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COMPARISON OF TRACE ELEMENT AND HEAVY METAL CONCENTRATIONS OF TOP AND BOTTOM SOILS IN A COMPLEX LAND USE AREA

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Abstract: The purpose of this study was to identify the heavy metal compositions in top and bottom soils in eastern parts of Mersin Province, which has a complex land use (industrial, agricultural and urban). Industrial and agricultural activities and settlement sites overlap in the subject area. 64 samples, 32 from each of 2 depths (0-15 cm and 100 cm), were taken in the scope of this study. Mineralogical compositions of soils were identified using XRD, main oxide components were identified using XRF and trace element and heavy metal components were identified using ICP-MS. Soil in the area is composed of mica, amphibole, serpentine, clay, feldspar, quartz, dolomite and calcite minerals. Clay mineral components are smectite, chlorite, illite and kaolinite; smectites are the prevalent type of clay found in the soil of the area. V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Sb and Pb heavy metals were analyzed. Cu, Zn, As, Cd, Sb and Pb heavy metals are noticeably enriched within the topsoil, while V, Cr, Mn, Fe, Co and Ni elements have similar distributions in top and bottom soil layers. Cu, Zn, Cd, Sb and Pb elements are likely abundant in topsoil due to high traffic and industrial activities. The abundance of As element in topsoil is due to agricultural activities. V, Mn, Fe, Cr, Ni and Co accumulated in top and bottom soils due to lithological factors in the study area.

Keywords: Topsoil; bottom soil; trace element and heavy metal concentration; environmental geochemistry

1. INTRODUCTION

The effects of first Industrial Revolution that started mid-18th Century and the 2nd Industrial Revolution that started in the early 20th Century are evident today in almost all countries around the world. As a result of these industrial revolutions, many natural and synthetic substances that had not been in use before have became a part of people's everyday lives. In parallel to industrial development, the majority of the population that once lived in rural areas began concentrating in urban areas, which had the natural consequence of regular and irregular release of the waste materials generated by dense populations into nature, resulting in heavy metal polluted soils. Heavy metal input to urban environments began in ancient times but the input considerably increased in the 1960s and thereafter (Coby et al., 2006). Heavy metal accumulations in soil can be lithological or anthropogenic or both (Krzysztof et al., 2004; Nadal, 2005; Zhang, 2006; Güler et al., 2010; Song et al., 2011; Sarı et al., 2013; Shao et al., 2014). Generally, As, Pb, Cd, Cu, Cr, Ni, Fe, Hg and Zn are the heavy metals that are associated with anthropogenic activities that generate soil pollution (Coby et al., 2006; Kumar et al., 2013; Yong & Mulligan, 2004).

The world's human population is increasing rapidly, especially in urban areas (Coby et al., 2006). As a result, agricultural areas, settlement areas, and areas with industrial activities are overlapping in many regions around the world today. Consequently, there is an intense pressure on soil and water resources due to pollution. Many studies carried out recently have revealed that there are notable heavy metal pollutions in soils at sites near urban and industrial areas (Nadal, 2005; Köleli & Halisdemir 2005; Lee et al., 2005; Zhang, 2006; Coby et al., 2006; Dao et al., 2010; Güler et al., 2010; Guillén et al., 2012; Kumar et al., 2013; Shao et al., 2014). As such, Mersin is a province that is located in southern Turkey on the shore of the Mediterranean Sea that is

experiencing rapidly increasing population and industrialization. In 1980, Mersin province had a population of 850,000 wih a rural area/urban area ratio of 50% to 50%. Today, the population is approximately 2,000,000 and the rural area/urban area ratio is 20% to 80%. These figures indicate that the increase of the provincial population is coupled with a great relative increase in urban population. The subject area of this study is located in the eastern part of Mersin Province where settlements, industrial facilities and agricultural activities are all present (Fig. 1). In the study area and it's immediate surroundings there is a glass factory, soda production factory, cement factory, automobile repair and service complex, fruit packaging and fruit juice factories, an organized industrial zone, marble factories, mine storage areas, industrial transportation stations, oil and petroleum products storage facilities, an abandoned oil refinery and thermal power station and a fertilizer factory as well as agricultural and settlement areas. The main pollutant factors for the soil and water resources of the area are the intensive agricultural and industrial activities as well as the settlement sites (Kurt, 2010).

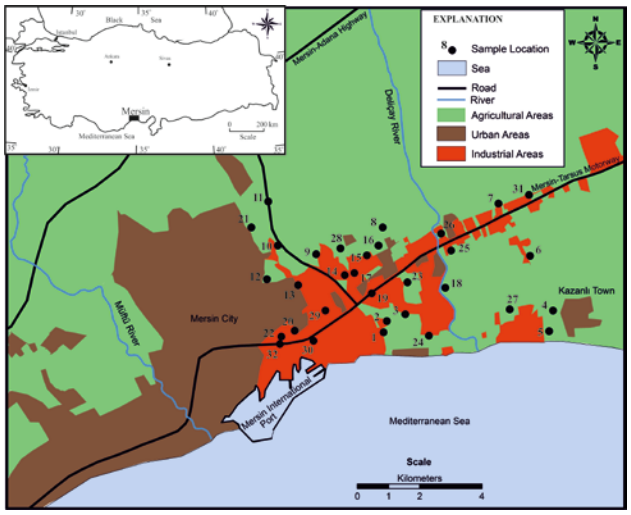

Figure 1. Land use map of the study area.

It has been concluded previously that the origins of heavy metals in the soil can be both lithological and anthropogenic (Kumar et al., 2013; Shao et al., 2014) and that one of the best way to identify the origin is profile distribution method (Blaser et al., 2000; Sterckeman et al., 2000; Shao et al., 2014). Consequently, profile distribution method was adopted in this study for the purpose of identifying the origins of the heavy metals in the soil of the area. Although there many studies have aimed to characterize the soil and water pollution in areas near the study area (Güler et al., 2010; Kurt, 2010; Köleli & Halisdemir, 2005; Kurt et al., 2012; Güler et al., 2012; Güler et al., 2013a; Güler et al., 2013b; Yıldırım & Güler, 2016) no study has investigaged this particular area, nor was profile distribution method used in the above-referenced studies.

Deltaic sediments of quaternary age are present in the study area. These deltaic sediments are fed from ophiolite and ophiolitic complications of Upper Cretaceous age, carbonate rocks of Jurassic-Cretaceous age and carbonate rocks of Tertiary age located in northern Mersin province.

2. MATERIALS AND METHODS

2.1. Soil sampling and preparation

For all geochemical studies, 32 topsoil samples (upper 15 cm) and 32 bottom soil samples (1 m) were collected from agricultural plots located around various industrial facilities and residences. Topsoil samples and bottom soil samples were collected at the same locations. Field work was completed within two days to rule out any seasonal effects. The sampling locations are shown in figure 1. All soil samples were taken by Edelman hand auger (Eijkelkamp Agrisearch Equipment, The Netherlands) and transported to the laboratory in tightly sealed 2-kg polyethylene bags to exclude loss or addition of moisture or pollutant. All soil samples were subsequently air-dried at room temperature and carefully disaggregated and homogenized in a ceramic mortar before sieving through a 2-mm nylon sieve to remove large particles and other debris. The <2 mm fraction was powdered in an agate mortar and used for further mineralogical (XRD) and geochemical (XRF and ICP-MS) analyses. All samples were preserved in nitric acid (20%) washed plastic tubes at 4°C laboratory conditions until analysis.

2.2. Reagents

37% HCl (Sigma Aldrich), 65% HNO_3 (Sigma Aldrich), 35% H_2O_2 (Sigma Aldrich) and 38-40% HF (Merck) were all of analytical grade. Ultra pure water (ELGA Purelab Prima, UK) was used in all procedures. The water used throughout the period of experimentation had a resistivity of 18 MΩ cm at room temperature.

2.3. Microwave-assisted digestion procedures

Microwave-assisted total digestion procedures were used in this study. Before each digestion, microwave polytetrafluoroethylene (PTFE) vessels were cleaned with 10 mL 65% HNO_3 heated for 10 min at 180°C (800W) in a microwave oven and

rinsed with ultrapure water. Topsoil samples and bottom soil samples were weighed to 0.25 g in microwave PTFE vessels. 6 ml HCl, 2 ml HNO_3, 1 ml H_2O_2 and 1 ml HF were added to the vessels. All samples were digested using the same microwave conditions (a 15-min gradual increase in temperature to 180°C, a 15-min step, at 180°C, 800W).

2.4. Analytical procedures

V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Sn, Sb, Ba and Pb element concentrations were determined in triplicate by Inductively Coupled Plasma–Mass Spectrometer (ICP-MS) after microwave-assisted total digestion. Inductively Coupled Plasma–Mass Spectrometer was an Agilent 7500ce ICP-MS (Agilent Technologies, Tokyo, Japan) equipped with Octopole Reaction System. The external standard calibration method was applied to all determinations using an internal standard mix (^{6}Li, ^{45}Sc, ^{72}Ge, ^{115}In and ^{209}Bi) in 2% HNO_3 matrix. NIST single-element reference standards were used to construct ten-point calibration curves. At regular intervals during analysis, calibration standards were analyzed to check accuracy. Extractant and ultra pure water blanks were frequently analyzed to check for contamination. Blanks were prepared and analyzed by completion of the full analytical procedure without samples. The analytical accuracy was checked by replicate measurement of several samples and by measuring certified reference materials. The relative error was less than ±4% for all results. SRM 2710 (Montana Soil) soil standard reference material was analyzed to check the recoveries of the method.

The clay fraction and mineralogical composition of samples was determined by a Rigaku Smart Lab (Japan) X-ray diffractometer (XRD). SiO_2, Al_2O_3, MgO, Na_2O, K_2O, CaO, Fe_2O_3 and P_2O_5 major oxides was determined by Rigaku ZSX Primus II (Japan) wavelength dispersive X-ray fluorescence spectrometer (WDXRD). Total organic matter contents of the soil samples were determined based on the Walkley-Black method (Walkley and Black 1934). Grain size distribution of the soil samples were determined based on the Bouyoucos hydrometer method (Bouyoucos, 1951).

3. RESULTS

3.1. Soil Mineralogy and Grain Size Distribution

A total of 64 samples, from 2 depths at 32 locations, were taken in order to characterize the mineralogy of the soils in the study area. Surface soil samples were taken from 0-15 cm while deep soil samples were taken from 100 cm depths. All soil mineralogies and clay components of the 64 soil samples were identified. Analyses indicated that soil samples were composed of mica, amphibole, serpentine, clay, feldspar, quartz, dolomite and calcite minerals. In clay component analysis graphs of soils, peaks of smectite, chlorite, illite and kaolinite type clay minerals were identified. According to clay mineralogy analysis, soils in the study area are composed of smectite, chlorite, illite, kaolinite and serpentine type clays. Smectite clays are generally the most common type of clays found in the soils of the area. In terms of mineralogy, there is no difference between the compositions of topsoil and bottom soil.

In terms of soil grain size, soils are composed of clay silt and sand-sized grains. In all soil samples, there is more soil of clay grain size than soil of sand grain size (Table 1). Amounts of organic substances in soils are given in Table 1. Generally, amounts of organic matter in topsoil and bottom soil are similar, both having low organic matter ratios (Table 1). In review of the physical characteristics of soils given in table 1, topsoil and bottom soil have similar physical characteristics.

And about the soil properties, Kurt et al., (2012) indicated that the region soil is alkaline soil type (the pH values vary between 7.5–8.5).

Table 1. Average, minimum and maximum degree of soil organic matter and grain size distribution of the soil samples.

		Soil Organic Matter (%)	Grain Size Distrubution		
			Clay (%)	Silt (%)	Sand (%)
TopSoil	**Mean**	**1.38**	**68.94**	**24.46**	**1.83**
	Minimum	1.16	64.71	21.57	0.00
	Maximum	2.57	73.52	34.67	5.34
Bottom Soil	**Mean**	**1.19**	**69.16**	**22.35**	**1.66**
	Minimum	0.35	67.05	20,64	0.00
	Maximum	2.41	76.87	31.19	4.89

3.2. Soil Geochemistry

32 samples of topsoil and 32 samples of bottom soil were taken from the study area for the purpose of soil geochemistry analysis. Average, minimum and maximum concentrations of major oxides of these samples are given in Table 2. Accordingly, soil samples contain SiO_2, CaO, Al_2O_3, MgO, K_2O, TiO_2, Na_2O and P_2O_5 main oxides in descending order of abundance (Table 2). As clearly seen in Table 2, topsoil and bottom soil have approximately the same concentrations of main oxides.

Table 2. Average, minimum and maximum concentrations of major oxides of soil samples.

		SiO_2 (%)	CaO (%)	Al_2O_3 (%)	MgO (%)	K_2O (%)	TiO_2 (%)	Na_2O (%)	P_2O_5 (%)
Topsoil	**Mean**	**40.81**	**27.30**	**10.83**	**4.33**	**2.15**	**1.20**	**0.33**	**0.34**
	Minimum	16.81	10.08	3.36	1.68	0.74	0.46	0.09	0.06
	Maximum	51.74	48.08	14.32	6.70	2.89	1.66	0.52	0.72
Bottom Soil	**Mean**	**41.19**	**25.77**	**10.99**	**4.30**	**2.15**	**1.31**	**0.31**	**0.15**
	Minimum	18.08	6.22	3.36	2.15	0.74	0.68	0.12	0.07
	Maximum	55.45	49.46	14.40	6.25	2.92	1.84	0.64	0.27

Table 3. Recovery table of SRM 2710 (Montana Soil) soil standard reference material.

	This Study	**NIST Certificated Value**	**Recovery (%) This Study**	**Recovery (%) Güler et al., 2010**
As (mg/kg)	614.26	626	98.1	97.3
Cd (mg/kg)	21.01	21.8	96.4	96.2
Co (mg/kg)	8.54	10	85.4	66.4
Cr (mg/kg)	37.61	39	96.4	59.7
Cu (mg/kg)	3029	2950	102.7	87.1
Mn (mg/kg)	9937	10100	98.4	68.8
Mo (mg/kg)	19.28	19	101.5	104.8
Ni (mg/kg)	14.7	14.3	102.8	86.2
V (mg/kg)	64.44	76.6	84.1	65.9
Zn (mg/kg)	6573	6952	94.5	79.3
Pb (mg/kg)	5364	5532	97.0	95.4

Table 4. Average, minimum and maximum concentrations of selected heavy metals sampled from topsoil and bottom soil.

		V (mg/kg)	Cr (mg/kg)	Mn (mg/kg)	Fe (mg/kg)	Co (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	As (mg/kg)	Cd (mg/kg)	Sb (mg/kg)	Pb (mg/kg)
Top Soil	**Mean**	**62.27**	**117.05**	**582.75**	**28713**	**20.84**	**227.68**	**42.51**	**128.02**	**9.22**	**0.51**	**1.27**	**43.46**
	Minimum	21.93	50.65	288.00	14193	6.42	74.85	15.15	54.68	4.96	0.09	0.46	13.05
	Maximum	92.20	198.03	929.44	37948	37.65	433.98	263.37	451.98	13.50	1.26	2.97	194.96
Bottom Soil	**Mean**	**66.38**	**121.53**	**554.32**	**29271**	**22.83**	**261.88**	**22.62**	**63.86**	**6.83**	**0.30**	**0.90**	**18.09**
	Minimum	14.50	0.73	241.39	10042	6.01	52.42	5.63	9.23	0.44	0.00	0.36	4.35
	Maximum	98.20	244.97	1095.26	40251	52.24	569.72	36.04	100.56	10.51	0.70	1.31	34.89
	Mean Top Soil/Mean Bottom Soil	**0.94**	**0.96**	**1.05**	**0.98**	**0.91**	**0.87**	**1.88**	**2.00**	**1.35**	**1.74**	**1.41**	**2.40**

Table 3 provides, as per SRM 2710 (Montana Soil) soil standards, recovery of this study as well as that of Güler et al., (2010). In this study, microwave total leaching method was adopted while five-stage sequential extraction method was adopted in Güler et al., (2010) (Vaisanen & Kiljunen, 2005). Recoveries of As, Cd, Co, Cr, Cu, Mn, Mo, Ni, V, Zn and Pb elements in respective order were 98.1%, 96.4%, 85.4%, 96.4%, 102.7%, 98.4%, 101.5%, 102.8%, 84.1%, 94.5% and 97.0%. Recoveries of As, Cd, Mo and Pb elements in this study were approximately similar to recoveries reported by Güler et al., (2010) (Tab. 3). However, the recoveries of Co, Cr, Cu, Mn, Ni, V and Zn in this study were higher than those in Güler et al., (2010) (Table 3).

Table 4 gives average, minimum and maximum concentrations of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Sb and Pb elements sampled from topsoil and bottom soil.

Average concentrations (ppm) of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Sb and Pb elements sampled from topsoil in respective order were 62.27, 117.05, 582.75, 28713, 20.84, 227.68, 42.51, 128.02, 9.22, 0.51, 1.27 and 43.46 (Table 4). Average

concentrations (ppm) of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Sb and Pb elements sampled from bottom soil in respective order are 66.38, 121.53, 554.32, 29271, 22.83, 261.88, 22.62, 63.86, 6.83, 0.30, 0.90 and 18.09 (Table 4). Topsoil/bottom soil ratios of average concentrations of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Sb and Pb elements in respective order are 0.94, 0.96, 1.05, 0.98, 0.91, 0.87, 1.88, 2.00, 1.35, 1.74, 1.41 and 2.40 (Table 4). If we assume 1.05 topsoil/bottom soil ratio of Mn element to be 1, V, Cr, Mn, Fe, Co and Ni are all 1 or near 1. This indicates that these elements were concentrated due to mostly lithological factors. On the other hand, topsoil/bottom soil ratios of Cu, Zn, As, Cd, Sb and Pb elements are all greater than 1. Considering that the soil sampled from a depth of one meter had formed in a period that wasn't subject to human influences, it is safe to assert that Cu, Zn, As, Cd, Sb and Pb elements were concentrated due to anthropogenic activities. Especially Cu, Zn, Cd and Pb elements had twice the concentration in topsoil in comparison to their concentrations in bottom soil (with topsoil/bottom soil ratios of Cu, Zn, Cd and Pb of 1.88, 2.00, 1.74 and 2.40, respectively). On the other hand, concentrations of V, Cr, Mn, Fe, Co and Ni elements in topsoil and bottom soil are similar; the origins of these elements are the ophiolitic rocks located in northern parts of Mersin Province.

Graphical comparisons of Cu, Zn, As, Cd, Sb, Pb, V, Cr, Mn, Fe, Co and Ni elements in top and bottom soils in the area subject to this study are given in figure 2 and figure 3. Concentrations of Cu, Zn, As, Cd, Sb and Pb elements in topsoil are generally higher than in bottom soil (Fig. 2). On the other hand, concentrations of V, Cr, Mn, Fe, Co and Ni elements are similar in top and bottom soils (with the exception of a few sample points) (Fig. 3). This data is further supported by the concentrations of V, Cr, Mn, Fe, Co and Ni elements in bottom and topsoils as given in Table 4. Bottom and topsoils sampled from the study area are similar in terms of main oxides (Table 2), organic substances and grain sizes (Table 1) and mineralogical compositions. On the other hand, top and bottom soils of the subject area are considerably different in terms of concentrations of Cu, Zn, As, Cd, Sb and Pb especially (Fig. 2 and Fig. 3). The difference is significant. It has been pointed out by many studies that the presence of several heavy metals in soil, namely As, Pb, Cd, Cu, Cr, Ni, Fe, Hg and Zn, is associated with anthropogenic activities (Ottesen & Langedal, 2001; Coby et al., 2006; Yang et al., 2011; Kumar et al., 2013; Yong & Mulligan, 2004). Some of these studies mentioned the sectors of origin of these anthropogenic pollutions (Ottesen & Langedal, 2001; Yang et al., 2011). In this study however, there is a complex land use in the study area (Fig. 1). Various industrial activities, green houses and other agricultural activities and settlements overlap in the area. Accordingly, Cu, Zn, As, Cd, Sb and Pb pollution was identified in the topsoils of the study area. Average concentrations of Cu, Pb, Zn, Cd and As elements in topsoils in various regions of the world are given in Table 5. Concentrations of these elements identified in this study are mostly similar to these other concentrations given in in Table 5. However, concentrations for the study area are quite lower than the average concentrations of certain foreign provinces (such as Avellino, Madrid and Luoyang). This is due to the great increase in industrialization and population of Mersin over the last 20 years. Likewise, Yang et al., (2011) pointed out that a city's topsoil pollution will increase in line with the industrialization age/history.

Distribution maps of Cu, Zn, Cd, As, Sb and Pb elements in topsoil and land use maps are given in figure 4. Distribution of Cu, Zn, Cd, Sb and Pb elements are similar to one another, being more concentrated in southwest-west sections where industrial activities are concentrated. On the other hand, As element is more concentrated in areas with more agricultural activity (Fig. 4).

Pearson's correlation coefficient has been used in many studies for the purpose of identifying correlations between heavy metals concentrated in soils as well as their origins (Manta et al., 2002; Andersen et al., 2010; Yang et al., 2011; Guo et al., 2012). These previous studies have pointed out that especially Cu, Pb and Zn elements result from industrial activities and increased vehicle traffic (Yang et al., 2011). Likewise, strong correlation coefficients between Cu, Zn, As, Cd, Sb and Pb elements, which exist in topsoils in greater concentrations in comparison to bottom soils of the study area, were identified in this study (Table 6). It can be seen from Table 6 that Zn element has high correlation with Cd, Sb and Pb elements while Pb element has high correlation with Cu, Zn, Cd and Sb elements. High correlation between these elements may indicate that the pollution in the sudy area is a result of high traffic and industrial activity.

As element has fairly low correlation with other elements. This indicates that the origin of As element differs from the origin of other elements in the area. In a study carried out in a nearby area, Kurt (2010) stated that As element exists in high concentrations in agricultural lands and that the origins of As element are mostly agricultural activities. It has also been pointed out that arsenic

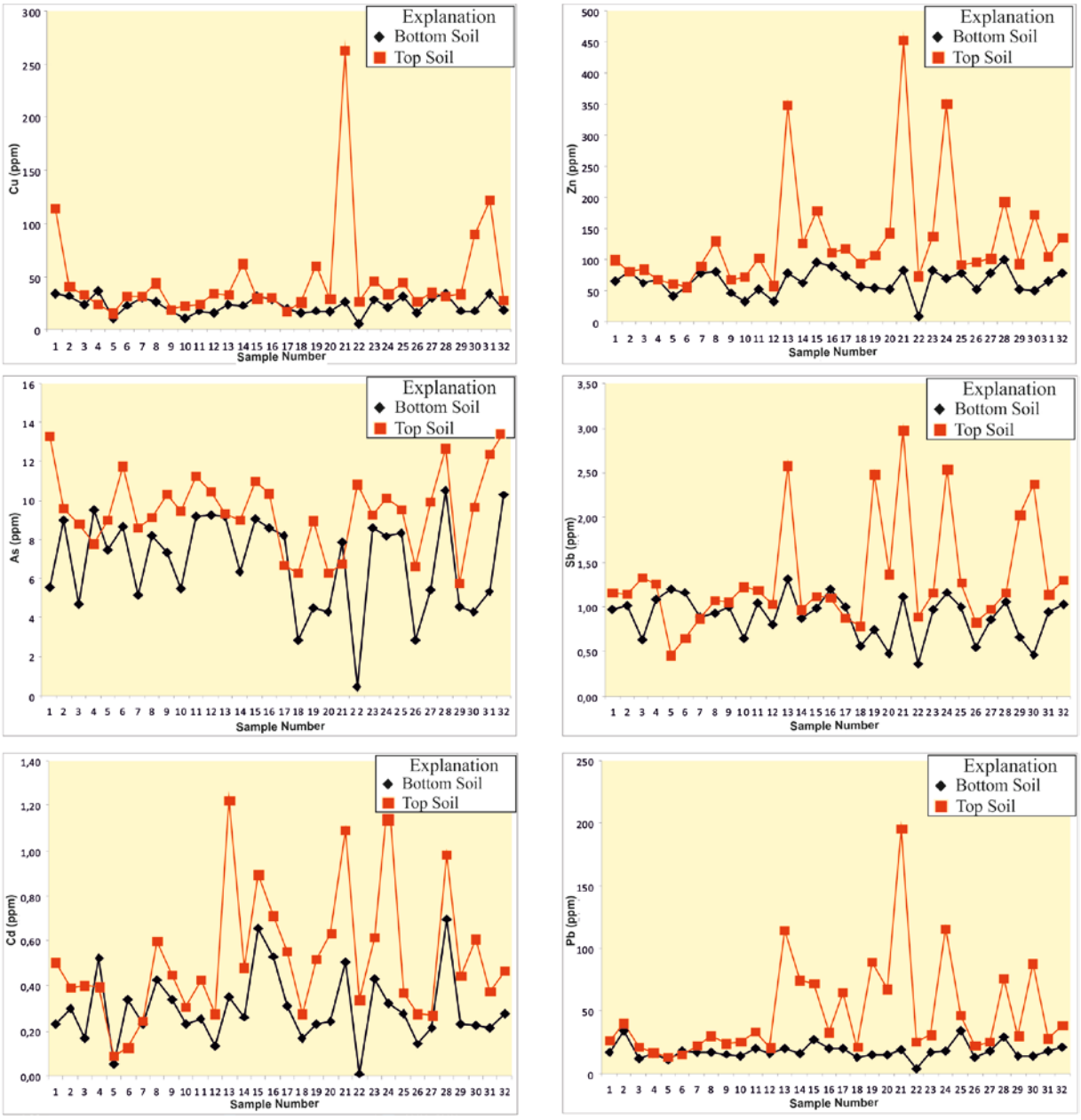

Figure 2. Comparison of selected heavy metal concentrations in topsoil and bottom soil samples.

can contaminate soil due to fossil fuels and waste substances resulting from burning as well as agricultural activities (Yong & Mulligan, 2004). The fact that As element has very low correlation with other elements that typically result from industrial activities and traffic suggests that the origins of As element in this area might be agricultural activities.

Cluster analysis is a statistical method that is commonly used in studies aiming to identify the distribution, behavior and origins of heavy metals in soils (Iqbal & Shah, 2011; Yaylalı-Abanuz, 2011; Barbieri et al., 2014; Kelepertzis, 2014; Karim et al., 2014). Results of cluster analysis of heavy metals found in topsoil of the study area are given in figure 5. There are two clusters, one consisting of Cu, Sb, Zn, Pb and Cd elements and the other consisting of V, Mn, Fe, Cr, Ni, Co and As elements. Cu, Sb, Zn, Pb and Cd elements have strong clustering behavior. There is also high correlation between these elements (Table 6) which are all concentrated in topsoil.

On the other hand, V, Mn, Fe, Cr, Ni, Co and As elements form another cluster. As element is in this group has only a weak clustering behavior, however. V, Mn, Fe, Cr, Ni and Co elements exhibit similar distributions in top and bottom soil (Fig. 3); their concentration in soil is due to lithological factors. As clustering behavior shows us that As element is neither of lithological origin nor, due to the weak correlation with Cu, Sb, Zn, Pb and Cd elements, is it associated with traffic or industrial activities. The origins of As element are more likely to be agricultural activities. As distribution in figure 3 further supports this.

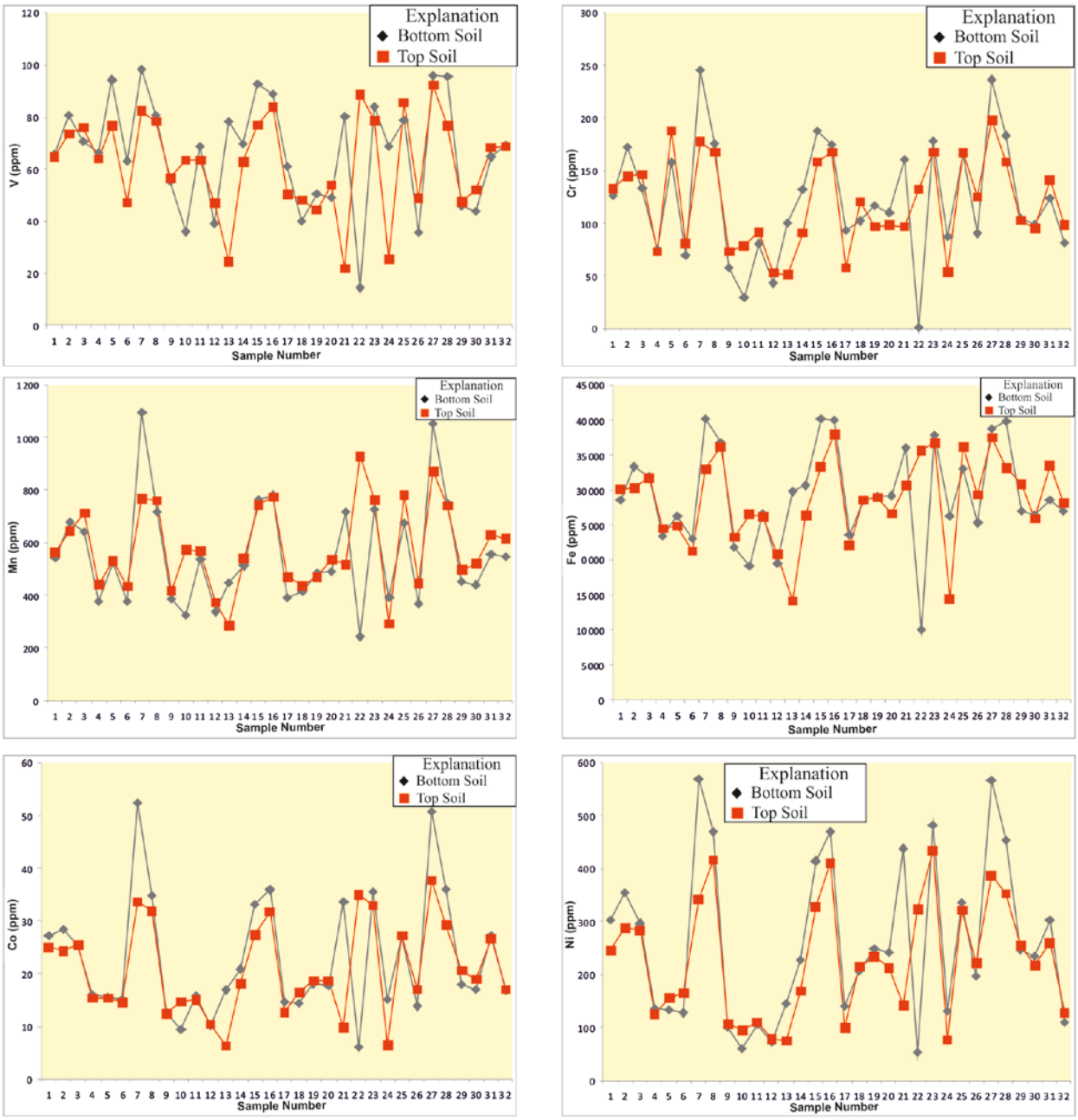

Figure 3. Comparison of selected heavy metal concentrations in topsoil and bottom soil samples.

Table 5. Comparison of mean selected element concentrations (mg/kg) in urban soils from cities of different countries.

City	Cu	Pb	Zn	Cd	As	Depth	References
Mersin (N=32)	**42.5**	**43.5**	**128.0**	**0.51**	**9.2**	0-15	This Study
Changchun (N=352)	29.4	35.4	90.0	0.13	12.5	0-15	Yang et al., 2011
Shenzen (N=84)	10.8	38.9	59.0	0.08	8.9	A Layer	Tao et al., 2001
Chengdu (N=168)	46.6	50.8	128.6	0.21	13.2	0-20	Shi, 2004
Luoyang (N=20)	111.3	257.0	364.2	1.30	ND	0-10	Zhang, 2006b
Galway (N=166)	33.2	78.4	99.3	ND	8.6	0-10	Zhang, 2006a
Madrid (N=55)	71.7	161.0	210.0	ND	ND	0-20	De Miguel et al., 1998
Hong Kong (=594)	22.3	89.7	146.0	2.18	ND	0-15	Li et al., 2001
Napoli (N=207)	72.0	141.0	163.0	0.37	12.2	0-15	Cicchella et al., 2008b
London	73.0	294.0	183.0	1.00	ND	ND	Thornton, 1991
Avellino	152.0	87.0	110.6	0.40	20.9	0-15	Cicchella et al., 2008a
ND:No data. N:Number of samples.							

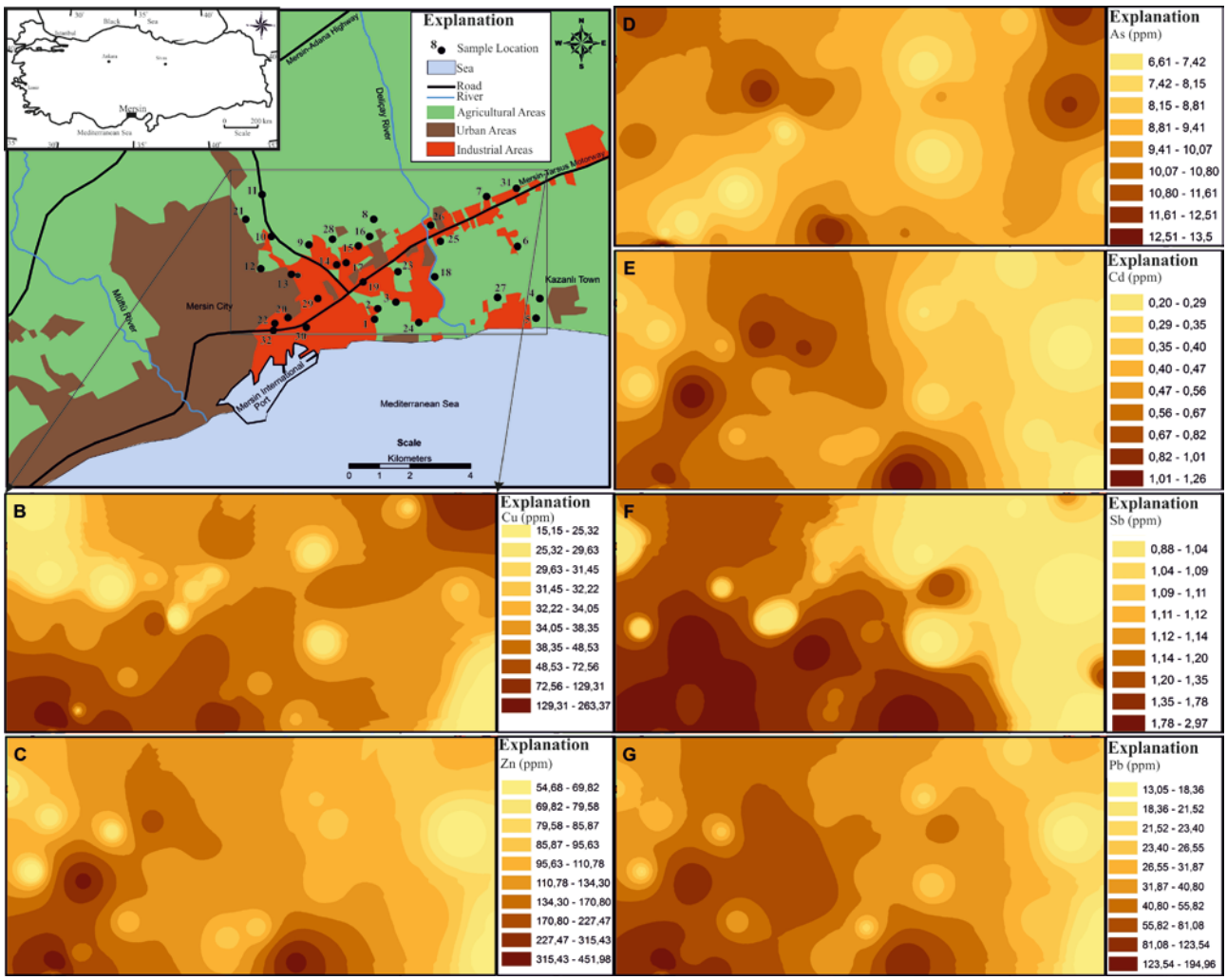

Figure 4. Distribution maps of Cu, Zn, Cd, As, Sb and Pb elements in topsoil and land use maps.

Table 6. Pearson's correlation matrix for topsoil metal concentrations.

	Cu	Zn	As	Cd	Sb	Pb
Cu	1					
Zn	**0.57**	1				
As	0.03	-0.05	1			
Cd	0.32	**0.88**	0.05	1		
Sb	**0.51**	**0.84**	-0.21	**0.75**	1	
Pb	**0.62**	**0.96**	-0.10	**0.84**	**0.82**	1

4. DISCUSSION

The study area is located in the eastern part of Mersin Province where settlements, industrial facilities and agricultural activities are present in an overlapping manner. There is a poorly planned and irregular complex land use in the area. Profile distribution method was employed in order to determine whether the origins of heavy metal concentrations are anthropogenic or lithological. Geological entity in the study area is deltaic sediments of quaternary age. Bottom (100 cm) and top (0-15 cm) levels of these sediments are similar in terms of main oxides such as SiO_2, CaO, Al_2O_3, MgO, K_2O, TiO_2, Na_2O and P_2O_5 and total organic matter, grain size and mineralogical composition. On the other hand, concentrations of certain heavy metals differ between top and bottom layers.

Concentrations of V, Cr, Mn, Fe, Co and Ni heavy metals are similar in top and bottom soils. The fact that concentrations of V, Cr, Mn, Fe, Co and Ni heavy metals are similar in top and bottom soils indicates that these elements are of lithological origin. These elements originate from ophiolitic rocks located northern Mersin Province. On the other hand, top and bottom soils of the subject area are considerably different in terms of concentrations of Cu, Zn, As, Cd, Sb and Pb.

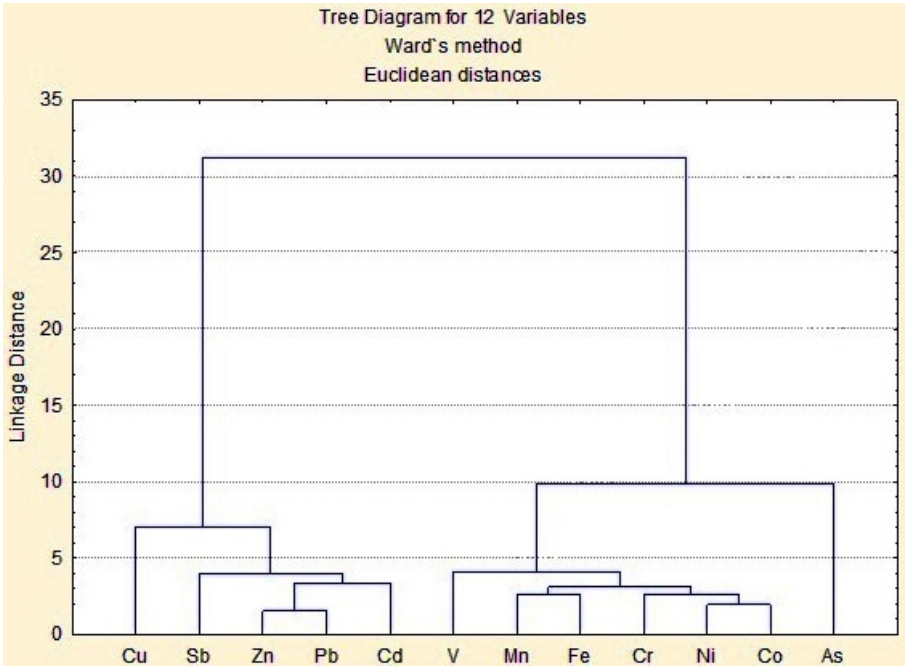

Figure 5. Results of cluster analysis of heavy metals in topsoil of the study area.

Concentrations of Cu, Zn, As, Cd, Sb and Pb elements in topsoil are much higher than those in bottom soil. As judged by Pearson's correlation coefficient method, Zn element has high correlation with Cd, Sb and Pb elements while Pb element has high correlation with Cu, Zn, Cd and Sb elements. In cluster analysis, Cu, Zn, Cd and Sb elements cluster together strongly. This indicates that these elements were introduced into topsoil interdependently. The fact that accumulations of these elements in topsoil are greater than bottom soil indicates that these elements accumulated in topsoil as a result of anthropogenic activities. When all the data is interpreted collectively, there is anthropogenic Cu, Zn, Cd, As, Sb and Pb pollution in topsoils and lithological V, Mn, Fe, Cr, Ni and Co accumulation in top and bottom soils of eastern parts of Mersin Province due to complex land use.

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