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HEAVY METALS BIOCONCENTRATION AND TRANSLOCATION IN PLANTS: THE INFLUENCE OF A THERMAL POWER SITE

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Abstract

Soil and plant samples were collected from agricultural areas under the influence of thermal power plant and ash samples were collected from ash storage area. In samples, As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, V, Zn, Al, Ca, Fe, K, Na and S were analyzed using ICP-MS. The aim of the study is to determine the set of elements mainly emitted from the components of the thermal power plant, as well as the major sources influencing the plant elemental levels. In the ash samples, significant enrichments of S, Mo, As, Ca, Cd and Cr were determined. Sugar beet leaves were considered to be a potential Na hyperaccumulator due to the translocation factor (TF) of 13525 calculated in its leaves. As a result of the Principal Component Analysis applied to the bioconcentration factors (BCFs) determined in plant parts, the main source of Co , Pb , Ni , Cr , Fe , Al, V, As, Mn and Cd was determined as geochemical background level of soil. Cu, Zn, and Mo enrichment in plant parts were found linked with agrochemicals used on the site, while another source of Cd was detected as phosphate fertilizers. Mo and S are identified as the main elements sourced from thermal power plant units.

Key words: bioconcentration, heavy metals, hyperaccumulation, principal component analysis, thermal power plant

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1. Introduction

Heavy metals (HMs) are one of the most important environmental concerns (Alloway, 2013; Kabata-Pendias, 1995; Pal et al., 2018). HM uptakes from soils and their translocation from plant roots to aerial parts have an important impact on HM bioaccumulation in food chain. However, in many parts of the world agricultural activities are realized in areas close to HM emitting sources such as fossil fuel power plants, mining sites, and industries.

Plant uptake of airborne metals (Hovmand et al., 1983; Lagerwerff, 1971), impact of traffic on metal translocation in plants (Wiseman et al., 2014), levels and enrichment of metals in soils and plants of highly industrialized areas (Hu et al., 2013; Panahandeh et al., 2018; Srinivasa Gowd et al., 2010; Yaylalı-Abanuz, 2011) are previously studied by some researchers. Thermal power sites are important sources of metal emissions and according to our knowledge, their influence on the metal enrichment in soils and plants and the translocation of these metals were not studied previously.

Here, metal levels in plants growing in an agricultural area surrounded by a thermal power production site, which is hosting a coal mine, two thermal power plants with a total annual capacity of 8.1 billion kWh, and a coal ash landfill site, were focused. Different from previous studies, the crustal elements and sulfur levels in the samples were also included in the study. Our aim is to identify the major elements released from thermal power plant units and to provide comprehensive information on the

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bioconcentration and translocation of HMs in regions under intense emissions. For this purpose, soil and plant samples were analyzed for their heavy metal, crustal element and sulfur levels. The enrichment factors (EFs) of studied elements in soil samples were determined and bioconcentration factors (BCFs) and translocation factors (TFs) were calculated for the plant parts. The elemental levels in soils and BCFs of plants were investigated statistically to identify the elements that are mainly originated from the thermal power site units. The findings of the study can be used to develop specific measures and controls on the emissions from thermal power plant sites, as well as for better understanding of the major anthropogenic activities influencing plant metal levels.

2. Material and methods

2.1. Study site

The study site is was located in the southeastern part of the Anatolian Peninsula, Turkey. The area is in the northwestern part of Elbistan Plain, which is mainly used for agriculture, and is close to Afşin town, which is at the 118 km north of Kahramanmaraş city. Sugar beet and sunflower are the main crops cultivated in this plain. The site drains its water to Harman Creek, which is in the Basin of Ceyhan River that is connected to Mediterranean Sea (Fig.1). There is a large mining area (~7.5 km x 2.5 km) on the site supplying lignite coal to the nearby thermal power plants having capacities of 1355 MW (TPS1) and 1440 MW (TPS2) (EUAŞ, 2018). The bottom ash from the power plants was deposited in a storage area (ASA, ~0.37 km x 1.03 km). As can be recognized from the wind rose in Fig. 1, even though the prevailing wind direction is southwest, the winds from other directions cannot be neglected in this area, except the winds from west (Esen and Tonbul, 2015).

The reported heavy metals, arsenic, and crustal element levels in Afsin-Elbistan lignite coals in the literature are presented with Table 1 (Karayigit et al., 2000; Kubešová et al., 2016). It is also known that, the ash content of Afsin-Elbistan lignites varies between 20.9% and 38.9% (Karayigit et al., 2000).

2.2. Sampling and sample preparation

The soils and plants (sunflower, sugar beet, eggplant and apricot) were collected from eight different sampling locations in the area, as well as two bottom ash samples (K1, K2) from ash storage area (ASA). Sampling points are selected under the prevailing winds by increasing the distance from possible sources. Soil samples were collected from all sampling points, where the sunflowers were sampled from SP1, SP6, SP7, and SP8, the sugar beets were collected from SP2, SP6, and SP7, while the eggplant was sampled from SP5, and the apricot was sampled from SP4.

All samplings were made in the same date. The distances of the sampling points (SPs) from the possible pollution sources are presented with Table 2.

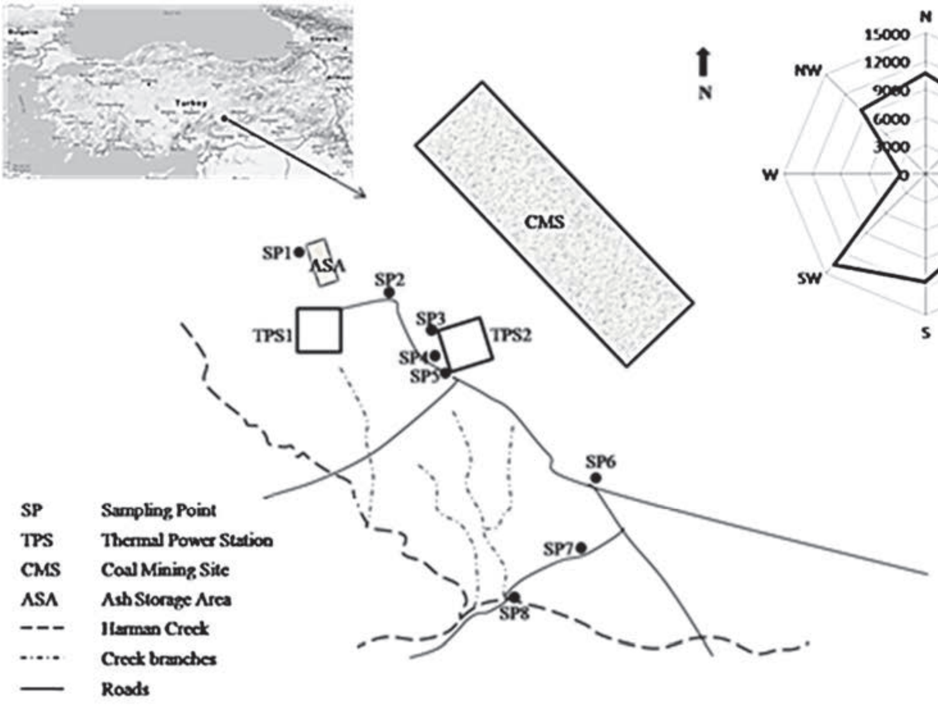


Fig.1. Study site and sampling locations with wind rose of Afşin town

Table 1. Element concentrations in Afsin-Elbistan lignites (Karayiğit et al., 2000, Kubesova et al., 2016) and their background levels in soils and earth crust (Champion, 2008; Pais and Jones, 1997)

Elements	***Coal***		***Coal Ash***		***Soil***		
	Kubesova et al. (2016)	***Karayiğit et al. (2000)***	***This Study***		***This Study***	***Range (Pais and Jones, 1997)***	***Earth Crust Average, (Champion, 2008)***
			K1	***K2***	***Range***		
Al, %	0.41-4.52	1.6	3.76	4.14	1.68-3.26	1-8.2	8.2
Ca, %	2.34-26.5	11.1	24.83	22.37	7.0-19.77	n.r.*	5
Fe, %	0.28-3.77	0.9	2.45	2.55	1.5-2.92	4.5-5.5	6.3
K, %	0.05-0.43	0.2	0.28	0.3	0.3-1.1	n.r.*	1.5
Na, %	0.01-0.07	0.1	0.06	0.06	0.01-0.93	n.r.*	2.3
S, %	<1.9-4.6	n.r.*	4.12	4.05	0.01-1.37	n.r.*	0.04
As, mg/kg	1.64-36.3	10	17.1	17.7	4.0-13.8	0.1-48	2.1
Cd, mg/kg	n.r.*	n.r.*	0.44	0.5	0.3-1.13	0.01-3	0.15
Co, mg/kg	1.24-17.3	3.9	12.2	12.3	10.2-22.8	1-40	30
Cr, mg/kg	17.5-465	146	203.7	229.2	55.8-100.9	5-1000	140
Cu, mg/kg	n.r.*	12	27.54	30.37	18.1-32.5	2-100	68
Mn, mg/kg	12.3-137	78	212	166	320-777	200-3000	1100
Mo, mg/kg	n.r.*	4.8	15.24	16.05	0.33-7.21	0.5-40	1.1
Ni, mg/kg	<9-147	16	101.2	102.9	79.4-205.4	1-200	90
Pb, mg/kg	n.r.*	6	10.84	13.22	7.79-19.2	3-189	10
V, mg/kg	20-320	161	233	267	47-79	3-230	190
Zn, mg/kg	5.53-64.9	27	49.6	55.9	30.96-130	10-300	79
*n.r.: not reported							

Table 2. Distances of possible sources from sampling points, km (ASA: Ash Storage Site, TPS1: Thermal Power Station 1, TPS2: Thermal Power Station 2, CMS: Coal Mining Site)

Sampling point	***ASA***	***TPS1***	***TPS2***	***CMS***
SP1	0.5	1.31	4.97	7.17
SP2	2.05	1.94	2.37	5.16
SP3	3.52	3.08	1.00	4.45
SP4	3.94	3.27	1.02	4.76
SP5	4.28	3.59	0.94	4.73
SP6	8.96	8.16	4.65	6.17
SP7	10.01	8.98	6.02	7.92
SP8	9.76	8.54	6.35	9.03

Soils were collected from the surface by using a core sampler (5 cm in diameter and 15 cm in length). At least five soil samplings were made at each location and the collected materials were combined. Five to seven plants were uprooted from the soil at each sampling point and the fruits (about 0.5 kg) were picked by hand. Two samples from power plant bottom ash storage area were also collected with the help of a shovel. Soil, plant, and ash samples were deposited into plastic bags and stored at 4°C until the immediate analysis.

2.3. Analytical methods

Soil and bottom ash samples above 2 mm in diameter were removed by screening, the materials <2mm were dried at 60°Cand homogenized. Plants were divided as root, leaves, seeds and/or fruits, the parts were washed with running tap water and rinsed with distilled water before they weredried at 60°C. Dried plant samples were ground by using an agate mortar and sieved under 80-mesh. The samples were sent to Acme Analytical Laboratories Ltd. (Vancouver, Canada), accredited under ISO 9002, for the analyses. For soil samples, 0.5 g of dried material under 80-mesh was first retained in 2 ml HNO_3 solution for 1 h and then 6 ml of 2:2:2 HCl–HNO_3–H_2O solution was added. The material was dissolved at 95°C for 1 h and analyzed with ICP-MS (Yaylalı-Abanuz, 2011). STD-DS7 was used as certified reference material during the analytical runs for the elements in soil and ash samples. For plant samples, 1.0 g of material was digested with first HNO_3 and then *aqua regia*, diluted to 20 ml and analyzed by ICP-MS. STD-V14 and STD-V16 were used as certified reference materials during the analytical runs for the elements in plant samples (Rogan et al., 2009).

2.4. Calculation of Enrichment Factor, Bioconcentration Factor and Translocation Factor

The enrichment factors of the elements in soils (EF_S) and in coal ash samples were calculated by the formula given in Eq. (1) proposed by Buat-Menard and Chesselet (Buat-Menard and Chesselet, 1979).

$$EF_S = (C_{E-S}/C_{RE-S})/(C_{E-AEC}/C_{RE-AEC}) \quad (1)$$

where: $C_{E\text{-}S}$ is the concentration of the studied element in sample; $C_{RE\text{-}S}$ is the concentration of the reference element in the sample; $C_{E\text{-}AEC}$ is the concentration of the studied element in reference material; $C_{RE\text{-}AEC}$ is the concentration of the reference element in reference material. Here Earth crust was used as the reference material (Table 1), while aluminum was used as the reference element since it is one of the most important elements in the Earth crust and aluminum concentrations in soil and coal ash samples were not exceeding its crust abundance. The average enrichments of elements in bottom ash samples was also calculated with respect to their concentrations in lignite coal (Karayigit et al., 2000) by using aluminum as the reference element in coal.

The magnitude of the *EF* is used to evaluate the enrichment of target element in the studied matrix (Yaylalı-Abanuz, 2011); *EF*<2 indicates a range between deficiency to minimal enrichment of the studied element, while 2<*EF*<5 represents a moderate enrichment, 5<*EF*<20 shows a significant enrichment, 20<*EF*<40 describes a very high enrichment, and *EF*>50 is the indication of extremely high enrichment.

Plant bioconcentration factors (BCFs) were determined by dividing the HM concentration in plant parts' to the concentration in soil (Yoon et al., 2006).

Translocation factors (TFs) were calculated by taking the ratio of HM concentration in plant shoots to that in plant root (Yanqun et al., 2005). Plants are exhibiting TF < 1 when they are stressed due to the metal level. However, TF > 1 indicates that plants tolerate the metal concentration and also utilize the studied metal. That's why TF > 1 is an indication of a hyperaccumulator plant (Chanu and Gupta, 2016).

2.5. Statistical analysis

Correlations analysis using Pearson correlation coefficients were applied to identify the interrelations between the elemental levels in samples and the distance of the sampling point from the pollution sources by using SPSS 24.0. The correlations among the bioconcentration factors of studied elements (As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, V, Zn, Al, Ca, Fe, K, Na, and S) were also investigated. Principal Component Analysis with Varimax rotation and Kaiser normalization was applied to this data set to describe the main factors influencing the elements' enrichment in plants. Sample size was tested by applying KMO and Bartlett's Test to data set by using SPSS 24.0 for Windows (IBM Inc., Chicago, Ill., USA). Kaiser-Meyer-Olkin Measure of Sampling Adequacy was determined as 0.540 and the significance of Bartlett's Test of Sphericity was <0.001; therefore the sample size was found suitable to be evaluated by using PCA. Major principal components (PCs) with significant clusters defined by factor loading coefficients higher than 0.5 and with Eigenvalues greater than 1.0 were extracted.

3. Results and discussion

3.1. Elemental levels detected in thermal power plant bottom ash and soil samples

The concentrations of elements in bottom ash samples were generally higher than their concentrations in lignite coal, except Na (Table 1) due to their enrichment in ash during the combustion process. The average enrichments of elements in bottom ash ($E_{A\text{-}C}$) were calculated with respect to their concentrations in lignite coal (Karayigit et al., 2000), and varied between 0.6 (Na) and 6.35 (Ni). The mean $E_{A\text{-}C}$ of the elements was determined as 2.38. The $E_{A\text{-}C}$ values of Pb, Mn, Cr, and Co were in the range of reported enrichments calculated for Indian bottom ashes, while $E_{A\text{-}C}$ values for As, Cu, Fe, Ni, and Zn were higher (Bhangare et al., 2011). However, enrichment factors of Mo and S in coal ash were found as 29.6 (very high enrichment) and 213 (extremely high enrichment), respectively (Table 3).

Co, Cr, Cu, Mn, V, Al, Fe, K and Na concentrations in all soil samples were below their average levels in Earth's crust (AEC), while As, Cd, and Ca levels were above the AEC in all samples. It is also observed that Mo, Pb, Zn levels in some soil samples and S levels in SP1, SP3, SP4, SP5, and SP6 soils were above their AEC. Kelly et al. (1996) investigated the Pb, Zn, Cd and Cu concentrations in industrial and agricultural soils of Wolverhampton, Britain. The range of these elements' soil levels in our study are generally closer to the measured range in agricultural soils of Britain, rather than the soils from industrial sites.

Table 3. Enrichment factors (EFs) of elements[1] in soil samples and coal ash regarding their abundance in Earth crust

Sample	*As*	*Cd*	*Co*	*Cr*	*Cu*	*Mn*	*Mo*	*Ni*	*Pb*	*V*	*Zn*	*Ca*	*K*	*S*
K_{Ave}^{*}	17.2	6.5	0.8	3.2	0.9	0.4	29.6	2.4	2.5	2.7	1.4	9.8	0.4	213
SP1	9.1	22.9	1.0	1.6	0.8	0.9	6.7	2.2	2.4	1.0	1.2	5.5	2.2	105
SP2	11.4	12.7	2.3	2.1	1.4	2.3	1.5	5.1	4.3	1.3	3.2	19.3	0.8	1.2
SP3	17.1	48.4	2.7	4.1	2.7	2.6	47.1	7.6	6.3	3.0	11.9	23.9	2.7	59.3
SP4	12.4	12.9	2.1	2.2	1.7	2.1	4.9	5.5	5.7	1.1	4.3	7.2	1.1	11.6
SP5	10.6	13.8	2.4	2.2	1.9	2.5	4.3	4.9	5.4	1.4	4.4	16.3	1.5	11.2
$SP6_{SF**}$	8.1	6.2	1.8	1.5	1.2	2.0	1.2	3.3	3.6	0.9	2.2	5.5	0.7	0.7
$SP6_{SB***}$	8.6	6.6	1.8	1.5	1.2	1.9	1.2	3.3	3.6	0.9	1.8	6.4	0.7	3.6
SP7	22.7	12.0	2.6	2.5	1.6	2.4	2.0	7.9	6.6	0.9	3.4	6.2	0.7	0.9
$SP8_{SF**}$	7.2	5.4	1.7	1.6	1.0	1.7	1.0	3.5	3.2	0.8	2.0	4.3	0.8	0.6
$SP8_{SB***}$	6.7	5.0	1.7	1.6	1.0	1.7	1.0	3.5	3.2	0.8	1.9	3.5	0.8	0.6
Scale: EF<2 : Deficiency to minimal enrichment, 2<EF<5 : Moderate enrichment, 5<EF<20 : Significant enrichment, 20<EF<40 : Very high enrichment, EF>40 Extremely high enrichment														

*[1] Enrichment factors for Fe and Na were <1.8 in all samples and not presented in the table, *Coal ash samples' average, **Sunflower field sample, ***Sugar beet field sample*

Among the studied elements, the enrichment factor (EF_S) values calculated for Fe and Na were <1.8 for all soil samples (Table 3). EF_S values for Co, Cr, Cu, Mn, V, and K elements in soils were in the range of minimal to moderate enrichments ($0.7<EF_S<4.1$). The concentrations of Fe, Na, K, Co, Cu, and Mn in bottom ash samples are lower or within the range of their levels in soils, while Cr and V levels in bottom ashes are exceeding the upper limit of soil concentrations.

Ni, Pb, and Zn levels in soils represented EF_S values between minimal enrichment to significant enrichment ($1.2<EF_S<11.9$), while the levels of these elements in coal ash are in the range of their soil concentrations. As and Cd were found as the elements that their EF_S values ≥5 in all soil samples. The coal ash concentrations of As, Mo, and Ca are much above the levels observed in soils, while coal ash Cd level was in soil range. In addition to that, as presented in Table 3, As, Cd, Mo, Ca, and S are the elements in coal bottom ash having $E_{A\text{-}C}$ values greater than 5.0 (between 6.5 for Cd and 213 for S), which corresponds a range from significant enrichment to extremely high enrichment. In most of the soil samples the elements of As, Cd, Ca and S showed EF_S values greater than 5.

SP3 was the most polluted soil with EF_S values of 48.4, 47.1, and 59.3 for Cd, Mo, and S, respectively. The highest EF_S was calculated for SP1 sulfur content (EF_S: 104.7) and this sample showed a very high enrichment of Cd (EF_S: 22.9). SP7 also had an EF_S of 22.7 for As. The sampling points SP6, SP7, and SP8 have a distance of more than 6 km from ASA, TPS1, and CMS and their distances from TPS2 are also more than 4 km. The soils from these sampling points have lower EF_S values for most of the studied elements. It should be noted that, according to the wind rose (Fig. 1), these points were under only the direction of north winds and therefore they have been effected only the emissions from CMS and/or TPS2. The sampling points SP1, SP2, SP3, SP4, and SP5 were in closer distances from the sources, been exposed to under winds of all of the pollution sources on the site which resulted with higher elemental concentrations and higher EF_S values in their soils. The studied soils can be ranked in decreasing order according to the sum of EF_S calculated as follows; SP3>SP1>SP5>SP4>SP7>SP2>SP8>SP6.

Srinivasa Gowd et al. (2010) determined the soil enrichment factor of some elements in two industrial areas in Uttar Pradesh, India. The average EF_S values they found for Cr (72.1), Cu (5.2), and Pb (7.97) were higher than the highest EF_S values of these elements calculated in our study, while the upper range of EF_S values in this study were higher than the EF_S of V (1.65) and Zn (8.16) in Indian industrial areas.

In a study conducted in Guadong Province, China, soil samples were collected from agricultural lands, industrial areas, waste disposal/treatment sites, urban areas, forest lands, and a water source protection area and EF_S values of major heavy metals were determined (Hu et al., 2013; Moolenaar and Beltrami, 1998; Yu et al., 2017). The highest EF_S's they have calculated for As, Cr, Cu, Ni, Pb, and Zn were much higher than the highest EF_S values of these elements in our study. However, the highest EF_S value calculated for Cd in China (20.9) was lower than the highest EF_S value calculated in our study area (48.4). In addition, average of the EF_S values of As, Cd, Ni, Pb, and Zn calculated for Chinese soils were lower than that calculated averages in this study. The EF_S values of Cr and Cu were compatible in both studies.

3.2. Elemental levels detected in plants and their bioconcentration and translocation

3.2.1. Elemental levels in plants

The plants were sampled from SP1, SP2, SP4, SP6, SP7, and SP8. The concentrations of studied elements in plant parts are presented in Table 4 and Table 5. Cd, Zn, Al, Fe, K concentrations in sunflower, sugar beet, eggplant, and apricot were in the plant range (Pais and Jones, 1997) in all sampling points.

Table 4. Heavy metal and metal concentrations detected in plant parts, ppm dw

Sampling Point	*Plant type*	*Plant part*	*As*	*Cd*	*Co*	*Cr*	*Cu*	*Mn*	*Mo*	*Ni*	*Pb*	*V*	*Zn*
SP1	**Sunflower**	**Root**	0.8	0.09	1.61	15.7	9.32	60	5.1	8.6	0.84	16	26.2
		Leaves	3.3	0.2	3.76	45.8	26.8	189	8.64	22.7	2.76	52	59.4
		Seeds	2.3	0.18	2.3	29.1	29.77	87	4.02	18.8	1.74	34	56.4
SP2	**Sugar beet**	**Root**	0.5	0.11	0.85	5.2	6.36	65	0.11	5.9	0.45	5	11.5
		Leaves	0.7	0.33	1.7	9.5	9.66	157	0.78	11.4	0.96	8	17.6
SP4	**Eggplant**	**Root**	1.6	0.27	1.43	9.7	7.77	63	1.82	10	1.1	11	43.9
		Leaves	4.4	0.36	2.3	14.2	11.35	160	7.93	18.8	2.79	16	41.6
		Fruits	0.6	0.21	0.2	6.6	7.21	32	4.59	1.6	0.27	<2	30.3
	Apricot	**Fruits**	0.1	<0.01	0.06	1.9	2.76	8	0.17	2.4	0.23	<2	5
SP6	**Sunflower**	**Root**	4.5	0.3	12.15	81.2	21.2	538	0.77	73.8	7.79	47	51.6
		Leaves	1	0.12	1.12	9.6	34.49	170	1.57	8.2	1.03	10	22.3
		Seeds	0.6	0.11	1.29	8.7	23.2	89	0.46	10.7	0.81	5	37.9
	Sugar beet	**Root**	0.3	0.08	0.41	2.6	4.35	62	0.08	2.5	0.19	2	12.3
		Leaves	0.9	0.33	1.63	10.8	15.4	253	0.65	11.8	1.16	10	25.9
SP7	**Sunflower**	**Root**	5.1	0.29	5.24	48.4	16.77	211	0.98	47.9	5.01	17	35.3
		Leaves	3.3	0.4	4.88	22.9	21.12	245	3.11	52	4.01	18	43.2

		Seeds	3.4	0.39	4.87	23.1	24.5	197	1.13	43.2	3.89	13	52.6
SP8	**Sunflower**	**Root**	0.9	0.18	2.87	16.5	11.75	123	0.56	15.7	1.63	14	26.2
		Leaves	1.3	0.22	2.11	16.3	29.3	209	2.08	14.1	1.88	15	37.5
		Seeds	<0.1	0.13	0.37	2.6	22.75	40	0.38	3.8	0.17	2	32.2
	Sugar beet	**Root**	0.5	0.09	1.21	7	5.2	82	0.1	8.2	0.76	6	21
		Leaves	0.8	0.24	1.85	10.6	12.32	266	0.66	12.8	1.06	9	30.2
Range in plants (Pais and Jones. 1997)		**Max.**	1.7	1	0.57	0.2	10	500	3	3.5	1	4.2	100
		Min.	0.009	0.1	0.3	0.02	1	10	0.1	0.3		0.27	10

Table 5. Crustal element concentrations detected in plant parts, ppm dw

Sampling Point	*Plant type*	*Plant part*	*Al*	*Ca*	*Fe*	*K*	*Na*	*S*
SP1	**Sunflower**	**Root**	0.25	1.52	0.192	2.7	0.144	0.49
		Leaves	0.82	8.69	0.606	3.15	0.02	1.57
		Seeds	0.46	4.46	0.363	4.21	0.013	0.91
SP2	**Sugar beet**	**Root**	0.1	1.29	0.104	0.98	0.087	0.11
		Leaves	0.2	3.77	0.214	4.15	1446	0.91
SP4	**Eggplant**	**Root**	0.14	1.95	0.164	2.43	0.055	0.19
		Leaves	0.31	5.93	0.329	5.26	0.015	0.5
		Fruits	0.01	0.67	0.022	4.65	0.009	0.23
	Apricot	**Fruits**	0.005	0.22	0.007	2.86	0.002	0.06
SP6	**Sunflower**	**Root**	1.84	6.06	1.623	1.19	0.184	0.1
		Leaves	0.16	6.13	0.178	4.35	0.007	0.65
		Seeds	0.18	1.71	0.169	3.2	0.003	0.26
	Sugar beet	**Root**	0.06	0.36	0.054	1.44	0.566	0.09
		Leaves	0.24	3.36	0.253	2.94	3181	0.75
SP7	**Sunflower**	**Root**	0.45	3.9	0.724	3.86	0.154	0.18
		Leaves	0.52	7.48	0.666	5.49	0.015	1
		Seeds	0.48	2.76	0.625	2.97	0.019	0.46
SP8	**Sunflower**	**Root**	0.35	1.3	0.324	2.23	0.435	0.2
		Leaves	0.38	7.4	0.325	3.17	0.011	0.74
		Seeds	0.04	0.89	0.04	2.34	0.003	0.21
	Sugar beet	**Root**	0.19	0.69	0.185	1.71	0.212	0.09
		Leaves	0.24	2.59	0.244	2.59	3887	0.53
Range in plants (Pais and Jones. 1997)		**Max.**	1000	5	100	9.75	n.a.*	0.96
		Min.	10		20			

*n.a.: not available

As, Mn, Mo, Ca, and S levels have not exceeded the plant range upper limit in sugar beet and apricot samples, but exceeded this limit in some sunflower and eggplant samples. However, the levels of Co, Cr, Cu, Ni, Pb, and V in plant parts have exceeded the upper limit for the plant rage in many of the samples. It was seen that, average As, Cd, Cr, and Pb concentrations of plant samples were found higher than the levels found in vegetables grown in suburban sites of Henan, China (Liu et al., 2006) and then the market vegetables in Zhejiang, China (Pan et al., 2016). Average Cd, Cr and Pb concentrations detected in studied plants were in their measured range in the herbs and vegetables grown in rural and agricultural sites of Turkey (Divrikli et al., 2006; Tüzen, 2003).

Average Mn level (150.3 ppm) were found much higher than the previous reports that indicates a range of 30.1 to 93 ppm in agricultural sites (Divrikli et al., 2006; Tüzen, 2003, Tokalıoğlu and Kartal, 2003). Studied plants' average Cu and Zn levels were in the ranges detected in the vegetables from both urban sites and rural sites in Turkey (Demirezen and Aksoy, 2006; Divrikli et al., 2006; Tüzen, 2003, Tokalıoğlu and Kartal, 2003). In general, the highest elemental concentrations were found in leaves of sugar beet and eggplant samples. The seeds have the lowest concentrations in all sunflower samples, while the highest concentrations were found in either the roots or leaves depending on the location of the sample.

3.2.2. Bioconcentration of elements in plants

Bioconcentration factors (BCFs) of HMs and crustal elements in plant parts are presented in Table 6 and Table 7, respectively, with available reference values (Pais and Jones, 1997). Co, Cr, and Pb metals' average BCF values in sunflower parts were higher than the upper limits reported for plants, while these elements' BCFs were also high in eggplant roots and/or leaves. BCF values calculated for As and Co in sugar beet leaves were also exceeding the reference upper limit for plants. BCFs for Cu, Mo, V, Zn, Al, Ca, and Fe were <1.00, while BCF range for Mo in studied plant parts was 0.17-5.25 ppm. Potassium BCFs were varies in a large range; between 2.45 and 12.45. Since Na levels in sugar beet leaves were very high, BCFs as high as 431000 were calculated. Sulfur (S) BCFs in plants were determined in the range of 0.36 and 100.00.

Table 6. Bioconcentration factors (BCFs) of studied metals and heavy metals for plant parts with reference values (Pais and Jones, 1997)

Plant	*Sample*	*BCF*	*As*	*Cd*	*Co*	*Cr*	*Cu*	*Mn*	*Mo*	*Ni*	*Pb*	*V*	*Zn*
SF[1]	**SP1**	**Roots**	0.09	0.24	0.10	0.13	0.30	0.10	2.08	0.08	0.07	0.15	0.49
		Leaves	0.37	0.54	0.23	0.37	0.85	0.33	3.52	0.20	0.23	0.50	1.11
		Seeds	0.26	0.49	0.14	0.24	0.94	0.15	1.64	0.17	0.14	0.33	1.06
	SP6	**Roots**	0.75	0.95	0.63	1.16	0.57	0.66	1.67	0.73	0.61	0.75	0.82
		Leaves	0.17	0.38	0.06	0.14	0.93	0.21	3.41	0.08	0.08	0.16	0.35
		Seeds	0.10	0.35	0.07	0.12	0.63	0.11	1.00	0.11	0.06	0.08	0.60
	SP7	**Roots**	0.16	0.58	0.15	0.19	0.44	0.17	1.27	0.13	0.13	0.24	0.43
		Leaves	0.22	0.71	0.11	0.19	1.10	0.28	4.73	0.12	0.15	0.25	0.62
		Seeds	0.02	0.42	0.02	0.03	0.86	0.05	0.86	0.03	0.01	0.03	0.53
	SP8	**Roots**	0.37	0.56	0.23	0.48	0.55	0.28	1.51	0.23	0.26	0.33	0.46
		Leaves	0.24	0.77	0.21	0.23	0.69	0.32	4.78	0.25	0.21	0.35	0.56
		Seeds	0.25	0.81	0.21	0.23	0.80	0.26	1.74	0.21	0.20	0.25	0.68
SB[2]	**SP2**	**Roots**	0.10	0.29	0.06	0.08	0.26	0.12	0.27	0.06	0.05	0.09	0.17
		Leaves	0.14	0.86	0.12	0.14	0.39	0.29	1.90	0.11	0.10	0.14	0.27
	SP6	**Roots**	0.09	0.30	0.06	0.08	0.20	0.11	0.22	0.07	0.06	0.11	0.35
		Leaves	0.14	0.80	0.09	0.12	0.47	0.36	1.47	0.10	0.08	0.16	0.50
	SP7	**Roots**	0.05	0.24	0.02	0.04	0.12	0.09	0.17	0.02	0.02	0.03	0.24
		Leaves	0.15	0.99	0.09	0.15	0.41	0.35	1.35	0.12	0.09	0.17	0.50
EP[3]	**SP5**	**Roots**	0.22	0.50	0.08	0.11	0.24	0.10	1.21	0.07	0.07	0.19	0.46
		Leaves	0.60	0.67	0.13	0.17	0.35	0.25	5.25	0.14	0.18	0.28	0.44
		Fruits	0.08	0.39	0.01	0.08	0.22	0.05	3.04	0.01	0.02	0.03	0.32
AP[4]	**SP4**	**Fruits**	0.03	0.03	0.00	0.03	0.12	0.02	0.20	0.03	0.02	0.04	0.08
Plant Range,	**(Pais&Jones, 1997)**	**Min.**	0.01	1.00	0.01	0.01	1.00	n.a.*	n.a.	0.10	0.01	n.a.	1.00
		Max.	0.10	10.00	0.10	0.10	10.00	n.a.	n.a.	1.00	0.10	n.a.	10.00

[*] n.a.: not available, [1] SF: Sunflower, [2] SB: Sugar beet, [3] EP: Eggplant, [4] AP: Apricot

Table 7. Bioconcentration factors (BCFs) of crustal elements for plant parts

Plant	Sample	BCF	Al	Ca	Fe	K	Na	S
SF[1]	**SP1**	**Roots**	0.09	0.17	0.08	2.45	0.15	0.36
		Leaves	0.30	0.96	0.26	2.86	0.02	1.14
		Seeds	0.17	0.49	0.15	3.82	0.01	0.66
	SP6	**Roots**	0.64	0.64	0.63	3.34	16.73	10.00
		Leaves	0.06	0.64	0.07	12.21	0.64	65.00
		Seeds	0.06	0.18	0.07	8.98	0.27	26.00
	SP7	**Roots**	0.11	0.16	0.11	4.96	43.50	20.00
		Leaves	0.12	0.90	0.11	7.04	1.10	74.00
		Seeds	0.01	0.11	0.01	5.20	0.30	21.00
	SP8	**Roots**	0.19	0.43	0.22	12.45	8.11	18.00
		Leaves	0.22	0.83	0.20	17.71	0.79	100.00
		Seeds	0.20	0.31	0.19	9.58	1.00	46.00
SB[2]	**SP2**	**Roots**	0.06	0.07	0.06	4.21	9.67	11.00
		Leaves	0.12	0.19	0.12	17.83	161000	91.00
	SP6	**Roots**	0.06	0.10	0.06	3.56	23.56	9.00
		Leaves	0.07	0.37	0.08	5.40	431000	53.00
	SP7	**Roots**	0.02	0.03	0.02	4.10	45.92	1.89
		Leaves	0.09	0.32	0.10	8.37	258000	15.75
EP[3]	**SP5**	**Roots**	0.00	0.07	0.01	9.89	0.60	1.77
		Leaves	0.14	0.59	0.13	11.19	1.00	3.85
		Fruits	0.06	0.19	0.07	5.17	3.67	1.46
AP[4]	**SP4**	**Fruits**	0.00	0.02	0.00	6.98	0.13	0.75

[1] SF: Sunflower, [2] SB: Sugar beet, [3] EP: Eggplant, [4] AP: Apricot

Average BCFs of As, Co, Cr, Mn, Ni, Pb, V, Al, Fe, and Na calculated for sun flower parts showed the same trend; the rank of their BCFs in decreasing order was as follows; Roots>Leaves >Seeds. The highest BCFs for Cd, Mo, Ca, Cu, K, and S in sunflowers were calculated for the leaves, while the highest Zn BCF was found for its seeds. BCF values of all studied elements in sugar beet leaves were higher than their BCFs in roots. The rank of BCFs in decreasing order was Leaves>Roots>Fruits for Cd, Co, Cr, Cu, Mn, Ni, Pb, V, K, and S in the eggplant samples. The highest As and Zn BCFs were calculated for roots, while the leaves showed the highest Mo, Al, Ca, and Fe BCFs, and the fruits resulted with the highest Na BCFs in eggplant sample. However, in general, the lowest element BCFs were found in the edible parts of the plants such as sugar beet roots, eggplant and apricot fruits, and sunflower seeds. Compared to the other plants'; BCF values calculated for As, Co, Cr, Cu, Zn, Ca, Al, Fe, and S in sunflower roots and leaves were the highest, while the BCFs for sunflower seeds were also higher than the eggplant and apricot fruits. In addition to that, it was observed that the rank of element BCFs differ according to plant type; this finding is compatible with the previous reports in the literature (Cataldo and Wildung, 1978).

3.2.3. Translocation of elements in plants

Translocation factor (TF) is the potential of a plant to transfer metals and other elements from its roots to aerial parts. TFs for sunflower plants collected from different sampling points were calculated for the leaves and seeds, and presented in Fig. 2a-b, respectively. It was observed that, higher average TFs for sunflower leaves were calculated for S (4.7), Ca (3.6), Mo (2.7), and Cu (2.1), while the lowest TF was calculated for Na (0.1). The average TFs for the other studied elements were found >1 in sunflower leaves. Previously reported TF values for sunflower leaves were lower than the values calculated in the content of this study, such as; TF_{Zn}= 0.44-0.57, TF_{Cu}= 0.32-0.45, TF_{Cd}= 0.31-0.52, and TF_{Pb}= 0.06-0.18 (Usman & Mohamed, 2009). In the content of the study, minimum TF value was calculated for Na (0.06) in sunflower seeds, and the only elements resulted with TFs > 1 in the seeds of the sunflowers were S (2.0), Cu (1.9), K (1.5), Zn (1.4), and Cd (1.1). TFs for sunflower leaves were higher than the TFs for the seeds, except Zn. TF_{leaves}/TF_{seeds} were the highest for Mn, S, Ca, and Mo elements in sunflowers and were between 2.2 and 3.3.

The average highest TFs were calculated for Na (13525), S (7.5), and Mo (7.3) the in sugar beet leaves, while the minimum TF was calculated for Zn (1.69). The other elements' TF values were all >1 (Fig. 3.). Reported TFs for sugar beet leaves were compatible with our results; TF_{Pb}= 0.27-1.75, TF_{Cd}= 1-2, TF_{Cr}= 0.1-1.8, TF_{Cu}= 0.6-1.8, TF_{Ni}= 0.2-2.6, TF_{Zn}= 0.8-1.9 (Yilmaz and Temizgul, 2012).

In eggplants, the average TF_{leaves} were determined for Al (31), Fe (15), Ca (8.9) and Mo (4.4), and the lowest for K (1.1). The highest average TF_{fruits} were found for Al (14), Fe (7.5), and Na (6.1) for the eggplant, while the lowest was for Co (0.1) (Fig. 4.). The previously reported TFs in eggplant leaves were lower that determined in this study, except Cd and Pb; TF_{Cr}= 0.2-0.6, TF_{Ni}=0.2-0.75, TF_{Cu}= 0.3-1.05, TF_{Cd}=1.3-2.3, TF_{Pb}= 0.05-1.9 (Wiseman, et al., 2014). When the values for Na were excluded, the sums of the average TF_{leaves} determined for the studied elements in decreasing order were as follows; 80.4 (eggplant) > 54.1 (sugarbeet) > 29.6 (sunflower).

According to the comprehensive study of Antoniadis et al. (2017), Na hyperacumulation in sugar beet leaves was not reported before in the literature. However, since TFs calculated for Na in sugar beet leaves were in the range of 5620-18335 (13525 in average), this plant can be considered as a hyperaccumulator for Na, and it has a high potential to be used in soil phytoremediation (Chanu and Gupta, 2016; Dushenkov et al., 1995).

3.3. Influence of the distance from the pollution sources on elemental levels in samples

In this part the correlations between the samples' elemental levels and the distances from the sources, which are presented with Table 2, are investigated. The statistically significant correlations are presented with Table 8. A negative correlation shows decreasing concentrations of an element with increasing distance from the source, which indicates the link between the element level in the sample and the corresponding pollution source. Oppositely, positive correlations shows that the element level in sample is unrelated with the pollution source.

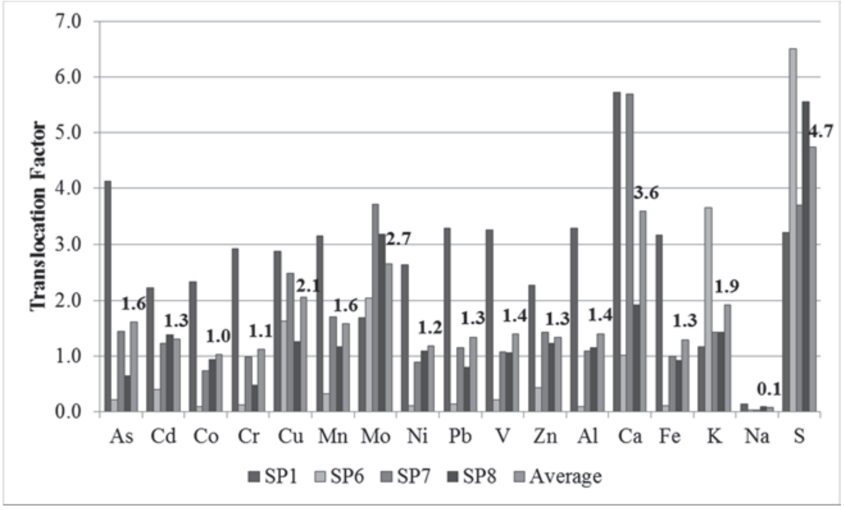
Detected significant negative correlations reveal that Mo, S, Cd, V, Cu, and Ca concentrations in studied samples may be related with the emissions from the thermal power plant components on the site.

On the other hand, it is understood that Co, Mn, Ni, Pb, Fe, and Al elements, whose levels in samples have positive correlations with distances from the pollution sources on the site, may not have been linked with the emissions from thermal power site. The major source of these elements in study area could be geochemical soil background levels, however the contributions from irrigation water, agrochemicals and fertilizers used in the area cannot be neglected.

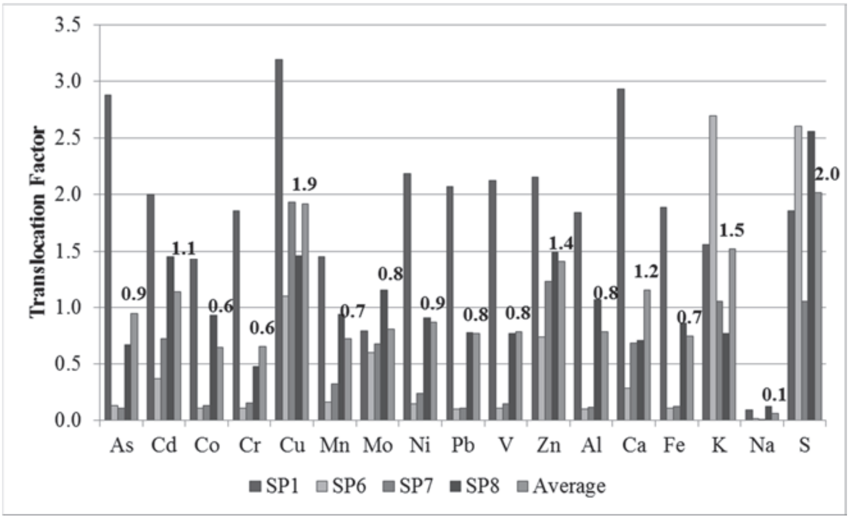
3.4. Principal component analysis

The correlation matrix determined for the calculated BCFs of the elements for studied plant parts (Table 9) showed that BCFs of a large cluster of elements' are very strongly correlated ($p \leq 0.01$). These elements are namely As, Cd, Co, Cr, Mn, Ni, Pb, V, Al, Ca, and Fe. Besides, Sulfur (S) has significant correlations with Cd, Cu, Mo, and K ($0.01 \leq p \leq 0.05$).

Principal component analysis (PCA) was carried out to identify the major sources linked with elements' enrichment in plant parts. The BCFs data set of the studied elements in plant parts were evaluated by PCA and four principal components were extracted. The variances explained by principal components (PCs) were all high and accounted for 90.795% of the total variance in the analysis (Table 10). In the component matrix (Table 11), high factor loading coefficients were obtained for the elements of Co (0.980), Pb (0.979), Ni (0.975), Cr (0.974), Fe (0.971), Al (0.956), V (0.904), As (0.870), and Mn (0.828) in first principal component (PC1) which explains 50.848% of the total variance.



(a)



(b)

Fig. 2. Translocation factors calculated for sunflower samples in sampling points SP1, SP6, SP7, and SP8; (a) TFs for the sunflower leaves, (b) TFs for the sunflower seeds

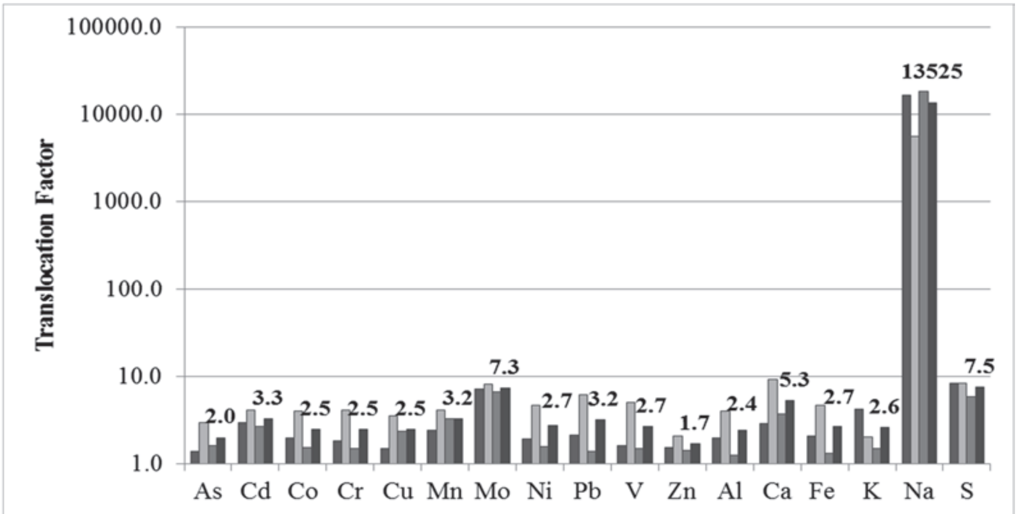


Fig. 3. Translocation factors (TFs) calculated for sugar beet leaves in sampling points SP2, SP6, SP7 and the average TFs

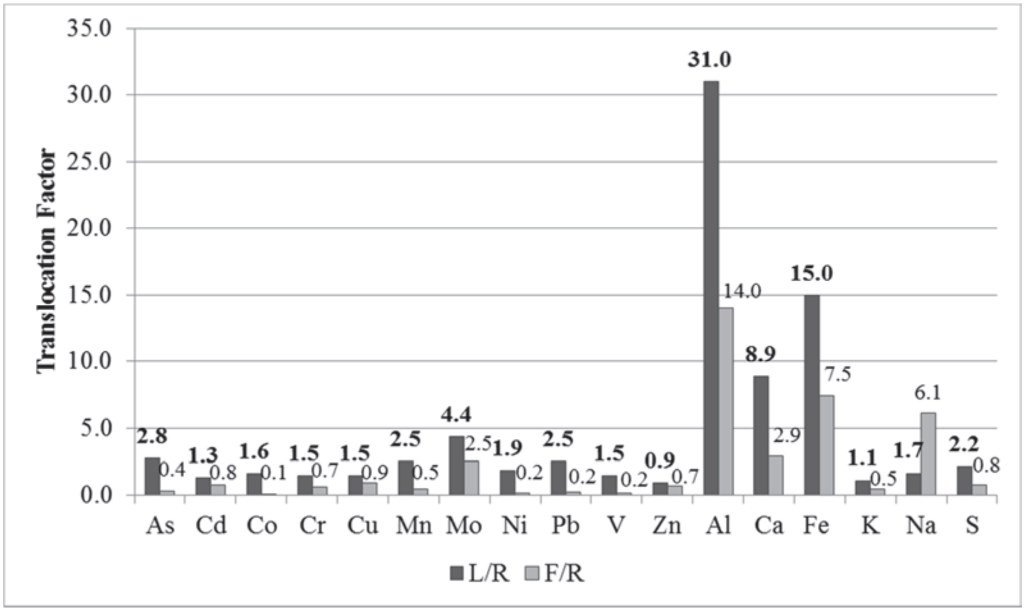


Fig. 4. Translocation factors calculated for eggplant leaves (L/R) and fruits (F/R) in sampling point SP5

Table 8. Statistically significant correlations detected between the elemental concentrations in the samples and the distances from the pollution sources on the site

Source	***Sample***	***Negative Correlations***		***Positive correlations***	
		p[1]		***p***[1]	
		≤0.01	***≤0.05***	***≤0.01***	***≤0.05***
ASA	**Soil**	-	Cd (-0.665)* S (-0.636)	Co (0.894) Mn (0.915)	Pb (0.640) Fe (0.730)
	SF$_R$[2]	Mo (-0.990)	-	-	-
	SF$_L$[3]	-	Mo (-0.959) V (-0.963)	-	-
	SF$_S$[4]	-	Mo (-0.964) Cu (-0.958)	-	-
	SB$_L$[5]	-	-	Mn (1.000)	-
TPS1	**Soil**	-	-	Co (0.886) Mn (0.901)	Al (0.651) Fe (0.759)
	SF$_R$[2]	Mo (-0.989) S (-0.946)	-	-	-
	SF$_L$[3]	-	Mo (-0.958) V (-0.965)	-	-
	SF$_S$[4]	-	Mo (-0.961) Cu (-0.953)	-	-
	SB$_R$[6]	S (-0.999)	-	-	-
	SB$_L$[5]	-	-	Mn (0.998)	Al (0.999)
TPS2	**Soil**	-	Ca (-0.730)	Al (0.854) Fe (0.838)	-
CMS	**Soil**	-	Ca (-0.745)	Al (0.824) Fe (0.815)	-
	SB$_L$[5]	-	-	Ni (1.000)	-

[1]Significance of Pearson correlation, [2]Sunflower roots, [3]Sunflower leaves, [4]Sunflower seeds, [5]Sugarbeet leaves, [6]Sugarbeet roots,
**Numbers in parenthesis are Pearson correlation coefficients (r)*

Cd is also member of this principal component with a lower factor loading coefficient of 0.536. These elements are highly correlated, and their soil concentrations are in the reported ranges (Pais and Jones, 1997). In addition, the elemental levels of Co, Mn, Pb, Fe, Al in soils and Mn and Ni in sugar beet leaves are found increasing with the distance from thermal power plant components. Therefore, PC1 is considered as natural soil background elemental concentrations. PC2 explains 17.228% of the total variance and high factor loadings of Cu (0.883), Ca (0.785), and Zn (0.768) elements are present in this component along with Mo (0.632). It is known that, the Bordeaux mixture and Burgundy solution are fungicides that are widely used chemicals in agriculture in Turkey (Kaplan, 1999). Bordeaux mixture contains $CuSO_4$ and $Ca(OH)_2$, while Burgundy solution is based on synthetic organic compounds carrying Mo in their molecules (Bodnar and Cutler, 1985). Zn deficiency in Turkish soils and plants is also common (Cakmak et al., 1999), and that's why $ZnSO_4$ is applied in soils and orchards

(Uçgun and Akgul, 2011) to fulfill this insufficiency. That's why, it is considered that PC2 represents the contribution of widely used agrochemicals in agricultural areas to the elemental levels and BCFs in plants. The high factor loading coefficients of K (0.930) and S (0.808) are found together with Mo (0.556) in PC3, which explains 13.272% of the total variance. As it was explained in Section 3.3, Mo and S are among the elements that their concentrations in plant parts decreases with increasing distance from the thermal power plant units of TPS1 and ASA. These units having similar distances from the sampling points (Table 2). The presence of crustal element K in this principal component indicates that the source has a similar structure with soil, which is supporting the idea that the main source of these elements in PC3 is the coal ash carried by winds from ASA.

PC4 explains 9.447% of the total variance and high factor loading coefficient of Na (0.950) is found in this component, as well as Cd (0.603). The fertilizers with phosphorus in their formula account for more than 50% of the total consumption in Turkey (Çolakoğlu et al, 2005), and that they have high heavy metal concentrations. Savru (2003) determined the Cd content of phosphate fertilizers produced in Turkey in the range of 3.96-28.9 ppm, while the main material used in the production of phosphate fertilizer is phosphate rock carrying metal impurities (Zhou et al., 2000). As Na is one of the major crustal metals in soils (Champion, 2008), its presence with Cd is considered as PC4 is linked with a metal contribution from phosphate fertilizers used in agricultural areas.

4. Conclusions

Metals and crustal element levels in soils and plants from an agricultural area hosting a thermal power plant complex were investigated. High enrichments of As, Cd, Mo, Ca, and S in coal ash and soils were observed. Translocation factors in plant leaves were found higher than the fruits and seeds, while sugar beet was identified as a possible Na hyperaccumulator with a translocation factor of 13525 in its leaves.

Table 9. Correlation matrix for the elements' BCFs in studied plant parts

*	*As*	*Cd*	*Co*	*Cr*	*Cu*	*Mn*	*Mo*	*Ni*	*Pb*	*V*	*Zn*	*Al*	*Ca*	*Fe*	*K*	*Na*	*S*
As	1	0.541^{a}	0.841^{a}	0.827^{a}	0.232	0.756^{a}	0.451^{b}	0.826^{a}	0.891^{a}	0.882^{a}	0.505^{b}	0.833^{a}	0.606^{a}	0.836^{a}	0.085	-0.137	-0.070
Cd		1	0.580^{a}	0.487^{b}	0.346	0.825^{a}	0.381	0.566^{a}	0.579^{a}	0.564^{a}	0.400	0.553^{a}	0.489^{b}	0.564^{a}	0.374	0.482^{b}	0.476^{b}
Co			1	0.972^{a}	0.267	0.850^{a}	0.189	0.988^{a}	0.988^{a}	0.937^{a}	0.546^{a}	0.976^{a}	0.505^{b}	0.983^{a}	-0.008	-0.092	0.052
Cr				1	0.237	0.811^{a}	0.129	0.972^{a}	0.972^{a}	0.903^{a}	0.502^{b}	0.954^{a}	0.469^{b}	0.973^{a}	-0.083	-0.113	-0.051
Cu					1	0.325	0.466^{b}	0.265	0.298	0.395	0.681^{a}	0.311	0.701^{a}	0.285	0.119	-0.107	0.442^{b}
Mn						1	0.337	0.847^{a}	0.857^{a}	0.828^{a}	0.465^{b}	0.843^{a}	0.640^{a}	0.855^{a}	0.166	0.337	0.327
Mo							1	0.166	0.273	0.370	0.314	0.266	0.807^{a}	0.233	0.392	-0.112	0.430^{b}
Ni								1	0.980^{a}	0.909^{a}	0.517^{b}	0.966^{a}	0.489^{b}	0.977^{a}	0.002	-0.080	0.063
Pb									1	0.949^{a}	0.537^{a}	0.972^{a}	0.576^{a}	0.980^{a}	0.030	-0.122	0.059
V										1	0.701^{a}	0.940^{a}	0.702^{a}	0.928^{a}	-0.017	-0.115	0.031
Zn											1	0.603^{a}	0.636^{a}	0.562^{a}	-0.226	-0.067	-0.058
Al												1	0.585^{a}	0.995^{a}	-0.059	-0.112	0.041
Ca													1	0.552^{a}	0.200	-0.042	0.395
Fe														1	-0.037	-0.089	0.040
K															1	0.088	0.710^{a}
Na																1	0.275
S																	1

** Numbers in the cells are Pearson correlation coefficients (r), a Correlation is significant at the 0.01 level (2-tailed), b Correlation is significant at the 0.05 level (2-tailed)*

Table 10. Total Variance Explained by PCA

Principal Component	*Initial Eigenvalues*			*Rotation Sums of Squared Loadings*		
	Total	*% of Variance*	*Cumulative %*	*Total*	*% of Variance*	*Cumulative %*
PC1	9.801	57.654	57.654	8.644	50.848	50.848
PC2	2.745	16.144	73.799	2.929	17.228	68.076
PC3	1.731	10.181	83.979	2.256	13.272	81.348
PC4	1.159	6.816	90.795	1.606	9.447	90.795

Extraction Method: Principal Component Analysis

Table 11. Component matrix

Element	***Component***			
	PC1	***PC2***	***PC3***	***PC4***
Co	0.980			
Pb	0.979			
Ni	0.975			
Cr	0.974			
Fe	0.971			
Al	0.956			
V	0.904			
As	0.870			
Mn	0.828			
Cu		0.883		
Ca		0.785		
Zn		0.768		
Mo		0.632	0.556	
K			0.930	
S			0.808	
Na				0.950
Cd	0.536			0.603

Extraction Method: Principal Component Analysis, Rotation Method: Varimax with Kaiser Normalization

Principal component analysis (PCA) showed that the background soil concentration is the major factor influencing the plant BCFs, which is followed by the agrochemicals such as $ZnSO_4$, $CuSO_4$, and Burgundy solution used in the agricultural sites, particulate emissions from coal ash storage site, and phosphate fertilizers used to improve crop yield.

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