

Determination of Heavy Metals in Soils Around Afsin-Elbistan Thermal Power Plant (Kahramanmaras, Turkey)

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In this study, heavy metal (V, Ti, Cr, Mn, Ni, Cu, Zn, As, Sn, Al, Mg and Fe) pollution of the soils around Afsin-Elbistan Thermal Power Plant have been investigated. When the average values of the 21 analysis results were compared with the crystal values, V:1.03, Ti:0.64, Cr:3.51, Mn:1.02, Ni:6.48, Cu:3.31, Zn:1.56, As:3.09, Sn:0.51, Al:0.71, Mg:1.25 and Fe:1.25 values were determined. According to these comparisons, the exchange rates in the study area are as follows: Ni > Cr > Cu > As > Mg and Fe > Zn. According to the relationships between distance and sampling locations of the samples (sample numbers 1-16) collected through a line from the area between power plant and Afsin district, distances (km) where the elements were determined in their maximum values are as follows: Ni:3, Mg:3, Cr:5, Ti:8, Mn:8, Cu:8, Fe:9, V:9, Zn:9, As:9, Sn:14 and Al:15. According to the results of XRD whole rock analysis, mineral associations found as clay, calcite, quartz, feldspar, mica, hematite and rarely clinoptilolite and opal-CT. Clay mineral assemblages are montmorillonite, illite, kaolinite, notronite and halloysite.

Key Words: Afsin-Elbistan, Thermal power plant, Polluted soil, Heavy metals, Turkey.

INTRODUCTION

Coal contains trace amounts of a wide range of elements including toxic metals and metalloids¹. Trace elements like Hg, Zn, Cd, As, Pb, Mn, Mo, Co, Ni, Cr and Se are situated in the inorganic part of the coal, Ga, Be and B are situated generally in the organic part of the coal, Ga, P, Ti, Sb and V are situated in both organic and inorganic parts of the coal². Coal combustion can mobilize trace elements by introducing them to terrestrial, aquatic and atmospheric environments and if leached, these elements may cause contamination of soil, surface water and groundwater³.

Contaminants that are thrown to the atmosphere with funnel gases in coal combustion systems are various gases like sulphur oxides, nitrogen oxides and carbon dioxides, solid fragments like soot and ashes and various carbon compounds⁴.

The purpose of this study is to determine the amounts of heavy metals (V, Ti, Cr, Mn, Ni, Cu, Zn, As, Sn, Al, Mg and Fe) in agricultural soils around Afsin-Elbistan Thermal Power Plant and to establish the probable relationships between these amounts and power plant.

Afsin-Elbistan Thermal Power Plant is located in the Afsin-Elbistan Valley, 154 km north of the Kahramanmaras city. Power plant consists of two units as A and B. A-unit was put into use in 1984 and has a total cocked power of 1355 MV. It consumes 28000 ton/day coal in full capacity. B-unit was put into use in 2004 and has a total cocked power of 1440 MV. It consumes 100000 ton/day coal in full capacity.

EXPERIMENTAL

Total 21 soil samples were taken from 5-10 cm deep in agricultural soils around Afsin-Elbistan Thermal Power Plant in August 2007. 16 Samples were taken between power plant and Afsin district and the samples were obtained from each 1 km of the outer boundary of the power plant. Other samples were taken from each 1 km between power plant and Elbistan district and one of them was taken from the west outer side of the power plant. Samples were taken with the help of 1/25000 scaled topographic map and GPS. There is 10-15 m height difference between the locations of the collected samples.

The samples were dried in drying oven at 105 °C for 24 h to dispose humidity. Dried samples were stained through the 2 mm plastic sieve and separated from pebbles. Afterwards, samples were formed into averagely 2 mm \geq particles by homogenizing them in an agate mortar.

In soil samples, total 34 elements (La, Ce, Pr, Nd, Sm, Eu, Gd, B, Rb, V, Yb, Li, S, P, Si, Na, K, Ti, Cr, Mn, Ni, Cu, Zn, As, Zr, Y, Sn, Sr, Te, Sc, Al, Mg, Ca and Fe) were analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES).

Three representative samples in 21 soil samples were analyzed by XRD. Their mineralogical compositions were determined by using PHILIPS PW 1140 type X-Ray Diffractometer with CuK_α radiation and goniometer speed of 2°/min in Hacettepe University, Ankara. Proportions of the minerals were determined from the powder diffractograms following an external standard method developed by Gundogdu⁵. In this method, all samples were mounted in the same way and the characteristic peak intensities (I) of minerals were normalized to that of the (104) reflection of dolomite. In other words, a K factor for each mineral (including clays with peaks between 19° and 20° 2 θ) was determined as $K = I_{\text{dolomite}}/I_{\text{mineral}}$ in a 1:1 dolomite-mineral mixture by weight. Percentages of mineral were calculated from the following equation: % of mineral, a = $100 \times K_a \times I_a / (K_a \times I_a + K_b \times I_b + \dots + K_n \times I_n)$. The relative error of this method is less than 15 %. X-ray diffraction patterns of the powders were evaluated using Jade 5.0 software (Materials Data, Inc., Livermore, CA).

RESULTS AND DISCUSSION

Lignites of Afsin-Elbistan lignite basin in the north of Kahramanmaras, Turkey were first established in 1967. This basin is situated at 1150 m high from sea level and has an area of 900 km². This area is a close basin that occurred when the Taurus Mountains were rised during Alpine Orogenesis⁶. Serpentine, granite and granodiorite, metamorphic series, Permo-Carboniferous deposits, continental and Quaternary deposits are seen in the area where Afsin-Elbistan Thermal Power Plant is placed and its surroundings (Fig. 1). Afsin-Elbistan lignite field, which covers about 120 km², has the largest proportion of low-ranklignite reserves of Turkey, containing 3.4 Gt of technically recoverable lignite⁷. A very thick lignite bed, ranging between 4 and 58 m in thickness and about 50 % moisture content on as received basis, is nearly horizontal and is being operated by an open-pit method⁸. Afsin-Elbistan lignite developed during the Pliocene-Pleistocene transition under freshwater conditions and has high volatile content of 60-70 % on dry ash-free basis and mean random huminite reflectance in the range of 0.24-0.29 % (avg. 0.27 %)⁹.

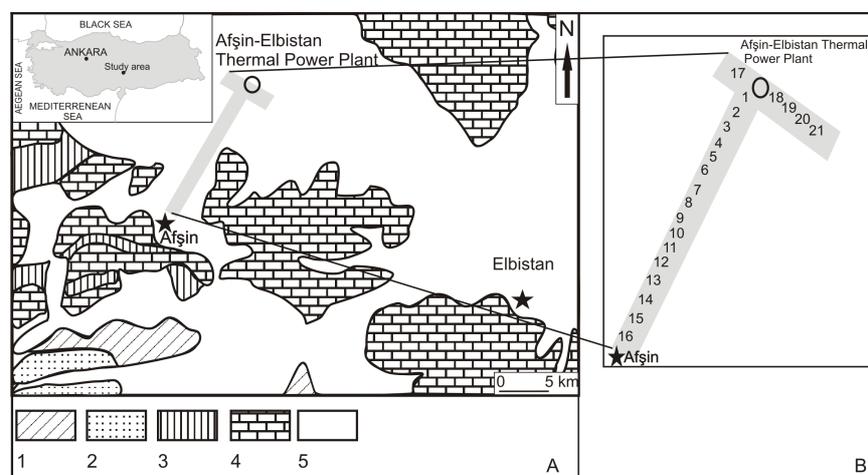


Fig. 1. Geological and sample maps of the study area. A) 1-Serpentine; 2-granite and granodiorite; 3-metamorphic series; 4-Permo-Carboniferous deposits; 5-continental Quaternary deposits (8). B). Sample map (Numbers show the sample locations)

According to the results of XRD whole rock analysis made on 3 samples collected from the study area (Samples no:1, 5 and 15), mineral associations are as follows: clay, calcite, quartz, feldspar, mica, hematite and rarely clinoptilolite and opal-CT. Clay mineral assemblages are montmorillonite, illite, kaolinite, notronite and halloysite.

In XRD patterns, peak values that are characteristic for the clay minerals in 14.56 Å and 15.51 Å were observed and especially clay peaks (4.43 Å, 4.44 Å) between 19°-20° (2θ) are determined. Calcite peaks in 3.01 Å and 2.27 Å, quartz peaks in 3.31 Å and 4.22 Å, feldspar peaks in 3.19 Å and 3.82 Å, mica peak in 10.21 Å and zeolite (clinoptilolite) peaks in 8.89 Å, 2.97 Å and 3.96 Å were observed (Fig. 2).

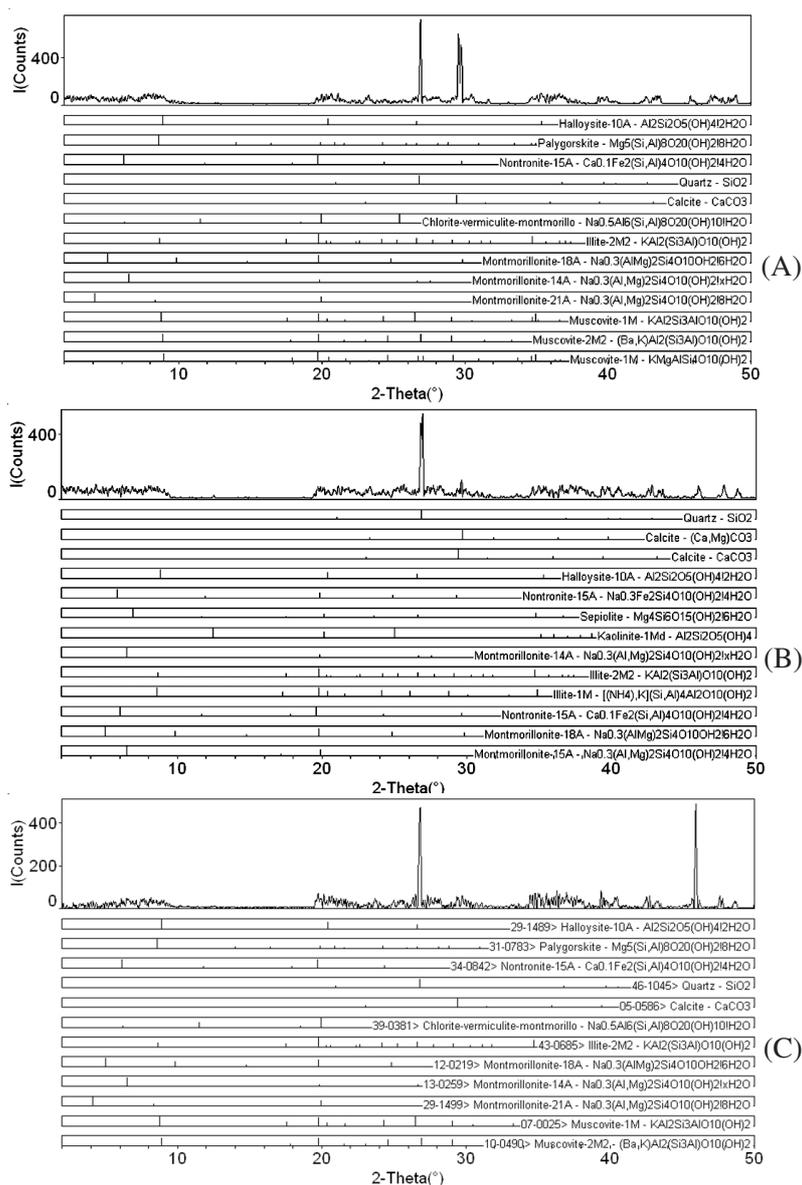


Fig. 2. Mineral determinations of the soil samples collected from the study area made by using the Jade 5.0 program for the XRD whole rock analysis (A: Sample no-1, B: Sample no-5 and C: Sample no-15)

Whole rock analysis results were evaluated according to the system developed by Gündođdu⁵ and clay mineral amounts in samples were determined as 68-73 %. According to these data, it is considered that elements (V, Ti, Cr, Mn, Ni, Cu, Zn, As, Sn, Al, Mg and Fe) mobilized with the funnel gases from the power plant were transported by the atmospheric agents, than penetrated to the soil by surface and rain waters and finally adsorbed by the clay minerals in soil. The negative charged surface of the clay minerals attracts the opposite charged ions in liquid¹⁰. Clay minerals absorb some cations and anions and hold them in exchangeable condition. Cations like Na⁺, K⁺, Ca²⁺ and Mg²⁺ between the layers of the clay minerals can exchange with both inorganic and organic cations¹¹.

An atomic plane consisting of OH and O ions is fixed on the outer surface of a clay mineral, these surfaces effect to the water layer that is hold relatively rigid. In this layer, cations are concentrated in near surfaces of the clay minerals. Anions attract the cations and reaches electrically neutral condition¹¹. The area is enriched by the elements (V, Ti, Cr, Mn, Ni, Cu, Zn, As, Sn, Al, Mg and Fe) transported by the volatiles and the evaluations of the results of the trace element analysis and their correlation matrixes support this situation.

In this study, trace elements in soil samples (La, Ce, Pr, Nd, Sm, Eu, Gd, B, Rb, V, Yb, Li, S, P, Si, Na, K, Ti, Cr, Mn, Ni, Cu, Zn, As, Zr, Y, Sn, Sr, Te and Sc) were determined as ppm and the major elements (Al, Mg, Ca and Fe) were determined as weight % (Table-1).

The minimum, maximum and average values of the heavy metals in the samples are as follows respectively: V: 21.25-81.85-54.42, Ti: 22.75-2936-1981.19, Cr: 60.01-165.93-122.92, Mn: 178.93-1249.00-537.88, Ni: 51.99-188.65-120.56, Cu: 14.90-77.20-120.56, Zn: 25.11-160.71-81.20, As: 1.12-23.75-6.18, Sn: 0.63-1.95-1.27 (ppm), Al: 3.07-8.01-5.49, Mg: 1.02-2.55-1.69 and Fe: 2.49-5.42-3.86 (% wt).

The relationships between the heavy metals in chemical analysis results of 21 soil samples collected from the study area was tested according to the Pearson Correlation Analysis technique, 1 and 5 % importance level (Table-2). Positive and negative correlations between elements determined according to the chemical analysis results were also shown. Elements showing positive relation and their relation levels were given as follows: There is high and medium level of positive correlation between Fe-Al, Cu-Mn, As-Zn, Ti-V, Zn-Fe, Fe-Mn, As-Al, Cu-Fe, As-Fe, Mn-Al, Ni-Cr, Fe-V, Zn-Cu, Cu-Cr, Al-V, Ni-Mg, Cu-V, Cu-Al, Zn-Al, Mn-V, As-V, Cr-V, As-Cu, Zn-Mn, As-Mn, Mn-Cr and Cr-Ti ($r_{\text{Fe-Al}} = 0.960$ [Sig(2ta) = 0.001], $r_{\text{Cu-Mn}} = 0.881$ [Sig(2ta) = 0.000], $r_{\text{As-Zn}} = 0.856$ [Sig(2ta) = 0.000], $r_{\text{Ti-V}} = 0.854$ [Sig(2ta) = 0.000], $r_{\text{As-Fe}} = 0.812$ [Sig(2ta) = 0.000] $r_{\text{Zn-Fe}} = 0.745$ [Sig(2ta) = 0.000], $r_{\text{Fe-Mn}} = 0.739$ [Sig(2ta) = 0.000], $r_{\text{As-Al}} = 0.737$

TABLE-1
ELEMENT DISTRIBUTION OF THE SOILS IN THE STUDY AREA (Al, Mg, Fe, Ca AND K IN WEIGHT %, OTHER ELEMENTS IN ppm)

S. No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	Min	Max	Average
Km	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	0	0	1	2	20			
Al (%)	3.74	4.51	3.07	4.27	3.52	4.25	5.42	7.32	7.73	7.57	5.40	6.73	7.70	7.25	7.60	8.01	4.64	4.66	5.74	3.09	3.13	3.07	8.01	5.49
Mg (%)	1.41	1.79	1.70	2.37	1.96	1.99	1.38	1.67	1.44	1.02	1.37	1.47	1.57	1.41	1.53	1.51	1.31	1.89	2.25	1.94	2.55	1.02	2.55	1.69
Fe (%)	2.91	3.26	3.14	3.40	2.99	3.48	3.47	4.45	5.12	5.42	3.50	4.31	4.96	4.72	4.83	5.35	3.15	3.22	4.00	2.92	2.49	2.49	5.42	3.86
Ca (%)	15.38	10.38	13.04	11.81	13.97	11.61	14.96	6.54	2.87	5.81	11.91	8.49	4.59	6.36	1.98	4.60	13.27	10.47	3.93	10.83	14.12	1.98	15.38	9.38
K (%)	0.81	0.96	0.95	0.98	0.88	1.01	1.01	1.29	1.41	1.43	1.23	1.25	1.54	1.51	1.52	1.42	0.85	1.01	1.19	0.57	0.87	0.57	1.54	1.13
La	12.06	23.37	20.83	21.62	18.93	21.63	24.43	33.09	35.60	37.75	28.26	31.68	36.42	35.93	37.31	36.81	23.36	22.05	25.70	17.09	17.73	12.06	37.75	26.74
Ce	10.71	36.41	30.33	32.17	25.53	31.69	38.05	58.51	64.63	64.64	45.39	54.58	64.67	61.05	66.24	63.53	35.28	32.36	41.32	21.75	24.49	10.71	66.24	43.02
Pr	9.20	20.48	22.58	21.93	20.98	21.89	24.65	20.10	17.83	22.04	23.97	21.72	19.83	20.65	18.90	19.82	23.91	20.25	15.56	19.08	20.70	9.20	24.65	20.29
Nd	13.45	38.39	19.21	34.09	27.86	35.71	38.74	56.47	61.28	62.19	43.56	50.42	59.26	58.48	40.68	59.53	37.38	38.32	48.02	35.12	31.83	13.45	62.19	42.38
Sm	1.78	5.66	5.61	5.62	4.30	5.40	5.52	8.70	9.66	10.33	6.97	8.25	9.96	9.31	11.27	9.96	5.61	5.71	6.94	4.13	3.97	1.78	11.27	6.89
Eu	0.56	1.36	1.13	1.27	1.09	1.31	1.33	1.96	2.19	2.45	1.62	1.90	2.21	2.18	2.18	2.31	1.39	1.42	1.71	1.01	0.89	0.56	2.45	1.59
Gd	2.56	8.20	7.65	8.25	6.87	8.12	8.23	11.96	13.46	14.65	9.78	11.29	13.50	12.94	14.70	13.79	8.26	9.11	11.09	6.95	5.96	2.56	14.70	9.87
B	10.32	35.14	30.55	35.20	37.03	48.85	34.74	46.26	51.83	53.82	42.80	44.17	55.50	51.20	52.93	53.52	33.85	40.62	46.75	30.57	32.00	10.32	55.50	41.32
Rb	28.33	155.87	135.23	158.42	115.75	141.25	168.27	237.06	253.03	245.62	188.44	226.85	276.25	250.88	277.17	261.63	158.41	154.48	196.59	79.77	113.11	28.33	277.17	182.02
V	21.25	50.70	21.46	46.68	47.28	54.78	47.85	65.26	79.78	81.85	51.25	62.29	73.74	70.53	26.77	74.98	51.86	62.51	70.77	53.34	27.92	21.25	81.85	54.42
Yb	0.75	2.23	1.76	2.04	1.74	2.11	2.13	3.12	3.49	3.57	2.47	2.90	3.40	3.36	3.27	3.45	2.25	2.36	3.19	1.75	1.52	0.75	3.57	2.52
Li		24.68	15.27	21.47	15.70	20.57	24.18	38.02	46.94	46.23	26.50	35.53	41.64	37.17	39.53	39.86	26.65	26.01	29.22	15.26	9.41	9.41	46.94	28.99
S	109.08	286.47	252.34	181.21	449.15	428.27	201.20	166.01	130.79	162.85	184.59	121.87	136.57	161.00	123.72	119.61	335.44	308.54	292.98	433.01	247.16	109.08	449.15	230.09
P	209.95	536.09	386.01	456.60	426.39	418.00	213.75	260.71	228.52	227.15	413.42	239.53	307.63	289.09	286.33	235.38	285.47	416.26	535.16	301.48	501.55	209.95	536.09	341.64
Si	307.34	226.45	146.98	646.58	623.04	1203.80	405.59	735.31	874.38	1103.00	1917.00	902.48	1233.40	928.65	338.21	1074.30	418.88	743.61	649.91	423.21	544.12	146.98	1917.00	735.54
Na	996.71	812.81	1767.71	644.94	1137.80	1757.90	1578.60	1009.49	1075.36	1892.41	2873.41	853.30	999.63	1624.10	1064.76	1008.50	1167.87	987.54	885.07	1209.21	1659.25	644.94	2873.41	1286.02
Ti	914.77	2071.80	22.75	1694.70	1529.60	2061.10	2096.60	2598.00	2936.50	2726.40	1940.60	2328.20	2468.10	2590.60	31.82	2324.60	2024.30	2161.20	2520.40	2621.70	1941.30	22.75	2936.50	1981.19
Cr	60.01	140.26	90.66	133.67	127.87	150.37	102.01	126.64	141.32	117.03	103.65	116.30	127.13	123.56	125.14	127.10	122.50	162.09	165.93	133.61	84.42	60.01	165.93	122.92
Mn	178.93	458.31	427.62	490.11	416.41	470.94	422.38	606.12	1249.00	639.00	471.99	548.17	642.69	625.56	678.67	632.87	400.67	475.25	649.45	474.63	336.68	178.93	1249.00	537.88
Ni	51.99	108.60	121.65	168.54	133.34	139.36	93.62	115.60	150.64	94.22	83.42	95.29	105.67	100.79	113.57	104.85	105.44	156.21	177.80	188.65	122.60	51.99	188.65	120.56
Cu	14.90	39.66	43.58	43.07	41.35	47.78	38.36	50.11	77.20	63.31	43.38	44.37	53.30	52.23	55.74	51.02	40.87	54.16	67.47	38.70	32.62	14.90	77.20	47.29
Zn	25.11	69.38	67.81	61.67	70.16	75.73	68.69	85.94	98.73	160.71	78.51	80.48	96.22	99.70	102.03	90.89	75.88	70.92	79.33	98.16	49.21	25.11	160.71	81.20
As	1.70	4.15	2.03	2.73	3.12	3.33	3.57	4.43	10.28	23.75	9.04	7.52	9.63	9.19	9.44	10.49	2.05	5.36	4.83	2.06	1.12	1.12	23.75	6.18
Zr 3	15.45	51.13	3.51	39.51	31.02	42.44	54.25	73.42	78.01	65.51	53.34	66.19	68.23	71.56	3.80	62.17	51.55	47.08	52.83	35.49	33.14	3.51	78.01	47.60
Y	7.45	22.60	18.83	20.70	17.58	21.19	20.95	30.61	34.09	37.24	25.36	28.89	33.58	34.74	35.00	35.17	22.77	23.23	28.31	16.94	16.00	7.45	37.24	25.30
Sn	0.63	1.17	1.49	0.78	1.09	1.15	1.31	1.60	1.14	1.78	0.82	1.52	1.95	1.11	1.95	1.20	1.23	0.89	0.79	1.80	0.63	1.95	1.27	
Sr	117.89	310.65	271.95	258.10	276.43	253.73	172.45	123.53	102.25	145.93	216.74	144.50	113.62	107.53	94.18	103.46	216.49	224.48	159.30	217.33	454.06	94.18	454.06	194.50
Te	1.38	4.61	2.05	5.44	2.46	4.43	4.04	6.90	7.52	9.69	5.12	5.76	7.42	6.38	6.40	8.98	4.74	5.95	6.80	5.58	4.35	1.38	9.69	5.52
Sc	5.03	13.37	11.37	13.88	11.21	13.04	13.04	18.37	20.29	19.95	13.69	17.10	20.00	18.40	20.14	19.72	13.85	16.69	20.28	11.78	8.46	5.03	20.29	15.22

TABLE-2
CORRELATION MATRIX INDEX OF THE HEAVY METALS IN 21 SAMPLES
COLLECTED FROM THE STUDY AREA

	V	Al	Mg	Ti	Cr	Mn	Fe	Ni	Cu	Zn	As	Sn
V	1											
Al	.671‡	1										
Mg	-.278	-.550‡	1									
Ti	.854‡	.368	-.062	1								
Cr	.610‡	.243	.261	.452†	1							
Mn	.640‡	.699‡	-.222	.408	.479†	1						
Fe	.688‡	.960‡	-.528†	.333	.262	.739‡	1					
Ni	.187	-.248	.670‡	.221	.699‡	.291	-.158	1				
Cu	.714‡	.656‡	-.132	.405	.677‡	.881‡	.715‡	.408	1			
Zn	.658‡	.644‡	-.467†	.398	.359	.580‡	.745‡	.085	.698‡	1		
As	.612‡	.737‡	-.595‡	.320	.121	.519†	.812‡	-.252	.598‡	.856‡	1	
Sn	0.50	.425	-.159	-.105	-.077	.195	.414	-.221	.274	.416	.384	1

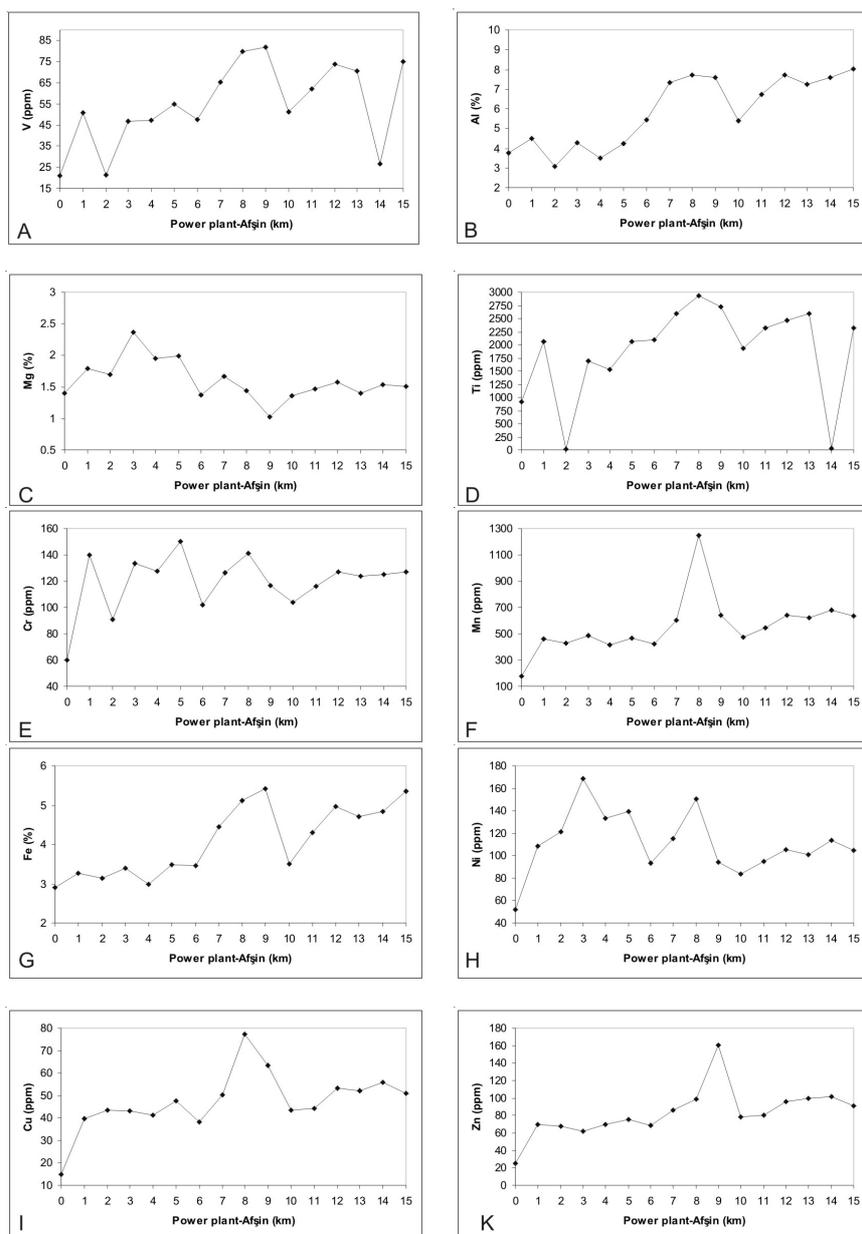
†Correlation is significant at the 0.05 level (2-tailed).

‡Correlation is significant at the 0.01 level (2-tailed).

[Sig(2ta) = 0.000], rCu-Fe = 0.715 [Sig(2ta) = 0.000], rCu-V = 0.714 [Sig(2ta) = 0.000], rMn-Al = 0.699 [Sig(2ta) = 0.002], rNi-Cr = 0.699 [Sig(2ta) = 0.000], rZn-Cu = 0.698 [Sig(2ta) = 0.000], rFe-V = 0.688 [Sig(2ta) = 0.001], rCu-Cr = 0.677 [Sig(2ta) = 0.001], rAl-V = 0.671 [Sig(2ta) = 0.001], rNi-Mg = 0.670 [Sig(2ta) = 0.001], rCu-Al = 0.656 [Sig(2ta) = 0.001], rZn-Al = 0.644 [Sig(2ta) = 0.002], rMn-V = 0.646 [Sig(2ta) = 0.002], rAs-V = 0.612 [Sig(2ta) = 0.003], rCr-V = 0.610 [Sig(2ta) = 0.003], rAs-Cu = 0.598 [Sig(2ta) = 0.000], rZn-Mn = 0.580 [Sig(2ta) = 0.006], rAs, Mn = 0.519 [Sig(2ta) = 0.0016], rMn-Cr = 0.479 [Sig(2ta) = 0.028] and rCr-Ti = 0.452 [Sig(2ta) = 0.000]. There is high and medium level of negative correlation between (rMg-Al = -0.550 [Sig(2ta) = 0.010], rFe-Mg = -0.528 [Sig(2ta) = 0.014] and rZn-Mg = -0.467 [Sig(2ta) = 0.033]).

According to Wedepohl¹², the average concentration levels of pollutant heavy metals in the upper crust are as follows: V: 53, Ti: 3117, Cr: 35, Mn: 527, Ni: 18.60, Cu: 14.30, Zn: 52, As: 2, Sn: 2.50 (ppm), Al: 7.74, Mg: 1.35 and Fe: 3.09 (% wt). When the average values of the 21 analysis results were compared with the crustal values, V:1.03 (54.42/53), Ti:0.64 (1981.19/3117), Cr:3.51 (122.92/35), Mn:1.02 (537.88/527), Ni:6.48 (120.56/18.60), Cu:3.31 (47.29/14.30), Zn:1.56 (81.20/52), As:3.09 (6.18/2), Sn:0.51 (1.27/2.50), Al:0.71 (7.74/5.49), Mg:1.25 (1.69/1.35) and Fe: 1.25 (3.86/3.09) values were determined. According to these comparisons, the exchange rates in the study area are as follows: Ni > Cr > Cu > As > Mg and Fe > Zn. The concentration values of the other elements are approximately same with the average concentration levels of the elements in the upper crust.

The relationships between distance and sampling locations of the samples (sample numbers 1-16) collected through a line from the area between power plant and Afsin district are shown in Fig. 3. According to this figure, distances (km) where the elements were determined in their maximum values are as follows: Ni:3, Mg:3, Cr:5, Ti:8, Mn:8, Cu:8, Fe:9, V:9, Zn:9, As:9, Sn:14 and Al:15.



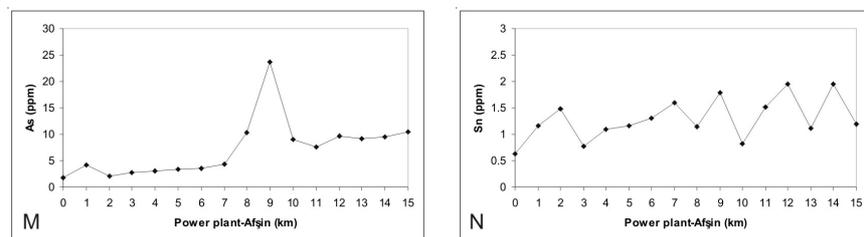


Fig. 3. Distance-element diagrams of the samples collected from the area between Thermal Power Plant and Afsin

Heavy metal concentrations of the samples (sample numbers: 1, 17 and 18) taken from west, south and east sides of the power plant were compared and it's seen that there is no similarity. In addition, samples taken from 1, 2 and 3 km of the power plant-Elbistan direction (sample numbers: 19, 20 and 21) and samples taken from 1, 2 and 3 km of the power plant- Afsin direction (sample numbers: 2, 3 and 4) show no similar heavy metal concentrations. The reason of this situation can be atmospheric events at the region.

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(Received: 29 January 2008;

Accepted: 14 July 2008)

AJC-6695