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Letters to Editor

Detection of Heavy Metal Concentrations in Soil Caused by Nigde City Garbage Dump

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Abstract

The aim of this study was to detect heavy metal concentrations in the creek which passes through Nigde city garbage dump. In this respect, the soil samples collected in the study area by GPS were analyzed using X-Ray Fluorescence Spectrometer. Traces of heavy metals were observed by using statistical programs on analysis results. Geological observations were taken into consideration.

According to the heavy metal concentrations in the Creek, the maximum values were as follows; (mg/kg) Ti: 4960, V: 520, Cr: 120, Mn: 810, Ni: 460, Cu: 410, Zn: 100 and Pb: 480. The concentration levels of heavy metals in soil caused by garbage dump are listed in the following order; Pb > Cu > V > Ti > Cr > Ni > Zn. High positive correlation were observed between Ti-Mn, V-Ni and Cr-Ni. Medium positive correlations were observed between V-Cr, V-Cu and Ni-Zn. It has been found by chemical analysis data collected from stations established throughout the creek that there is an effect of morphological structure and no geological anomaly has been formed. According to chemical analysis results, statistical programs give important accuracy. Heavy metals, which give anomaly, differ throughout the creek. The source of these heavy metals was determined as Nigde city garbage dump. For this reason, it was suggested that, in order to refine the study area, a modern, organized storage system must be used instead of wild storage system in storing the urban wastes, and recyclable products must be used in the industry.

Keywords: heavy metals, contamination, garbage, Nigde

Introduction

Soil can be defined as "a natural body consisting of generally unconsolidated layers or horizons of mineral and/or organic constituents of variable thickness which differ from parent rock; in morphological, physical, chemical and mineralogical properties" [1].

The number of studies on heavy metal concentrations of urban waste has recently increased [2-5]. Routine studies for detection of heavy metals in sediment samples continue rapidly [6-10]. Findings heavy metal levels of sediments in creek beds and river beds is an important indicator for the detection of environmental contamination [4]. Piling of urban wastes continually in one area causes a considerable increase of heavy metals in soil [11-12]. Serious hazards come into existence in soils which are exposed to heavy metal contamination and the improvement of such areas constitutes one of the main problems [13-14]. Soil research conducted in urban areas give significant information on ecological balances (growing of plants, ground water plates, heavy metal content, etc.) [15]. Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, and Pb are main pollutant metals among heavy metals. Decays caused by these heavy metals have been observed in many plant species examined in laboratories and natural environments. It is known that among the heavy metals, Co, Cd and Ni decrease photosynthesis and inhibit, prevent stomatal

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activity [16-17]; Cd, Cr, Zn and Mn cause necrosis and chlorosis [18]; Cu, Hg, Cd, Mn, Co and Zn prevent seed sprouting [19-20]; Ni, Hg, Cd, Cu and Pb disturb hormonal balance [21-22].

For this reason we wanted to detect heavy metal concentrations in the creek which passes through Nigde city garbage dump. In this respect, heavy metal concentrations which disturb the ecological balance were studied. The region has an important place as a result of agriculture and husbandry activities performed throughout and down The Creek. The average concentration levels of pollutant heavy metals in the upper crust, Northern Europe soil, crust and boundary values accepted by Turkish Ministry of Environment Soil Contamination Regulation are given in Table 1.

Experimental

Study Area

Nigde province is located in (37° 10-N, 33° 10 W) the Central Anatolia Region, among Central Taurus Mountains. Five different tecto-stratigraphical units exist in relation to geology, lithology, structural position and age. These units are: Nigde group, Aladag Group, Ulukisla-Eregli Group, Melendiz Group, and Quaternary Group [27]. Lower levels of the Tertiary units are from Paleocene-Lutetian aged and composed of flysch structured sandstone, limestone shale, mudstone and siltstone alternated. These units are called Camardi Formation. Pontian (Upper Miocene) aged lake sediments formed by gray clayey limestone, mudstone, clay and marl alternation overlain uncomfortably on Camardi Formation. These units, which cover extensions in the study area, are called the Gokbez Formation. Ignimbrites of Lower Pliocene that overlay the Gokbez Formation are lateral -vertical transitional with this formation. This unit, which is called Incesu Ignimbrite, is the oldest member of the Melendiz Group. A small amount old alluviums, hillside debris and large amount of current alluvion gather on all these units. Alluviums are usually composed of loose pebble, sand, mil, and clay (Quaternary) [28-32].

The garbage dump of Nigde province is 10 km away from city centre and covers an area of 0.1 km^2. It is 1 km away from new residential centre. Agriculture and husbandry activities are performed in topographically lower portions of the study area. Surface waters in and around

Table 1. The concentration levels of pollutant heavy metals in upper crust [23], the soil [24], boundary values accepted by Turkish Ministry of Environment [25] and Northern Europe [26] (mg/kg).

Elements	Nigde Garbage		Upper Crust [23] (C)	Northern Europe Soil [26] (D)	Crust [24]	Acceptable limit [25]	B/A	B/C	B/D
	Unpolluted Soil Mean (A)	Polluted Soil Mean (B)							
Ti	2286.7	4649	3117	2601	5 000	-	**2**	**1.5**	**1.8**
V	38.3	178	53	37	110	-	**4.6**	**3.4**	**4.8**
Cr	31.7	81	35	32	100	100	**2.6**	**2.3**	**2.5**
Mn	523.3	669	527	426	1000	-	**1.2**	**1.3**	**1.6**
Ni	15.3	133	18.6	10	75	30	**8.6**	**7.2**	**13.3**
Cu	15.7	222	14.3	10	50	50	**14**	**15.5**	**22.2**
Zn	53.3	74	52	43	70	150	**1.4**	**1.4**	**1.7**
Pb	16.7	267	17	17	12.5	50	**15.9**	**15.7**	**15.7**



Fig. 1. Garbage dump and area in which the leakage water flows in (arrows show the flow direction of leakage water).

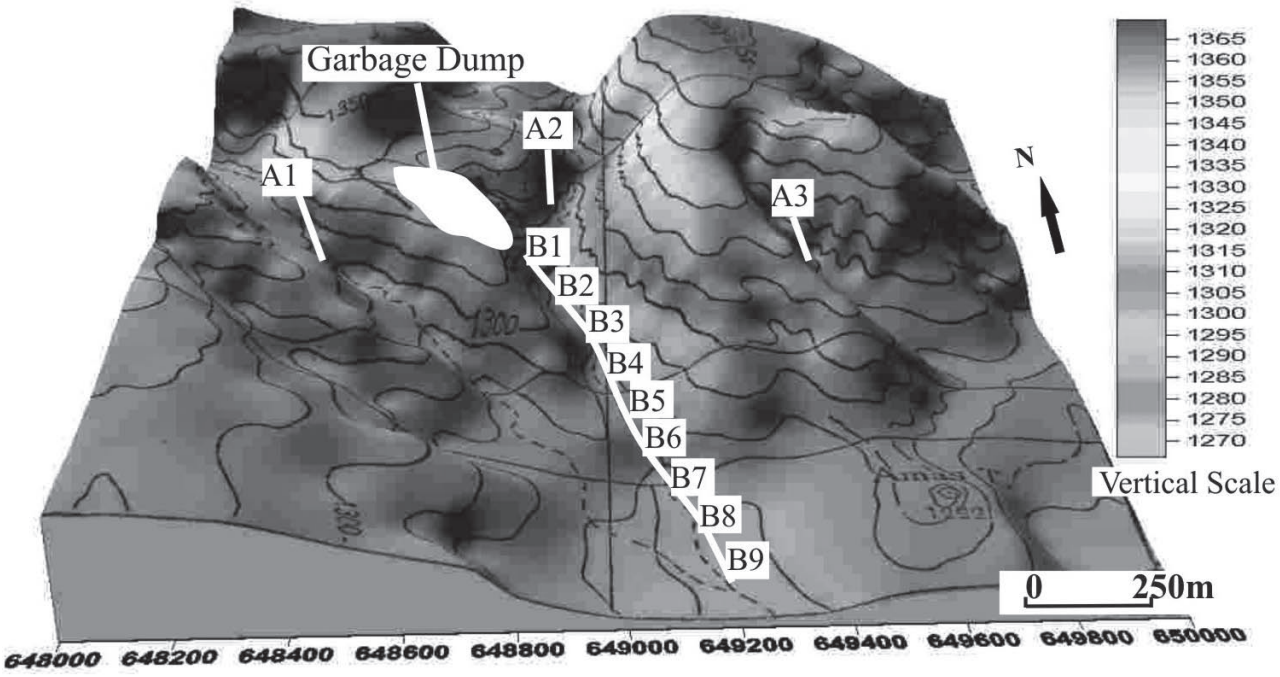


Fig. 2. Study area and samples locations.

the garbage dump flow in agricultural and husbandry areas, which are situated near the study area (Fig. 1). Since the year 1990, a daily average of 250 tons of garbage have been collected from houses and offices located in Nigde city borders and dumped in garbage dump using primitive storage methods. Collected garbage is stored in garbage dump using primitive storage methods. The contents of this garbage are as follows: 10% paper, nylon, pet bottle; 5% metals like sheets and cans; 1% cloth, bone; 15% ash (October-May, winter months); and 69% domestic garbage. A daily 150-200 kg amount of paper, plastic, metal, etc. have been collected for recycling purposes [33].

Sampling and Analyses

A total of 12 soil samples were collected; 9 samples from the area that lies from the creek which runs through the garbage dump located on the Gokbez Formation to the valley, and 3 from the western, eastern, and northern portions that are outside the garbage dump and topographically higher (Fig. 2). The area which was thought to be polluted because of Nigde garbage dump was defined as the creek passing through the dump and reaching the valley. Soil samples belonging the polluted area were taken from the creek. Unpolluted soil samples were taken from the region at the upper levels of garbage dump which was close to the damp, but garbage was not effective. Samplings were collected in May 2006. Each specimen taken was marked on the sampling map using Magellan brand SporTrac GPS. All samplings were taken in 5-10 cm depth from the surface. Samples which are called group B were taken throughout the creek in which the leakage water from the garbage dump flows in. First sampling was systematically taken in every 100 m beginning from the boundary of garbage dump. Samples which are called group A were taken as reference samples from western, eastern, and northern portions (A1, A2, and A3) of study area of garbage dump and area which is outside its sphere of influence, and to explain the geological characteristics of the area. All soil samples were taken with a stainless steel specimen shovel. Samples were kept in plastic bags for analysis.

Soil samples were dried in drying oven at 105°C for 24 hours to dispose humidity. Dried samples were strained through the 2 mm plastic sieve and separated from pebbles. Afterwards, samples were formed into average 2 mm> particles by homogenizing them in an agate mortar. Double sided film tablets of 32 mm in diameter were prepared from each specimen. For Ti, V, Cr, Mn, Ni, Cu, Zn and Pb elements, measurements in samples tablets were made in electronic control system with spectro xepos bechtop x-ray fluorescence spectrometer. Both group results obtained from chemical analysis results were compared. The source of heavy metal was commentated according to this comparison.

Results

The direction of ground water in garbage dump and its surrounding area is south by southwest. Average level of ground water is 50 m from the surface [32]. The direction of ground water is consistent with the creek that runs through the garbage dump. Sulfurous spring water observed in the garbage dump is affected from the garbage dump [34]. Surface waters are completely drained in natural ways. Rain waters that drop on garbage dump and

surface waters in the surrounding area flow in the creek, and they flow into the agricultural areas that topographically constitute the lowest portion of the creek.

The result of the chemical of the soil samples collected from the study area is presented in Table 2. Samples marked as A1, A2 and A3 were taken from the region outside the effective area of garbage damp area. However, samples marked as B1, B2, B3, B4, B5, B6, B7, B8 and B9 were taken from the polluted region that is under the effect of garbage damp. Table 2 shows minimum, maximum and average values of heavy metal contents of these samples.

Maximum values of heavy metal concentrations (Table 2) in the creek that runs through the garbage dump and concentration levels of heavy metal concentrations in the crust (Table 1) [24] are as follows (mg/kg): Ti: 4960-5000, V: 520-110, Cr: 120-100, Mn: 810-1000, Ni: 460-75, Cu: 410-50, Zn: 100-70 and Pb: 480-12.5. When ratios in the crest are taken into consideration, heavy metals like V, Cr, Ni, Cu, Zn and Pb have shown anomaly, whereas Ti and Mn have not. These elements observed in the study area are the leading reasons of pollution.

According to the chemical analysis results, arithmetic average values of A1, A2, and A3 samples which have been taken to detect the rate of heavy metals in garbage dump and area which is outside its sphere of influence have been observed as follows: (mg/kg) Ti: 2286.7, V: 38.3, Cr: 31.7, Mn: 523.3, Ni: 15.3, Cu: 15.7, Zn: 53.3 and Pb: 16.7. When the average of analysis results of A1, A2 and A3 compared with the average of analysis results of B1, B2, B3, B4, B5, B6, B7, B8 and B9 exchange rate in soil has been observed as follows; Ti: 2, V: 4.6, Cr: 2.6, Mn: 1.2, Ni: 8.6, Cu: 14, Zn: 1.4 and Pb: 15.9. Similar results were obtained and all the metals studied have shown anomaly. In this respect, exchange rates that belong to the study area were given in Fig. 3.

The relationship between the heavy metals in chemical analysis results of 9 soil samples collected from the study area was tested according to correlation analysis [5; 35] technique 1% and 5% importance level (Table 3). In the table that was created to determine positive and negative correlation between elements determined according to chemical analysis results, there were no elements with high or middle level negative relation. However, high and middle level positive relation was determined. Elements showing positive relation and their relation levels were given as this: There is high level of positive correlation between Ti-Mn, V-Ni and Cr-Ni (r Ti-Mn=0.942 [Sig(2ta)=0.057], $r_{V\text{-}Ni}$=0.854 Sig(2ta)=0.003], r Cr-Ni=0.824 Sig(2ta)=0.006]). There is a medium level of positive correlation between V-Cr, V-Cu and Ni-Zn ($r_{V\text{-}Cr}$=0.742 Sig(2ta)=0.022], $r_{V\text{-}Cu}$=0.688 Sig(2ta)=0.041], $r_{Ni\text{-}Zn}$=0.752 Sig(2ta)=0.020]).

Hierarchical Cluster Analysis dendogram of the samples collected from 9 stations in the route were drawn by taking account of distance coefficient according to their chemical analysis results [5]. In view of this dendogram, groups of stations no. 3, 4, and 5 were connected to the groups of stations no. 6 and 7. These groups were the most alike stations among themselves. Stations no. 8 and

Table 2. The results of the chemical analysis of the soils samples from the study area (mg/kg) Nigde Garbage Soil.

		Ti	V	Cr	Mn	Ni	Cu	Zn	Pb
Unpolluted	A1	2340	35	30	530	15	16	50	20
	A2	2330	40	35	520	16	17	60	10
	A3	2190	40	30	520	15	14	50	20
mean		**2286.7**	**38.3**	**31.7**	**523.3**	**15.3**	**15.7**	**53.3**	**16.7**
Polluted	B1	4960	520	120	810	460	410	100	250
	B2	4680	370	90	680	130	260	70	190
	B3	4510	120	80	630	80	330	60	180
	B4	4460	160	60	640	70	260	70	230
	B5	4450	90	70	590	80	290	80	310
	B6	4460	90	90	620	120	100	90	480
	B7	4470	90	70	550	70	90	70	370
	B8	4950	80	60	760	100	130	70	160
	B9	4900	80	90	740	90	130	60	230
Min		4450	80	60	550	70	90	60	160
Max		4960	520	120	810	460	410	100	480
Mean		**4649**	**178**	**81**	**669**	**133**	**222**	**74**	**267**

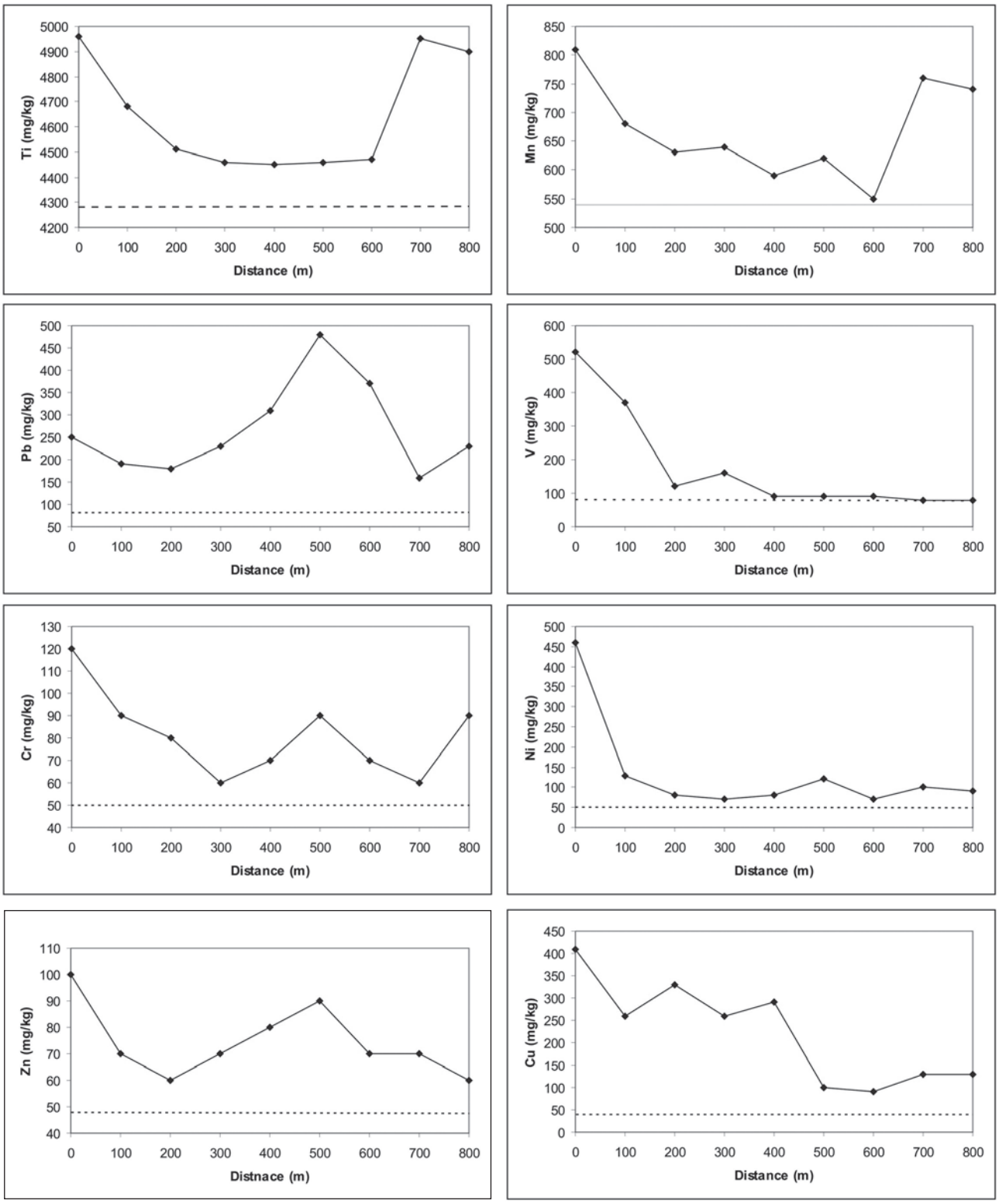


Fig. 3. Element-distance distribution of samples systematically taken according to distance from the area of garbage leakage water flow (- - - - - - – A group elements average).

9 were connected to the previous groups from the outside. Station no. 1 was connected to groups from the outermost. Among the other stations, stations no. 3, 4, and 5, in which the slope of hill was high, have showed similar characteristics. Stations no. 5 and 6, in which the slope of hill was lower than the previous stations, and stations no. 8 and 9, which have the lowest slope, have showed similar characteristics (Fig. 4).

A table has been formed according to Model Summary and Anova in Regression data [36] of chemical

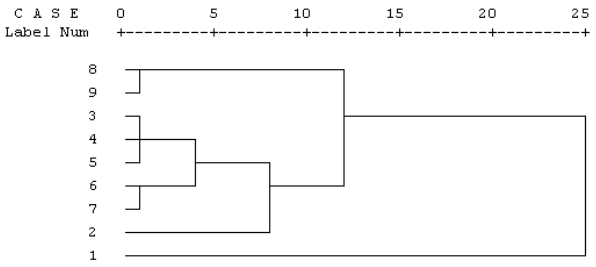


Fig. 4. Hierarchical cluster analysis dendogram of the soil samples in the creek that runs through the Nigde city garbage dump.

analysis results taken in relation to Pb (Table 3). The clarity level of regression equation for Model Summary is $R^2 = 99.1\%$ and it gives an important rate of accuracy. 7 (Zn, Ti, Cu, Cr, V, Mn and Ni) clarifying variant explain the exchange of Pb element according to Anova as high level.

Discussion

V, Cr, Ni, Cu, Zn and Pb. elements have shown anomaly when maximum levels of these data were compared with concentration levels in the soil [24; 34]. These elements which were observed in the study area are among the main reasons for the contamination. There is a Pb > Cu >V > Ti > Cr> Ni> Zn > Mn line up between the exchange rates of analysis results in soil. The exchange rates of pollutant heavy metals in the study area can be determined with their background values and samples distances (Fig. 3).

For the Ti, V, Cr, Mn, Ni, Cu and Zn elements, the points where the maximum contamination was detected in the samples taken from the area in which the contamination detected was observed in B1 specimen that was taken from the ending point of garbage dump. For the Pb element, it was observed in B6 specimen taken from the 500 m below the garbage dump.

It is considered that heavy metals which have high and medium levels of positive correlation can be from the same

Table 3. Correlation coefficients between metal concentrations.

	Ti	V	Cr	Mn	Ni	Cu	Zn	Pb
Ti	1.000							
V	.416	1.000						
Cr	.431	.742(*)	1.000					
Mn	.942(**)	.545	.516	1.000				
Ni	.550	.854(**)	.824(**)	.661	1.000			
Cu	.096	.688(*)	.432	.296	.588	1.000		
Zn	.101	.545	.570	.235	.752(*)	.306	1.000	
Pb	-.517	-.247	.110	-.526	-.047	-.427	.492	1.000

N:9; *Correlation is important at 0.05 level.; ** Correlation is important at 0.01 levels.

Table 4. Model summary and anova according to regression values.

Model summary						
Model		R	R Square	Adjusted R Square	Std. Error of the Estimate	
1		.996(a)	.991	.932	27.0974	
a Predictors: (Constant), Zn, Ti, Cu, Cr, V, Mn, Ni						
ANOVA(b)						
Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	85065.729	7	12152.247	16.550	.187(a)
	Residual	734.271	1	734.271		
	Total	85800.000	8			
a Predictors: (Constant), Zn, Ti, Cu, Cr, V, Mn, Ni						
b Dependent Variable: Pb						

origin. It was found that stations with similar characteristics include approximately the same amount of elements. No geologically different concentration was found (Fig. 4). Model Summary from multivarity statistical work explains why data give a value close to 100% and Pb in statistical means in Anova explains other heavy metals in a high ratio.

When polluted and unpolluted soil in Nigde city garbage damp region were compared, an increase in heavy metal ratios was observed. Because the heavy metal contents of unpolluted soil were concordant with the heavy metal ratios of upper crust soil, it was tought that the pollution in the region was not geologically based. When polluted soil is compared with upper crust and Northern Europe soils, an endogen-based pollution under the influence of Nigde city garbage dump was seen.

For data obtained by chemical analysis results, positive and negative relation between the elements were determined. No negative relations between the elements were found. However, there was a high and middle level relation between the elements. The elements that have high and middle level relation were thought possibly to be antropogenic in relation with garbage damp area. No negative relation shows that the sources of elements cannot be different. (Table 3)

In Turkey, 68% of domestic solid wastes are organic wastes, and the remaining percentage is composed of materials like paper, carton, textile products, leather, metal, wood, glass and ash. Among the 3215 municipalities in Turkey, only 11 of them use an organized garbage storage system. In Nigde, garbage storage is performed by wild storage system, where garbage is unloaded in an area randomly. For this reason, it will be appropriate to maintain organized garbage storage system over a medium or long term.

Refinement activities must be done for the non-recyclable products in the area which is considered to be the source of contamination in the study area. However, wastes like glass, paper, carton, plastic and metal must be reused as industrial products by recycling methods. These wastes must be used as sources of raw material in various sectors. Recycling the domestic wastes must be rearranged in accordance with the system by providing environmental awareness.

Conclusions

Five different tecto-stratigraphical units exist in the study area, which are formed regionally by Nigde group, Aladag Group, Ulukisla-Eregli Group, Melendiz Group, and Quaternary group.

V, Cr, Ni, Cu, Zn and Pb elements have shown anomaly according to the relationship between maximum levels of heavy metal concentrations in the creek which runs through the garbage dump and concentration levels in the soil. These elements which were observed in the study area are among the main reasons for the contamination. According to the samples collected from a clean area and heavy metal concentrations of the area which is under the influence of garbage dump, the exchange rates in the soil are lined up as follows among themselves: Pb > Cu > V > Ti > Cr > Ni > Zn > Mn.

According to the Hierarchical Cluster Analysis dendogram data of the chemical analysis results collected from the 9 stations, it was observed that there were similarities between the stations, differences have been formed morphologically, and there was no geological anomaly.

Surface waters in the Nigde province city garbage dump and leakage water caused by the chemical, biological and physical occurrences of the wastes have given rise to the accumulation of heavy metals. It was suggested that organized storage system must be used instead of primitive storage system in Nigde and other similar areas where primitive storage systems are used.

Recycling of wastes like glass, paper, carton, plastic and metal must be provided by refining the study area. Wastes must be recycled in the industry instead of being unloaded in storage areas.

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