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ORIGINAL ARTICLE

Ecological assessment of heavy metals in soil around a coal-fired thermal power plant in Turkey

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Abstract

In this study, heavy metal concentrations in agricultural surface soil (0–5 cm) samples collected from the area around the Kangal lignite-fired thermal power plant were determined using energy-dispersive X-ray fluorescence spectrometry. Also, the pH values of agricultural soil samples were measured to assess the level of acidification. Geo-accumulation index (I_{geo}), enrichment factor (E_F), contamination factor (C_F), contamination degree (C_D), modified contamination degree (mC_D), and pollution load index (I_{PL}) were estimated to assess the heavy metals pollution in soil samples. The average concentration of Fe, Ti, Mn, Cr, Ni, Zn, Zr, Co, Cu, Pb, As, Sn and Hg was found as 39,065 ± 5096, 2262 ± 738, 721 ± 119, 713 ± 236, 610 ± 199, 82 ± 37, 65 ± 26, 64 ± 19, 29 ± 3, 17 ± 7, 9 ± 7, 3 ± 1 and 2 ± 1 mg kg^{-1}, respectively. The values of pH varied from 7.5 to 8.2 with an average value of 8.0 (moderately alkaline). The I_{geo}, E_F and C_F results reveal that the study area is heavily or very highly contaminated with Cr, Ni, and Hg. On the basis of the I_{PL} value, the soil samples are polluted with heavy metals. However, the mC_D indicates moderate heavy-metal contamination of the soil samples.

Keywords Soil pollution · Heavy metals · Geo-accumulation index · Enrichment factor · Contamination factor · Pollution load index · Lignite-fired power plant

Introduction

Energy is an essential commodity for economic and technological developments and social life. Turkey is a developing country and demands more energy to sustain economic development and population growth. In 2018, Turkey's installed electrical power capacity reached 88,526 MW and approximately 68% of the total electricity production was obtained from fossil fuels such as coal (lignite coal 15%, imported coal %11 and hard coal %1) and natural gas (31%) (EPİAŞ 2018). Lignite coal is an important primary energy source in Turkey's energy production because it is available in abundance, domestic and economic. Turkey's lignite reserves are estimated to be approximately 17.5 billion tons, which corresponds to approximately 2.1% of the total world coal reserves (MTA 2018). However, Turkish lignite coal has a low quality and contains high concentrations of sulfur, ash, dust, and moisture (Gören et al. 2017). Therefore, the majority of lignite coal produced annually is used to produce electrical energy in thermal power plants (MTA 2018). Turkey's installed power capacity of lignite-fired thermal power plants (LFTPPs) was 9.7 GW in February 2018 (TEİAŞ

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2018). The use of lignite coal as fuel in thermal power plants leads to major environmental problems such as the generation of acid gases (SO_2, SO_3, NO, and NO_2), fly ash, bottom ash and coal slag. Turkish LFTPPs produce more than 13 million tons of fly ash each year (Yüksek and Kaya 2017). Heavy metals contained in fly ash have potential risks for human health and soil and water ecosystems.

Soil is the ultimate target and sinks for environmental contaminants such as heavy metals dispersed in the natural environment by human activities (IAEA-TECDOC 2004). Environmental contaminants entering a soil system through discharge or emissions behave differently from site to site depending on the soil absorption properties, texture, density, humidity, and other factors (IAEA-TECDOC 2004). Heavy metals known as trace metallic elements are naturally occurring elements that have a high atomic weight and a density that is at least five times greater than that of water (Tchounwou et al. 2012). Heavy metals are also classified as human carcinogens or systemic toxicants according to the International Agency for Research on Cancer because heavy metals are known to induce multiple types of organ damages, even at low exposure (Tchounwou et al. 2012).

During the past decade, many researchers have studied the effects of coal-fired thermal power plants (CFTPPs) on the pollution (or contamination) of environmental samples (soil, water, plant, etc.) with heavy metals and/or radionuclides (Gür and Yaprak 2010; Agrawal et al. 2010; Demaku et al. 2011; Çayır et al. 2012; Lu et al. 2013; Xinwei et al. 2013; Okedeyi et al. 2014; Iruretagoiena et al. 2015; Özkul 2016; Howladar et al. 2016; Noli and Tsamos 2016; Verma et al. 2016; Huang et al. 2017; Zhao et al. 2017; Liu et al. 2017; Ćujić et al. 2017). Gür and Yaprak (2010) investigated the effect of radionuclide emission on the environment from Yatağan, Yeniköy and Kemerköy LFTPPs which are located in southwestern Anatolia of Turkey. They found that the average activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in surface soil samples from around these three LFTPPs were within the worldwide intervals reported by UNSCEAR. Agrawal et al. (2010) measured the concentration of Cd, Pb, As and Ni in soil samples collected from around four large CFTPPs in Singrauli region in India using an atomic absorption spectrophotometer (AAS). They found that soils from various selected sites in each direction were largely contaminated with metals. Demaku et al. (2011) analyzed the concentrations of heavy metals (Pb, Zn, Cu, Cd, Fe and Ni) in soil, water, sludge and coal ash in the region of two CFTPPs (Kosova A and Kosova B) in Kosova using an inductively coupled plasma optical emission spectrometry (ICP-OES) and AAS. They found that the concentration of heavy metals in water, sludge, soil, and ash was higher compared to the standards. Çayır et al. (2012) determined the activity concentration of radionuclides and level of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn, Al, and Fe) in soil samples from the surroundings of Afsin-Elbistan CFTPP in Kahramanmaraş province (Turkey). They found that emissions of A and B units of the CFTPP had enhanced element concentrations in the soil of the surrounding area. Xinwei et al. (2013) determined the concentrations of heavy metals (Cu, Cr, Co, Mn, Ni, Pb, Zn and V) and natural radionuclides (^{226}Ra, ^{232}Th and ^{40}K) in soil samples around Baqiao CFTPP in Xi'an (China) using X-ray fluorescence and gamma-ray spectrometry, respectively, and assessed the heavy metal contamination level of soils calculating the pollution load index. They revealed that coal combustion for energy production has affected the natural radioactivity level and heavy metals (Cu, Pb, Zn, Co, and Cr) concentrations of soil around the CFTPP. Okedeyi et al. (2014) determined the concentration of metals (Fe, Cu, Mn, Ni, Cd, Pb, Hg, Cr and Zn) in soil and plant (*Digitaria eriantha*) samples within the vicinity of three CFTPPs (Matla, Lethabo and Rooiwal) in South Africa using ICP-OES and graphite furnace AAS. They calculated metal pollution index, accumulation factor, enrichment factor, and geo-accumulation index to assess the metal pollution of samples. They indicated that the soils were moderately enriched with metals, exception for Pb. Özkul (2016) investigated the heavy metal pollution of soil samples collected from the close vicinity of Tunçbilek CFTPP in Turkey using an inductively coupled plasma mass spectroscopy (ICP-MS). He estimated geo-accumulation index and enrichment factor to assess heavy metal pollution of soils. He found that the enrichment factors of As, Cr, Hg, Ni and Pb in most of the sampling sites indicated moderate significant to extremely high enrichment in the soils. Howladar et al. (2016) studied the quality of the soil samples taken from different distances from the Barapukuria CFTPP area in Dinajpur (Bangladesh). Noli and Tsamos (2016) analyzed the concentration of As, Ba, Co, Cr, Sr, Sc, Th, U, Zn in soil and water samples from the vicinity of a CFTPP in Northern Greece by using neutron activation analysis (NAA). They found that the obtained data in most of the cases did not exceed the normal levels and the investigated area was only slightly contaminated. Verma et al. (2016) investigated the heavy metal (Pb, Ni, Cr, Mn, and Fe) contamination of groundwater samples from site around ash pond of Parichha CFTPP in Jhansi (India) by using AAS. They indicated that the concentrations of heavy metals measured in groundwater samples were above the limits prescribed by WHO for groundwater. Huang et al. (2017) determined the concentrations of Pb, Cd, Hg, As, Cu and Cr in soil and cabbage samples collected from the area surrounding the Jinsha CFTPP in Guizhou Province (China) using an inductively coupled plasma atomic emission spectrometry (ICP-AES). They indicated that the CFTPP contributed to the Pb, Cd, As, Hg, Cu and Cr pollution in nearby soils, particularly Hg pollution. Liu et al. (2017) analyzed the contents of heavy metals (Hg, Cd, As, Ni, Pb, Cu, Cr and Zn) in soil samples from the near the Xilingol CFTPP in

Inner Mongolia using ICP-MS and assessed the level of soil pollution with heavy metals and ecological risks by calculating potential ecological risk index. They identified three risk categories: (1) Hg and Cd were high-risk heavy metals, (2) Ni, Pb, Cu and Cr were medium-risk heavy metals and (3) Zn was a low-risk heavy metal. Ćujić et al. (2017) measured the concentrations of heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn) in soil samples which were collected in the vicinity of the largest CFTPP (Nikola Tesla) in Serbia and calculated enrichment factor, geo-accumulation index, contamination factor and pollution load index to assess the soil pollution due to heavy metals. They indicated that operation of the CFTPP had no significant negative impact on the surrounding environment with regard to the content of heavy metals.

As can be seen from the literature review above, the heavy metal contamination of environmental samples from the surroundings of CFTPPs has generally been investigated by determining the concentration of up to nine metals using analytical chemical methods (ICP-OES, ICP-AES, ICP-MS, and AAS) and calculating up to four ecological indices. This study differs from the similar studies in the literature as follows: (1) it is the first detailed study investigating the heavy metal pollution of agricultural soil samples around the Kangal LFTPP in which poor-quality lignite coal has been used as fuel, (2) the determination of the concentration of selected thirteen heavy metals (Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Zr, Sn, Hg and Pb) in one hundred and forty agricultural soil samples collected from the close area of the Kangal LFTPP is performed using an energy-dispersive X-ray fluorescence (EDXRF) spectrometric method and (3) the potential soil pollution due to heavy metals is assessed by estimating six ecological indices (geo-accumulation index, enrichment factor, contamination factor, contamination degree, modified contamination degree and pollution load index).

Materials and methods

Collection of samples

Kangal (39° 14′ 10″ N–37° 23′ 20″ E) is a district of Sivas province in Central Anatolia of Turkey. The Kangal Basin has a very short and cool summer, long and hard winter season, and rainy spring and autumn seasons. Two wind directions dominate the study area: west-northwest (WNW) and east-southeast (ESE). However, the wind intensity belongs to the light wind category (1.6–3.3 m/s). Moderate conditions prevail in the region. The effect of wind around the plant, therefore, remains limited. The Kangal LFTPP is located 25 km southwest of Kangal district at a latitude of 39° 04′ 40″ N and longitude of 37°17′45″ E. Kangal has available lignite coal reserves of 92 million tons. The lignite basin formed in a Pliocene depositional environment is composed of two coal seams with thicknesses of approximately 10 m (Şen and Saraç 2000). Clay-bearing tuffits with a thickness of 3–5 m occur between these two coal seams (Şen and Saraç 2000). Kangal lignite has an average sulfur content, moisture content, calorific value and fly ash fraction of 3, 51%, 1100 kcal/kg and 21%, respectively (Gören et al. 2017). Kangal LFTPP has a total installed capacity of 457 MW and 1811 GW h gross production (Gören et al. 2017). The Kangal LFTPP has been in production for 29 years since 1989. The annual consumption of lignite coal of the Kangal LFTPP is approximately 6,832,889 tons. It produced 1,423,843 tons fly ash in 2015 (Gören et al. 2017).

Agricultural surface soil samples were collected from one hundred and forty sites in the northern, eastern and western agricultural areas of the Kangal LFTPP, as shown in Fig. 1. Sampling strategy includes random sampling. Agricultural soil samples were collected to a depth of 5 cm from each site with a stainless steel shovel in April 2015 and October 2016. Each site was recorded using a handheld global positioning system. Each sample of about 2 kg was transported to the sample preparation laboratory in a thick plastic bag. Small stones, sand, grass, and other foreign materials were removed and kept in the laboratory atmosphere.

Sample preparation, pH measurement, and XRF analysis

The following procedure was used for the pH measurement of each soil sample: 10 g of air-dried soil sample was placed into a 50-mL beaker. 25 mL of distilled water was added to the beaker and left for 24 h. The pH was then measured using a pH meter (LaMotte 5 series).

The samples were dried at 110 °C until a constant weight was reached. Then, the soil samples were ground and homogenized manually by means of an agate. Each soil sample of 5 g was transferred into a sample cup which consists of a top and a bottom ring, 4-μm prolene foil serving for the sides and the bottom (Wien et al. 2005). Analyses of the major oxides, minor elements and trace heavy metals in the soil samples were performed using EDXRF spectrometer (Spectro Xepos) equipped with a thick binary Pd/Co alloy anode X-ray tube (50 W, 60 kV) (Turhan et al. 2018). The EDXRF spectrometer has an HAPG polarizer to improve the sensitivity to elements in the Na–Cl range and a band-pass filter to improve the performance for element detection in K–Mn range. The EDXRF spectrometer optimizes the excitation using polarization and secondary targets. It has an autosampler for up to 12 items and software modules. The target changer with up to eight polarization and secondary targets offers many different excitation conditions, ensuring the optimal determination of all elements from K to U (Turhan et al. 2018). The EDXRF spectrometer employs

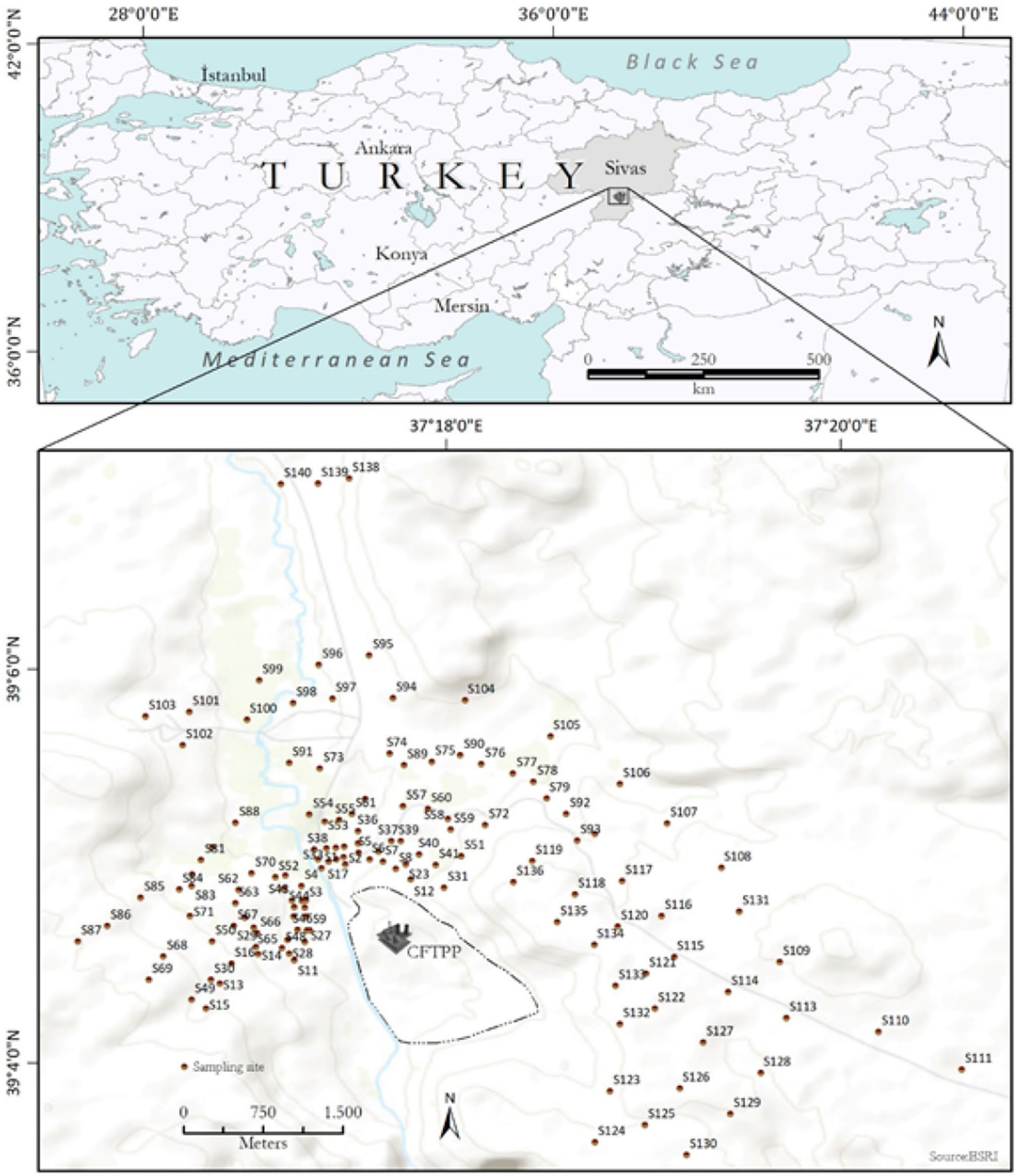

Fig. 1 Sampling sites in the investigated area

sophisticated calibration techniques such as "standardless" calibration, usually based on the Fundamental Parameters (FP) method. Soil certified reference material (NIST SRM 2709) was used for the quality assurance for the EDXRF system. The results obtained with the EDXRF system on the certified reference material (NIST SRM 2709) are given in Table 1. The analysis procedures were completed by placing the sample cups prepared for each soil sample into the

Table 1 Results of the certified soil reference material compared to the certified values

Element	Concentration (mg kg^{-1})	
	Certified	Analyzed
As	17.7 ± 0.8	19.0 ± 0.2
Ba	968 ± 40	995 ± 2
Co	13.4 ± 0.7	11 ± 2
Cr	130 ± 4	145.1 ± 0.3
Cu	34.6 ± 0.7	33.3 ± 0.5
Fe	35,000 ± 1100	34,360 ± 20
Hg	1.4 ± 0.1	1.1 ± 0.2
Mn	538 ± 17	566 ± 1
Ni	88 ± 5	78 ± 1
Pb	18.9 ± 0.5	18.1 ± 0.4
V	112 ± 5	112 ± 0.8

automatic sampler and counting them once for 2 h. The overall uncertainty of the analytical procedure is between 4% and 15%. The detection limit of Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Zr, Sn, Hg and Pb was determined as 2, 1, 1, 1, 3, 0.5, 0.5, 0.5, 0.5, 1, 2.5, 0.8 and 0.8 mg kg^{-1}, respectively.

Ecological parameters

The heavy metal pollution of the soil due to anthropogenic activities can be estimated with different ecological parameters or pollution indicators such as the geo-accumulation index, enrichment factor, contamination factor, contamination degree, modified contamination degree, and pollution load index.

The geo-accumulation index (I_{geo}), which was originally introduced by Muller (1969), was used to assess the degree of heavy metal pollution in the soil samples collected from the study area by comparing preindustrial and current heavy metal concentrations (Muller 1969). The I_{geo} was estimated using the following equation:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5 \times B_n}\right), \tag{1}$$

where C_n is the metal concentration of the soil sample, B_n is the average geochemical reference or background value of the earth's crust, and the constant 1.5 represents natural fluctuations because of possible differences in the reference values and very small anthropogenic influences (Özkul 2016; Muller 1969). In estimating this index, Yaroshevsky's earth composition was taken as reference values (Yaroshevsky 2006). The I_{geo} values consist of seven categories, as shown in the second row of Table 2.

The enrichment factor (E_F) was used to distinguish the anthropogenic metal source from natural process metal concentrations arising from human activities and to assess the degree of metal contamination (Buat-Menard and Chesselet 1979; Li et al. 2017). The E_F was estimated using the following equation based on the standardization of a measured element against a reference element (Özkul 2016; Abanuz 2011):

$$E_F = \frac{\left(C_n/C_{Ref}\right)_{Sample}}{\left(C_n/C_{Ref}\right)_{Background}}, \tag{2}$$

where C_n is the concentration of any element or metal and C_{Ref} is the concentration of a reference element or metal in the examined environment. On the basis of literature, the enrichment factor is estimated using one of the elements Al, Ca, Sc, Ti, Mn, Fe, Sr and Zr as reference element (Sengupta et al. 2010; Özkul 2016; Huang et al. 2017; Ćujić et al. 2017; Abunuz 2011). In this study, the enrichment factor was estimated in reference to Al and Yaroshevsky's Earth crust composition (Yaroshevsky 2006). The concentration of Al in each soil sample was measured using the EDXRF spectrometer. The E_F values consist of five classifications as given in the third row of Table 2.

The contamination factor (C_F) can be used for the determination of soil contamination. The C_F is estimated using the following equation (Hakanson 1980):

$$C_F = \frac{\left(C_n\right)_{Sample}}{\left(C_n\right)_{Background}}, \tag{3}$$

where C_n is the concentration of each metal measured in the soil samples. The C_F values consist of four classifications as given in the fourth row in Table 2.

The contamination degree (C_D) was first suggested by Hakanson (1980) to simplify contamination control. The contamination degree of the study area was estimated as the sum of the C_D estimated for each sample (Hakanson 1980; Devanesan et al. 2017):

$$C_D = \sum_{i=1}^{n} C_{Fi}, \tag{4}$$

where C_F is the contamination factor given in Eq. (3). The C_D values consist of four classifications as given in the fifth row in Table 2.

The modified contamination degree (mC_D) was introduced to assess the overall degree of contamination in a given area and estimated using the following equation (Devanesan et al. 2017):

$$mC_D = \frac{C_D}{n}, \tag{5}$$

Table 2 Ecological parameters and contamination levels

Ecological parameter	Value	Contamination category (soil quality)
Geo-accumulation index	$I_{geo} \leq 0$	Practically uncontaminated
	$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated
	$1 \leq I_{geo} < 2$	Moderately contaminated
	$2 \leq I_{geo} < 3$	Moderately to heavily contaminated
	$3 \leq I_{geo} < 4$	Heavily contaminated
	$4 \leq I_{geo} < 5$	Heavily to extremely contaminated
	$I_{geo} \geq 5$	Extremely contaminated
Enrichment factor	$E_F < 2$	Deficiency to minimal enrichment
	$2 \leq E_F < 5$	Moderate enrichment
	$5 \leq E_F < 20$	Significant enrichment
	$20 \leq E_F < 40$	Very high enrichment
	$E_F \geq 40$	Extremely enrichment
Contamination factor	$C_F < 1$	Low contamination
	$1 \leq C_F < 3$	Moderate contamination
	$3 \leq C_F < 6$	Considerable contamination
	$C_F \geq 6$	Very high contamination
Contamination degree	$C_D < 8$	Low contamination
	$8 \leq C_D < 16$	Moderate contamination
	$16 \leq C_D < 32$	Considerable contamination
	$C_D \geq 32$	Very high contamination
Modified contamination degree	$mC_D < 1.5$	Very low contamination
	$1.5 \leq mC_D < 2$	Low contamination
	$2 \leq mC_D < 4$	Moderate contamination
	$4 \leq mC_D < 8$	High contamination
	$8 \leq mC_D < 16$	Very high contamination
	$16 \leq mC_D < 32$	Extremely high contamination
	$mC_D \geq 32$	Ultra high contamination

where C_D is the contamination degree given in Eq. (4) and n is the number of analyzed metals. The values of mC_D consist of seven classifications as given in the last row in Table 2.

The pollution load index (I_{PL}) was used to assess the metal contamination levels of soil and estimated using the following equation (Ćujić et al. 2017; Lu et al. 2013):

$$I_{PL} = \sqrt[n]{\prod_{i}^{n} C_{Fi}}, \tag{6}$$

where C_F is the contamination factor given in Eq. (3) and n is the number of analyzed metals. If the I_{PL} value estimated for the entire sampling sites in the investigated area is higher than one, the area is polluted with metals.

Results and discussion

pH value and chemical composition of soils in the study area

The pH values of the soil samples varied from 7.5 (slightly alkaline) to 8.2 (moderately alkaline) with an average value of 8.0 (moderately alkaline). The pH values indicate that the soil samples are alkaline.

Descriptive statistics and the earth's crust averages for major and minor oxides in the soil samples are given in Table 3. The soil samples mainly consist of SiO_2, CaO, MgO, Al_2O_3, and Fe_2O_3. All minor oxides (Na_2O, K_2O, TiO_2, SO_3, P_2O_5, and Cr_2O_5) constitute approximately 2% of the soil. The average concentration of SiO_2 is approximately two times lower than the earth's crust average of 53.54%. Such soils generally have a basic rock feature and are clayey and dark-colored. The average concentrations of CaO, MgO and Fe_2O_3 are 2.2, 1.5 and 5 times higher than the earth's crust average of 9.41%, 5.44%, and 1.11%, respectively.

Table 3 Descriptive statistical data for major and minor oxides in the soil samples

	Concentration (%)										
	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	TiO_2	SO_3	P_2O_5	Cr_2O_5
Average	29.47	21.08	8.41	7.09	5.54	0.74	0.71	0.38	0.23	0.15	0.10
Median	28.77	20.26	8.22	6.47	5.56	0.69	0.63	0.36	0.20	0.14	0.11
SD	6.60	5.17	2.97	2.61	0.80	0.25	0.27	0.12	0.14	0.05	0.03
SE	0.56	0.44	0.25	0.22	0.07	0.02	0.02	0.01	0.01	0.01	0.01
Min	5.65	7.19	2.16	1.49	2.61	0.20	0.26	0.20	0.07	0.09	0.02
Max	55.50	41.95	21.19	19.59	8.05	1.68	1.72	0.75	1.38	0.52	0.19
Skewness	0.47	1.51	0.72	2.00	−1.03	1.40	1.63	1.37	5.07	3.26	−0.15
Kurtosis	3.62	4.90	2.53	5.69	4.31	2.47	2.11	1.44	37.24	16.28	−0.26
N	140	140	140	140	140	140	140	140	140	140	140
Earth's crust	53.54	9.41	5.44	15.87	1.11	2.66	1.09	0.97	0.05	0.19	–

SD standard deviation, *SE* standard error, *N* number of sample

Heavy metal concentration of the soil samples and pollution assessment

The descriptive statistics and the earth's crust average for the heavy metal concentrations in the soil samples are given in Table 4. The analyzed average heavy metal concentration is in the order of Fe > Ti > Mn > Cr > Ni > Zn > Zr > Co > Cu > Pb > As > Sn > Hg. The concentration of Cd in the soil samples is below the detection limit of 2 mg/kg. From Table 4, the skewness and/or kurtosis have a negative value which indicates the flat distribution for the heavy metals. Table 5 reports the comparison of heavy metal concentration in the study with those reported for CFTPPs in different countries. The spatial distribution maps of heavy metal concentrations in the soil samples obtained by ordinary kriging and the quantile classification method is shown in Fig. 2 (Ćujić et al. 2017).

The values of the I_{geo} and E_F of heavy metals estimated for the soil samples are given in Tables 6 and 7, respectively. The values of the C_F, C_D, and contribution of each heavy metal to the average value of C_D, mC_D and I_{PL} are listed in Table 8.

The titanium (Ti) concentrations in the soil samples varied from 1179.0 (S105 on the north-eastern side) to 4481.0 mg kg^{-1} (S133 on the eastern side) with an average value of 2261.7 mg kg^{-1}. The average Ti concentration is approximately two times lower than the earth's crust average of 4500 mg kg^{-1} (Yaroshevsky 2006). The I_{geo} values for Ti varied from −2.5 to −0.6 with an average value of −1.6. On the basis of the I_{geo} values, no contamination was detected. The E_F values for Ti varied from 0.6 to 1.8 with an average value of 1.1. The average E_F value indicates deficiency to minimal enrichment. The C_F values for Ti varied from 0.3 to 1.0 with an average value of 0.5. The average C_F value reflects low contamination.

The chromium (Cr) concentrations in the soil samples varied from 125.3 (S106 on the north-eastern side) to 1327.0 mg kg^{-1} (S26 on the western side) with an average

Table 4 Descriptive statistical data for the heavy metal concentrations of the soil samples

Heavy metal	Concentration (mg kg^{-1})								
	Average	Median	SD	SE	Min	Max	Skewness	Kurtosis	Earth crust
Ti	2261.7	2177.5	738.3	62.4	1179.0	4481.0	1.4	1.6	4500
Cr	713.2	722.9	236.0	19.9	125.3	1327.0	−0.1	−0.3	83
Mn	720.8	712.2	118.7	10.0	309.0	1116.0	0.1	1.4	1000
Fe	39,064.8	38,905.0	5096.0	430.7	18,220.0	56,290.0	−0.9	5.4	46,500
Co	63.9	67.5	19.1	1.6	12.0	104.0	−0.6	−0.2	18
Ni	610.1	620.9	198.7	16.8	89.5	971.0	−0.7	−0.3	58
Cu	28.8	28.5	3.4	0.3	18.1	40.8	0.6	3.5	47
Zn	81.8	75.8	36.8	3.1	50.2	376.5	4.3	29.4	83
As	9.0	6.9	7.3	0.6	3.2	98.7	7.6	67.7	1.7
Zr	65.3	63.7	26.1	2.2	28.1	152.2	1.5	2.1	170
Sn	3.3	3.0	1.1	0.1	3.0	9.3	4.5	18.9	2.5
Hg	1.7	1.5	1.2	0.1	1.0	13.2	7.0	65.7	0.083
Pb	17.0	15.4	6.8	0.6	1.9	59.0	2.3	10.2	16

Table 5 Comparison of heavy metal concentrations in soil samples of investigated area with those reported for CFTPPs production areas worldwide

Heavy metal	TPP (Country)											
	Seyitömer LFTTP (Turkey)	Kolaghat CFTTP (India)	Afşin-Elbistan LFTTP (Turkey)	Baqiao CFTTP (China)	Matla CFTPP (South Africa)	Lethabo CFTPP (South Africa)	Rooiwal CFTPP (South Africa)	Tunçbilek LFTPP (Turkey)	Xilingol CFTPP (Inner Mongolia)	Jinsha CFTTP (China)	Nikola Tesla CFTTP (Serbia)	Kangal LFTPP (Turkey)
	Average concentration (mg kg^{-1})											
Cr	356	103	62	99	63	58	70	–	32	53	32	713
Mn	923	1263	–	626	215	187	183	288	–	–	610	721
Fe	124,544	–	13	–	1836	1744	1735	–	–	–	29,030	39,065
Co	86	19	–	18	–	–	–	–	–	–	13	64
Ni	–	55	90	30	32	34	24	558	16	–	56	610
Cu	115	74	30	40	56	40	56	20	8	36	18	29
Zn	65	170	89	125	87	58	75	58	27	–	80	82
As	–	3.5	–	–	–	–	–	28	13	26	–	9
Hg	–	–	–	–	0.1	0.2	0.1	0.6	0.02	0.7	–	1.7
Pb	16	23	27	40	52	19	74	21	12	46	24	17
References	Güleç et al. (2011)	Mandal and Sengupta (2006)	Çayır et al. (2012)	Lu et al. (2013)	Okedeyi et al. (2014)	Okedeyi et al. (2014)	Okedeyi et al. (2014)	Özkul (2016)	Liu et al. (2017)	Huang et al. (2017)	Ćujić et al. (2017)	This study

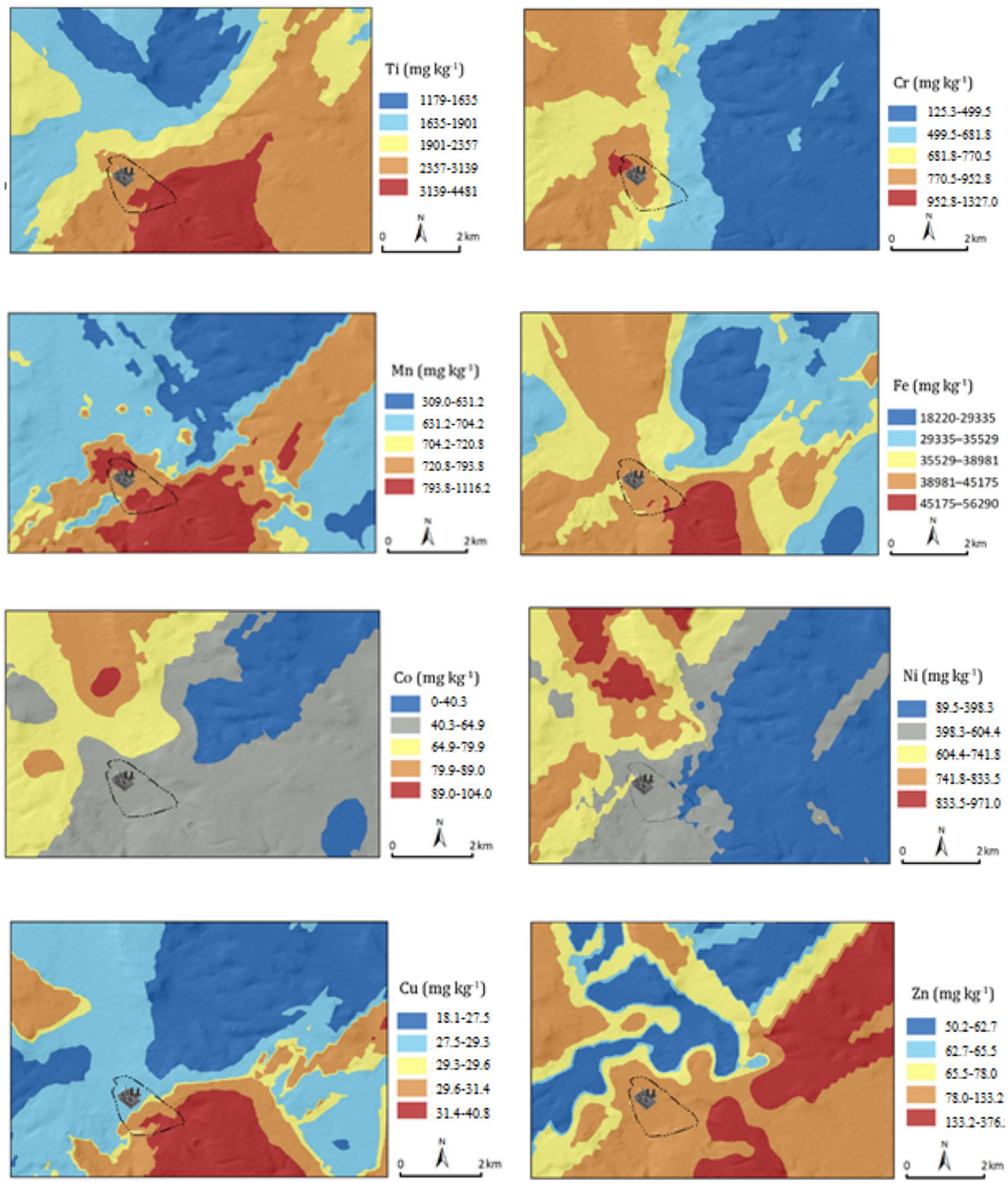

Fig. 2 Spatial distribution of metal concentrations in the soil samples

value of 713.2 mg kg^{-1}. The average Cr concentration is approximately nine times higher than the earth's crust average of 83 mg kg^{-1}; while, the average Cr concentration is lower than the ultrabasic rocks average of 2000 mg kg^{-1} (Yaroshevsky 2006). From Table 5, the average Cr concentration is higher than those obtained for TPPs in various

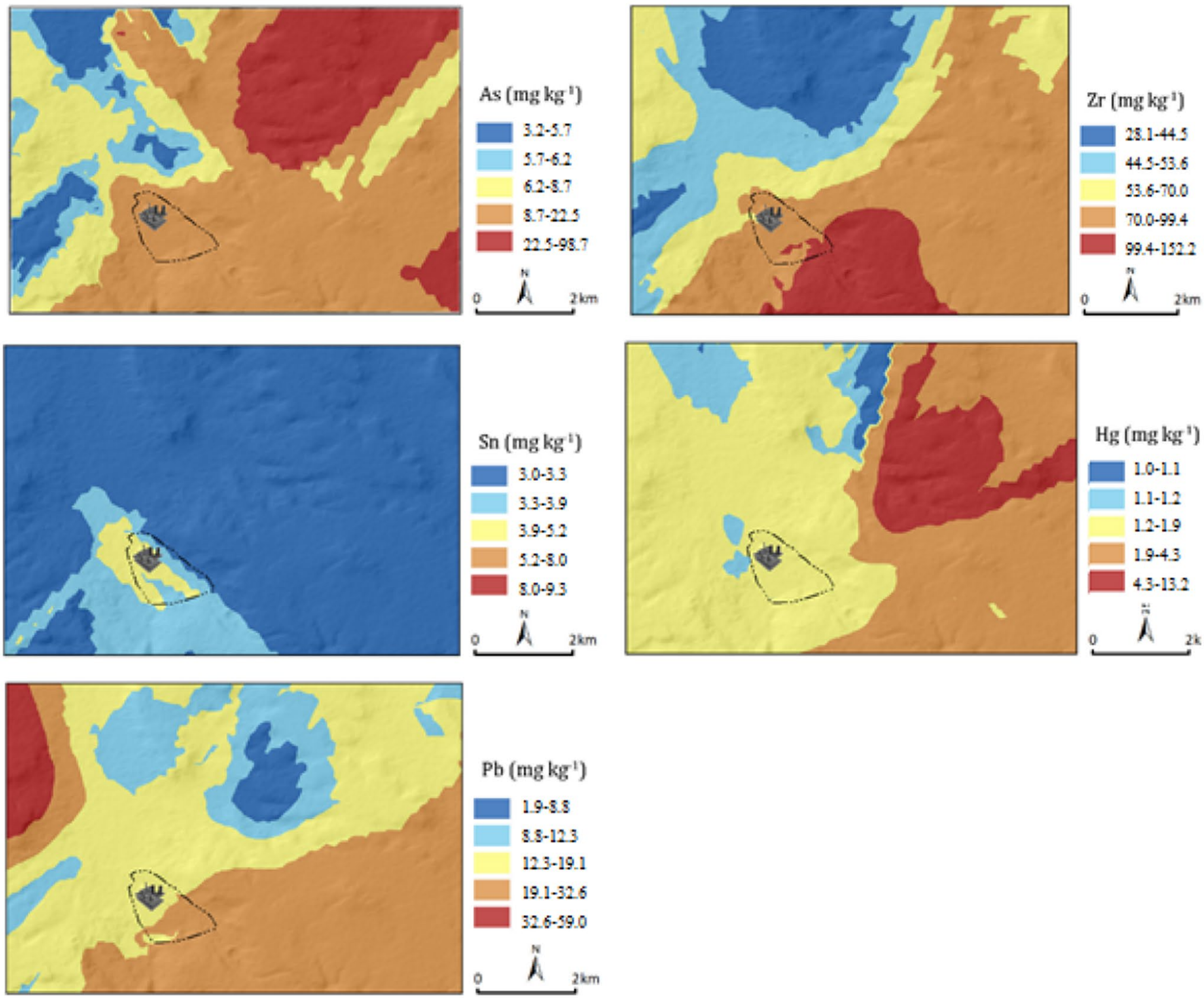

Fig. 2 (continued)

Table 6 Geo-accumulation index values of heavy metals estimated for the soil samples

Heavy metal	I_{geo} value			Contamination category
	Min	Max	Average	
Ti	−2.52	−0.59	−1.64	Practically uncontaminated
Cr	0.01	3.41	2.42	Moderately to heavily contaminated
Mn	−2.28	−0.43	−1.08	Practically uncontaminated
Fe	−1.94	−0.31	−0.85	Practically uncontaminated
Co	−1.17	1.95	1.15	Moderately contaminated
Ni	0.04	3.48	2.70	Moderately to heavily contaminated
Cu	−0.79	−1.96	−1.30	Practically uncontaminated
Zn	−1.31	1.60	−0.69	Practically uncontaminated
As	0.33	5.27	1.59	Moderately contaminated
Zr	−3.18	−0.74	−2.06	Practically uncontaminated
Sn	−0.32	1.31	−0.25	Practically uncontaminated
Hg	3.01	6.73	3.64	Heavily contaminated
Pb	−3.66	1.30	−0.59	Practically uncontaminated

Table 7 Enrichment factor values of heavy metals estimated for the soil samples

Heavy metal	E_F value			Enrichment level
	Min	Max	Average	
Ti	0.3	1.0	0.5	Deficiency to minimal enrichment
Cr	4.1	37.0	20.1	Very high enrichment
Mn	0.7	2.0	1.6	Deficiency to minimal enrichment
Fe	0.8	2.8	1.9	Deficiency to minimal enrichment
Co	1.5	16.2	8.4	Significant enrichment
Ni	4.3	48.8	25.5	Very high enrichment
Cu	0.6	1.9	1.4	Deficiency to minimal enrichment
Zn	1.2	4.1	2.1	Moderate enrichment
As	14.4	166.0	11.8	Significant enrichment
Zr	0.4	1.2	0.8	Deficiency to minimal enrichment
Sn	0.9	8.6	3.0	Moderate enrichment
Hg	9.4	365.2	46.3	Extremely enrichment
Pb	0.3	8.0	2.3	Moderate enrichment

countries. The I_{geo} values for Cr varied from 0.01 to 3.41 with an average value of 2.42. The average I_{geo} value reflects moderate to heavy contamination. The E_F values for Cr varied from 4.1 to 37.0 with an average value of 20.1. The average E_F value indicates significant to very high enrichment. The C_F values for Cr varied from 1.5 to 16.0 with an average value of 8.6. The average C_F value denotes very high contamination. The contribution of *Cr* to the average contamination degree is 15%.

The manganese (Mn) concentrations in the soil samples varied from 309.0 (S111 on the east side) to 1116.0 mg kg^{-1} (S132 on the east side) with an average value of 720.8 mg kg^{-1}. The average Mn concentration is lower than the earth's crust average of 1000 mg kg^{-1} (Yaroshevsky 2006). From Table 5, the average Mn concentration is higher than those obtained for Baqiao, Matla, Lethabo, Rooiwal, Tunçbilek, and Nikola TPPs; while, the average Mn concentration is lower than those obtained for Seyitömer and Kolaghat TPPs. The I_{geo} values for Mn varied from -2.3 to -0.4 with an average value of -1.1. On the basis of the I_{geo} values, no contamination was detected. The E_F values for Mn varied from 0.7 to 2.0 with an average value of 1.6. The average E_F value implies minimal to moderate enrichment. The C_F values for Mn varied from 0.3 to 1.1 with an average value of 0.7. The average C_F value indicates low contamination.

The iron (Fe) concentrations in the soil samples varied from 18,220.0 (S105 on the northeast side) to 56,290.0 mg kg^{-1} (S116 on the east side) with an average value of 39,064.8 mg kg^{-1}. The average Fe concentration is lower than the earth's crust average of 46,500 mg kg^{-1} (Yaroshevsky 2006). From Table 5, the average Fe concentration is higher than those obtained for Afşin-Elbistan, Matla, Lethabo, Rooiwal and Nikola TPPs; while, the average Fe concentration is lower than that obtained for Seyitömer TPP. The I_{geo} values for Fe varied from -1.9 to -0.3 with an average value of -0.9. On the basis of the I_{geo} values, no contamination was detected. The E_F values for Fe varied from 0.8 to 2.8 with an average value of 1.9.

Table 8 Contamination factor, contamination degree, modified contamination degree and pollution load index

Metal	C_F value			Contamination category	Contributions to average contamination degree (%)
	Min	Max	Average		
Ti	0.26	1.00	0.50	Low	0.9
Cr	1.51	15.99	8.59	Very high	15.1
Mn	0.31	1.12	0.72	Low	1.3
Fe	0.39	1.21	0.84	Low	1.5
Co	0.67	5.78	3.55	Considerable	6.2
Ni	1.54	16.74	10.52	Very high	18.4
Cu	0.39	0.87	0.61	Low	1.1
Zn	0.60	4.54	0.99	Low	1.7
As	1.88	58.06	5.29	Considerable	9.3
Zr	0.17	0.90	0.38	Low	0.7
Sn	1.20	3.72	1.31	Moderate	2.3
Hg	12.05	159.04	20.75	Very high	36.4
Pb	0.12	3.69	1.06	Moderate	1.9
C_D	21	273	55	Very high	
mC_D	1.3	17.0	3.4	Moderate degree of contamination	
I_{PL}	0.73	3.63	1.66	Polluted by heavy metals	

The average E_F value indicates minimal to moderate enrichment. The C_F values for Fe varied from 0.4 to 1.2 with an average value of 0.8. The average C_F value denotes low contamination.

The cobalt (Co) concentrations in the soil samples varied from 12.0 (S106 on the northeast side) to 104.0 mg kg^{-1} (S97 on the north side) with an average value of 63.9 mg kg^{-1}. The average Co concentration is approximately four times higher than the earth's crust average of 18 mg kg^{-1}; while, the average concentration of Co is lower than the ultrabasic rocks average of 200 mg kg^{-1} (Yaroshevsky 2006). From Table 5, the average Co concentration is higher than those obtained for Kolaghat, Baqiao and Nikola TPPs; while the average Co concentration is lower than that obtained for Seyitömer TPP. The I_{geo} values for Co varied from − 1.27 to 1.95 with an average value of 1.15. The average I_{geo} denotes no to moderate contamination. The E_F values for Co varied from 1.5 to 16.2 with an average value of 8.4. The average E_F value denotes moderate to significant enrichment. The C_F values for Co varied from 0.7 to 5.8 with an average value of 3.6. The average C_F value denotes considerable contamination. The contribution of Co to the average contamination degree is 6%.

The nickel (Ni) concentrations in the soil samples varied from 89.5 (S106 on the north-eastern side) to 971.0 mg kg^{-1} (S95 on the northern side) with an average value of 610.1 mg kg^{-1}. The average Ni concentration is approximately ten times higher than the earth's crust average of 58 mg kg^{-1}; while, the average Ni concentration is lower than the ultrabasic rocks average of 2000 mg kg^{-1} (Yaroshevsky 2006). From Table 5, the average Ni concentration is higher than those obtained for TPPs in various countries. The I_{geo} values for Ni varied from 0.04 to 3.48 with an average value of 2.70. The average I_{geo} value denotes moderate to heavy contamination. The E_F values for Ni varied from 4.3 to 48.8 with an average value of 25.5. The average E_F value denotes significant to very high enrichment. The C_F values for Ni varied from 1.5 to 16.7 with an average value of 10.5. The average C_F value denotes very high contamination. The contribution of Ni to the average contamination degree is 18.4%.

The copper (Cu) concentrations in the soil samples varied from 18.1 (S106 on the north-eastern side) to 40.8 mg kg^{-1} (S129 on the south eastern side) with an average value of 28.8 mg kg^{-1}. The average Cu concentration is lower than the earth's crust average of 47 mg kg^{-1} (Yaroshevsky 2006). From Table 5, the average Cu concentration is higher than those obtained for Tunçbilek, Xilingol and Nikola TPPs while the average Cu concentration is lower than those obtained for Seyitömer, Kolaghat, Baqiao, Matla, Lethabo, Rooiwal, and Jinsha TPPs. The I_{geo} values for Cu varied from − 0.8 to − 2.0 with an average value of − 1.3. On the basis of the I_{geo} values, no contamination was detected. The E_F values for Cu varied from 0.6 to 1.9 with an average value of 1.4. The average E_F value denotes deficiency to minimal enrichment. The C_F values for Cu varied from 0.4 to 0.9 with an average value of 0.6. The average C_F value denotes low contamination.

The zinc (Zn) concentrations in the soil samples varied from 50.2 (S105 on the northeast side) to 376.5 mg kg^{-1} (S131 on the east side) with an average value of 81.8 mg kg^{-1}. The average concentration of Zn is slightly lower than the earth's crust average of 83 mg kg^{-1} (Yaroshevsky 2006). From Table 5, the average Zn concentration is higher than those obtained for Seyitömer, Lethabo, Rooiwal, Tunçbilek, Xilingol, and Nikola TPPs while the average Zn concentration is lower than those obtained for Kolaghat, Afşin-Elbistan, Baqiao and TPPs. The I_{geo} values for Zn varied from − 1.3 to − 1.6 with an average value of − 0.7. On the basis of the I_{geo} values, no contamination was detected. The E_F values for Zn varied from 1.2 to 4.1 with an average value of 2.1. The average E_F value denotes minimal to moderate enrichment. The C_F values for Zn varied from 0.60 to 4.5 with an average value of 1. The average C_F value denotes low contamination.

The arsenic (As) concentrations in the soil samples vary from 3.2 (S140 on the north-eastern side) to 98.7 mg kg^{-1} (S106 on the north-eastern side) with an average value of 9.0 mg kg^{-1}. The average concentration of As is approximately five times higher than the earth's crust average of 1.7 mg kg^{-1} (Yaroshevsky 2006). From Table 5, the average As concentration is higher than that obtained for Kolaghat while the average As concentration is lower than those obtained for Tunçbilek, Xilingol and Nikola TPPs. The I_{geo} values for As varied from 0.3 to 5.3 with an average value of 1.6. The average I_{geo} value denotes no to moderate contamination. The E_F values for As varied from 4.4 to 166.0 with an average value of 11.8. The average E_F value denotes significant enrichment. The C_F values for As varied from 1.9 to 58.1 with an average value of 5.3. The average C_F value indicates considerable contamination. The contribution of As to the average contamination degree is 9.3%.

The zirconium (Zr) concentrations of the soil samples varied from 28.1 (S105 on the northeastern side) to 152.2 mg kg^{-1} (S133 on the eastern side) with an average value of 65.3 mg kg^{-1}. The average Zr concentration is lower than the earth's crust average of 170 mg kg^{-1} (Yaroshevsky 2006). The I_{geo} values for Zr varied from − 3.2 to − 0.7 with an average value of − 2.1. On the basis of the I_{geo} values, no contamination was detected. The E_F values for Zr varied from 0.4 to 1.2 with an average value of 0.8. The average E_F value indicates deficiency to minimal enrichment. The C_F values for Zr varied from 0.17 to 0.90 with an average value of 0.38. The average C_F value denotes low contamination.

The tin (Sn) concentrations of the soil samples varied from 3.0 (S133 on the eastern side) to 9.3 mg kg^{-1} (S17 on the western side) with an average value of 3.3 mg kg^{-1}. The average Sn concentration is slightly higher than the earth's crust average of 2.5 mg kg^{-1} (Yaroshevsky 2006). The I_{geo} values for Sn varied from −0.3 to 1.3 with an average value of −0.3. On the basis of the I_{geo} values, no contamination was detected. The E_F values for Sn varied from 0.9 to 8.6 with an average value of 3.0. The average E_F value denotes minimal to moderate enrichment. The C_F value for Sn varied from 1.2 to 3.7 with an average value of 1.3. The average C_F value denotes moderate contamination.

The mercury (Hg) concentrations of the soil samples varied from 1.0 (S85 on the western side) to 13.2 mg kg^{-1} (S107 on the northeastern side) with an average value of 3.3 mg kg^{-1}. The average Hg concentration is significantly higher than the earth's crust average of 0.083 mg kg^{-1}. From Table 5, the average Hg concentration is higher than those obtained for TPPs in various countries. The I_{geo} values for Hg varied from 3.1 to 6.7 with an average value of 3.6. The average I_{geo} value denotes heavy contamination. The E_F values for Hg varied from 9.4 to 365.2 with an average value of 46.3. The average E_F value denotes very high to extreme enrichment. The C_F values for Hg varied from 12 to 159 with an average value of 21. The average C_F value indicates very high contamination. The contribution of Hg to the average contamination degree is 36.4%.

The lead (Pb) concentrations of the soil samples varied from 1.9 (S106 on the northeastern side) to 59.0 mg kg^{-1} (S103 on the northwestern side) with an average value of 17.0 mg kg^{-1}. The average Pb concentration is slightly higher than the earth's crust average of 16 mg kg^{-1} (Yaroshevsky 2006). From Table 5, the average Pb concentration is higher than those obtained for Seyitömer and Xilingol TPPs while the average Pb concentration is lower than those obtained for Kolaghat, Afşin-Elbistan, Baqiao, Matla, Lethabo, Rooiwal, Tunçbilek, Jinsha and Nikola TPPs. The I_{geo} values for Pb varied from −0.4 to 1.3 with an average value of −0.6. On the basis of the I_{geo} values, no contamination was detected. The E_F values for Pb varied from 0.3 to 8.0 with an average value of 2.3. The average E_F value reflects minimal to moderate enrichment. The C_F values for Pb varied from 0.1 to 3.7 with an average value of 1.1. The average C_F value denotes moderate contamination.

The C_D values of all metals estimated for the soil samples varied from 21 to 273 with an average value of 55, indicating that the investigated area is highly contaminated with heavy metals. The mC_D values of all metals estimated for the soil samples varied from 1.3 to 17.0 with an average value of 3.4, indicating that the study area is moderately contaminated with heavy metals. The I_{PL} values of all metals estimated for the soil samples varied from 0.73 to 3.6 with an average value of 1.66, indicating that the study area is contaminated with heavy metals.

The Pearson correlation coefficient matrix of metals in the soil samples is presented in Table 9. Significant positive correlation coefficients ($p \le 0.01$; higher than 0.4) were obtained for the following metals: Ti versus Mn (0.77), Fe (0.46), Cu (0.77), Zn (0.77), Zr (0.96), Pb (0.74); Cr versus. Ni (0.51); Mn versus Fe (0.73), Cu (0.77), Zr (0.77), Pb (0.57); Fe versus Co (0.41), Cu (0.75), Zr (0.47); Co versus Ni (0.82); Cu versus Zn (0.60), Zr (0.78), Pb (0.67); Zn versus Zr (0.74), Pb (0.67) and Zr versus Pb (0.76). The strong correlation between these metals indicates that the contaminants in the soil samples from the study area have a common source, which originates from lignite coal seams (Ćujić et al. 2017).

Table 9 Pearson correlation coefficient matrix of the heavy metals in soil samples

	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Zr	Sn	Hg	Pb
Ti	1												
Cr	−0.21	1											
Mn	**0.77**	0.33	1										
Fe	**0.46**	0.26	**0.73**	1									
Co	−0.45	0.25	−0.12	**0.41**	1								
Ni	−0.67	**0.51**	−0.21	0.30	**0.82**	1							
Cu	**0.77**	0.004	**0.77**	**0.75**	0.01	−0.22	1						
Zn	**0.77**	−0.24	**0.56**	0.35	−0.33	−0.56	**0.60**	1					
As	0.22	−0.32	−0.02	−0.23	−0.52	−0.52	−0.09	0.14	1				
Zr	**0.96**	−0.19	**0.77**	**0.47**	−0.44	−0.67	**0.78**	**0.74**	0.24	1			
Sn	0.05	0.33	0.18	−0.01	−0.30	−0.01	−0.05	−0.03	0.05	0.05	1		
Hg	0.26	−0.24	0.10	−0.07	−0.12	−0.31	0.24	0.19	0.01	0.24	−0.14	1	
Pb	**0.74**	−0.11	**0.57**	0.32	−0.31	−0.54	**0.67**	**0.67**	0.05	**0.76**	−0.10	0.19	1

Bold value indicates significant correlation at $p \le 0.01$

Conclusions

This study was carried out to assess the environmental consequence of the operation of the Kangal LFTTP in Sivas province of Turkey, with regard to the acidification and heavy metals in soils. For this assessment, (1) a total of 140 agricultural soil samples were collected around Kangal LFTPP using random sample technique, (2) the pH value was measured for each soil sample, (3) major, minor and trace element concentration were analyzed for of each soil sample and (4) the geo-accumulation index, enrichment factor, contamination factor, contamination degree, modified contamination degree and pollution load index were estimated for each soil samples.

The random sample technique used may have some advantages and disadvantages compared to other sample techniques (directed random composite sampling, benchmark sampling, landscape-directed benchmark sampling, and grid sampling), but the use of a repeatable technique is crucial to monitoring soil pollution. Furthermore, random selection of 140 samples without any sample size calculation can be regarded as one of the limits of this study.

The average pH of the soil samples was measured as 8.0. This pH value shows that the investigated area is of moderate alkaline. In this case, the investigated area was not affected by the acid gases emitted from the Kangal LFTPP to the atmosphere.

The concentrations of selected thirteen heavy metals (Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Zr, Sn, Hg, and Pb) were analyzed using EDXRF spectrometry which is a common method for highly accurate and reproducible non-destructive element analyses. The average Cr, Co, Ni, As, Sr, Sn, Hg and Pb concentrations are higher than those reported for the earth crust. The average concentration of Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Hg and Pb is in agreement with heavy metal concentrations obtained for some coal (or lignite)-fired TPPs in the world using different analytical methods ICP-AES, ICP-OES, ICP-MS, etc. Although EDXRF technique includes some advantages such as easy sample preparation and instrument operation, the detection limits determined for elements are high compared to other instrumental techniques such as ICP-AES, ICP-OES, and ICP-MS.

On the basis of the geo-accumulation, enrichment factor and contamination degree index for these metals, the soil samples from the study area are heavily contaminated with Cr, Ni, and Hg. On the basis of the average contamination degree index of 273, the degree of contamination of the soil samples is very high. When the average value of the modified contamination degree modified index of 17.0 is taken into account, the pollution in the soil is moderate. As a result, the soil samples are contaminated with heavy metals when the average value of the pollution load index is taken into consideration. Since the heavy metal concentrations of the agricultural area around the Kangal LFTTP are not known before the installation of the plant, taking the average values of earth crust as a reference or background value may be the negative aspect of the heavy metal pollution assessment method.

Consequently, the data obtained in this study can be used as a valuable database or guiding information or reference point for monitoring the eco-toxic metals pollution for the next decades. Based on this study, it can be investigated how the eco-toxic metal accumulation in the agricultural area around the thermal power plant is dependent on soil parameters and how this pollution changes with soil profile. In the last decade, new lignite deposits including fertile agricultural lands in Turkey and the private sector is encouraged to establish a new thermal power plants to areas where the lignite deposits. In this case, the number of lignite-fired thermal power plants will increase rapidly in the next decade. From this perspective, this study raises an awareness of the negative impacts of thermal power plants on the environment.

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