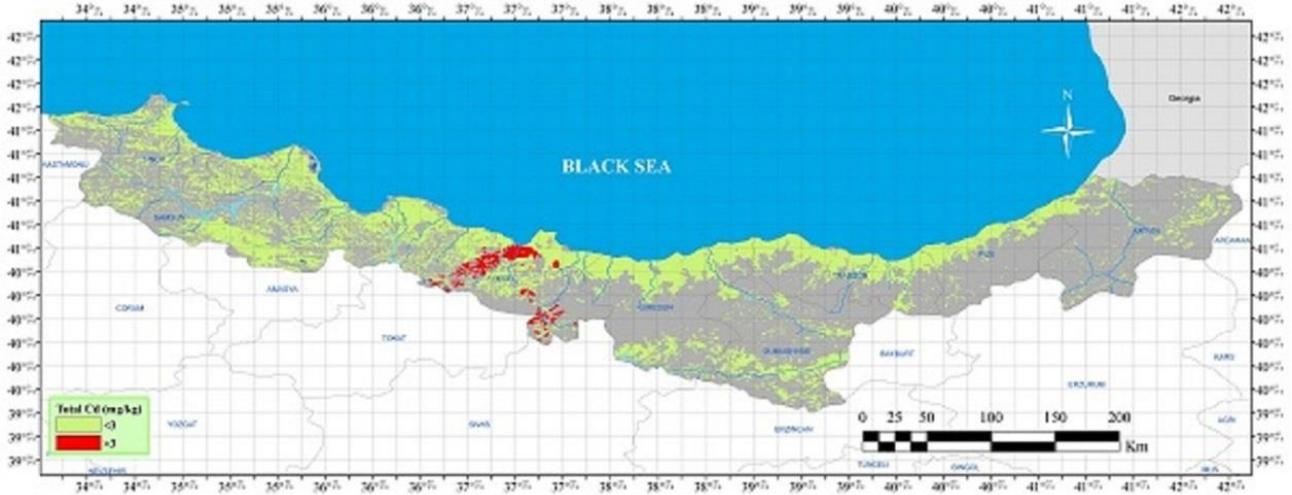


Figure 6. Interpolation mapping of cadmium in the study area

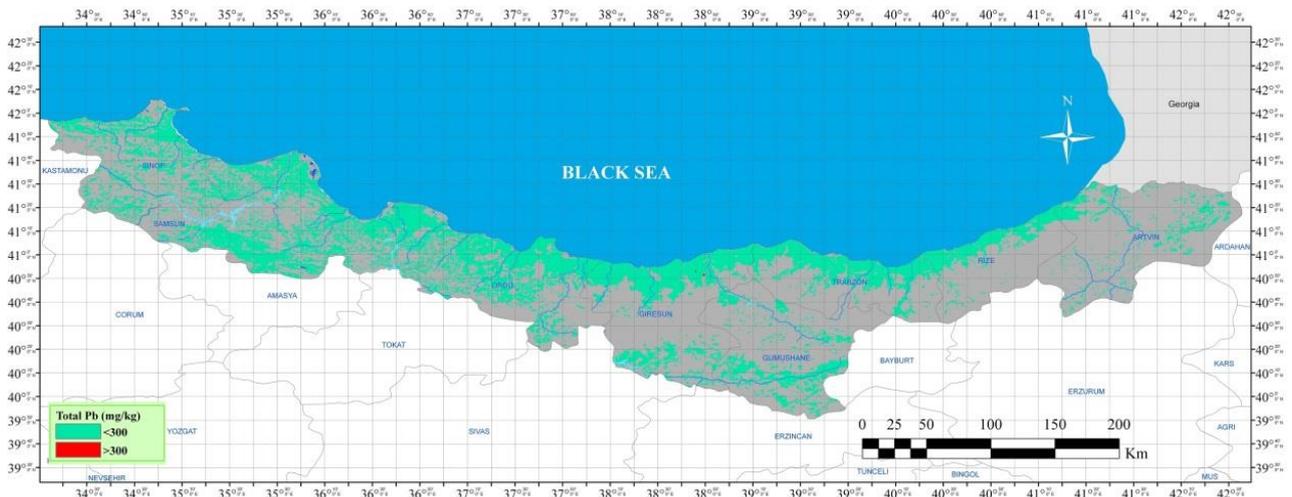


Figure 7. Interpolation mapping of lead in the study area

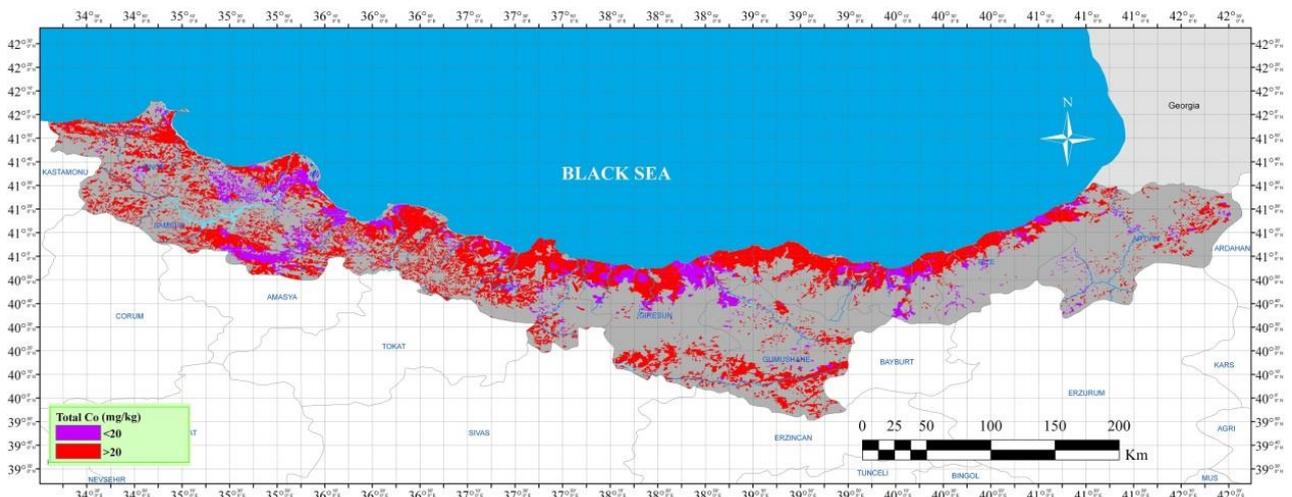


Figure 8. Interpolation mapping of cobalt in the study area

Table 4. Total sample number for each provinces' arable land and exceed threshold level of sample number and ratio for each heavy metal (HM).

HM	Provinces and their total sample number															
	Sinop		Samsun		Ordu		Giresun		Gümüşhane		Trabzon		Rize		Artvin	
	432	889	596	466	319	371	159	168	#	%	#	%	#	%	#	%
Cu	--	--	7	2	9	2	14	3	6	2	6	2	--	--	2	1
Zn	--	--	--	--	--	--	5	1	4	1	2	1	--	--	--	--
Ni	241	56	300	34	36	6	98	21	90	28	78	21	2	1	11	7
Cd	--	--	11	10	98	16	--	--	--	--	--	--	--	--	--	--
Pb	--	--	--	--	--	--	4	1	--	--	--	--	--	--	--	--
Co	375	87	571	64	478	80	318	68	256	80	259	70	113	71	123	73

Moreover cadmium concentration were not determined exceeded the threshold level in soils taken from all studied provinces except for Samsun and Ordu including less than 16%. Nickel concentration exceeded limited level in soils taken from all investigated arable land soils. But it shows very variable from province to province. The highest common distribution of nickel concentration that is over limited value were determined in cultivated soils of Sinop whereas, only 1% of the total samples located in Rize province was found exceed threshold level. Cobalt is the same as nickel and it is also very common in the study soil samples. On the other hand, it doesn't show very variable and about more 65% soil samples taken from all provinces exceeded limited level.

Conclusion

The present study examined the distribution and spatial parent of heavy metals in the agricultural fields located in Central and East Parts of Black Sea Region 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. These region soils have generally acidic reaction and their pH values are low and very low (5.5-4.5) due to high precipitation and leaching process (Ozyazici et al., 2011). As expected, solubility of heavy metal concentration increased with a decrease in pH (Martinez and Motto, 2000). 31% of the total soil samples (1092) have low pH (< 5.5). Except for Co and Ni distribution in total soil samples, all other heavy metal elements were determined about less than 10% in soil samples and they have not common places in the study area. Therefore, natural contents of heavy metals in arable soils depend primarily on its geogenic source from the parent materials in the area. However, changes in composition are possible during transport of heavy metal containing dust particles and, for some elements, also agricultural practices (Kloke, 1980). Particularly, the Cd, Cu and Zn contents were slightly raised, possibly due to excessive P fertilization, wrong fertilizer addition to low pH soil like ammonium sulphate (to increase acidity leading to high solubility) and field traffic. In addition it was found only Ni concentration over the threshold level. It is thought that this high level of Ni concentration dose not stems from the contaminations, but that this result is related to the parent material of the soils that were formed from magmatic rocks which include high amounts of nickel.

Such studies could help validate procedures of spatial predictions that have limited measured data. This may be suitable for many problems and contributes to the knowledge of the content in soil monitoring where heavy metal changes are relatively for large area such as agricultural soils of the Central and East Part of the Black Sea Region.

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