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Environmental assessment of heavy metal and natural radioactivity in soil around a coal-fired power plant in China

Xinwei Lu · Wen Liu · Caifeng Zhao · Cancan Chen

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Abstract Concentrations of heavy metals and natural radionuclides in soil around a major coal-fired power plant of Xi'an, China were determined by using XRF and gamma ray spectrometry, respectively. The measured results of heavy metals show that the mean concentrations of Cu, Pb, Zn, Co and Cr in the studied soil samples are higher than their corresponding background values in Shaanxi soil, while the mean concentrations of Mn, Ni and V are close to the corresponding background values. The calculated results of pollution load index of heavy metals indicate that the studied soils presented heavy metal contamination. The concentrations of ^{226}Ra, ^{232}Th and ^{40}K in the studied soil samples range from 27.6 to 48.8, 44.4 to 61.4 and 640.2 to 992.2 Bq kg^{-1} with an average of 36.1, 51.1 and 733.9 Bq kg^{-1}, respectively, which are slightly higher than the average of Shaanxi soil. The air absorbed dose rate and the annual effective dose equivalent received by the local residents due to the natural radionuclides in soil are slightly higher than the mean values of Shaanxi. 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 coal-fired power plant.

Keywords Heavy metal · Radioactivity · Environmental assessment · Soi · Coal-fired power plant · Multivariate statistical analysis

X. Lu (✉) · W. Liu · C. Zhao · C. Chen
School of Tourism and Environment, Shaanxi Normal University, Xi'an 710062, People's Republic of China
e-mail: luxinwe@snnu.edu.cn

X. Lu
Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, People's Republic of China

Introduction

Coal, an abundant natural resource and fossil fuel, plays an important role in energy generation, and ~27 % of the world's energy consumption originates from the incineration of coal [1]. China depends largely on coal resource for energy requirements, which contribute more than 70 % of the total power generated in China [2]. Coal combustion generates emissions of potentially toxic trace elements besides major pollutants (particulates, carbon, sulfur and nitrogen oxides) [3]. It is the main anthropogenic source of toxic air pollution and a large contributor to global warming and acid rain. Elements bound in coal are mobilized during coal combustion and may be released associated with particles or as vapors. Environmental pollution by coal-fired power plants (CFPP) all over the world is cited to be one of the major sources of pollution affecting the general environment in terms of land use, health hazards and air, soil and water in particular [4]. During the coal combustion process, the burn-out of all combustible matter results in a significant enrichment of the ashes in incombustibles, which are partitioned between the bottom ash (or slag) that falls inside the boiler, and the fly ash that is suspended in the flue gas together with vapors of volatile elements and compounds and carried up the stack following [3].

Bottom ash is the coarse-grained fraction and fly ash is the finer sized particles [5], ranging from 0.5 to 200 μm [6], which has a greater tendency to absorb trace elements (such as Cu, Pb, Zn, Cr, U, Th, and so on) during combustion owing to its relatively small size and large surface area [5–9]. Depending on the emission control system, most of the fly ash is recovered by collection devices, but the collection efficiency is always <100 % [10], so that some fly ash is released into the atmosphere and deposited on the soil around the CFPP. The atmospheric deposition of fly ash containing heavy metals and natural radionuclides from CFPP can induce long-term changes in soil quality [5]. Thus, to investigate the concentrations of heavy metals and natural radionuclides in soil around CFPP and to assess their environmental risk is becoming an emerging and interesting topic. While heavy metal contamination and natural radioactivity level of soil around CFPP have been studied extensively in developed countries [3, 10–12], few dada are available for developing countries [13–15], including China [14, 15].

The main objective of this study is to (1) determine the concentration of heavy metals and natural radionuclides in soil around a major CFPP of Xi'an, China, (2) calculate the pollution load index and radiological parameter to know the heavy metal contamination level and radiological hazard, respectively, and (3) identify the relationship between heavy metals and natural radionuclides and analyze their possible sources and the effects of human activities.

Materials and methods

Background of study area

Xi'an, the capital of Shaanxi province, is located in the middle of Wei river valley (107°40′–109°49′E and 33°39′–34°45′N) and is the largest city in northwestern China (Fig. 1). The city, over 800 m above sea level, is bounded by Qinling Mountain on its south and east and by Loess Plateau at the north. The climate of Xi'an city is a typical temperate continental semi-humid climate with the annual average temperature and precipitation of 13–15 °C and 500–700 mm, respectively. The predominant wind direction in winter and autumn is northeast, while in summer and spring it is southwest [16]. The main soil type is ustalfs. The total urban area of Xi'an city is ~3,580 km^2 and the urban population is 6,470,000 in 2009. Xi'an is an important center of economy, education, culture, manufactory and high-tech industries in northwestern China.

Baqiao CFPP with a 150 m-high stack and 3.7×10^9 kWh annual production capacity, situated at the northeastern extremity of Xi'an (Fig. 1), has operated since 1951. The annual consumption of coal in Baqiao CFPP is about 860,000 tons, mainly from the Weibei coalfields of Shaanxi province, resulting in ~184,000 tons of fly and bottom ash per year. The electric precipitator system was installed in 2003 to reduce the particulate emission through the 150 m-high stack.

Sampling and sample preparation

Soil samples were collected around Baqiao CFPP from 44 sites, as marked in Fig. 1. At every sampling site, 4 topsoil (0–20 cm) samples were collected from the four corners of a square area corresponding to 4 m^2 using a stainless steel shovel. All soil samples that were toughed by the metallic digging tool were carefully eliminated from the samples before packing to avoid cross-contamination. For each sampling site, a total of ~1.5 kg composite soil sample was taken from the mixed sample using a quartile method. Forty-four soil samples were collected around the CFPP, at a distance of 100, 400 and 1,000 m in this manner (Fig. 1). The collected soil samples were stored in polyethylene bags for transport and storage. The exact location (longitude and latitude) of each sample site was measured by GPS instrument. All soil samples were air-dried naturally in the laboratory at room temperature for about 2 weeks, after which they were tapped lightly using a wooden mallet and then sieved through a 0.9 mm nylon sieve to remove little stones, debris and plant roots before halving.

One half of the sieved soil samples were dried at 110 °C for about 36–48 h in an oven, homogenized, ground and then sieved through a 0.16 mm mesh. Each sample was then transferred to a gas-tight, radon impermeable, cylindrical polyethylene plastic container (7.0 cm height and 6.5 cm diameter), weighted and hermetically sealed. The sealed samples were stored for about 30 days before counting so as to allow ^{226}Ra and ^{224}Ra to reach the secular equilibrium with their short-lived decay products [3, 17]. After that period, the soil samples were analyzed for natural radionuclide concentration using γ-ray spectrometry. For measuring the heavy metal concentration, a total 100 g of the other half sieved soil sample was ground with a vibration mill and sieved through a 0.075 mm nylon mesh. Four gram of milled soil sample and 2.0 g of boric acid were weighed out placed in the mold, and pressed into a 32 mm diameter pellet [18].

Analytical methods

The concentrations of the natural radionuclides ^{226}Ra, ^{232}Th and ^{40}K in the soil samples were determined by a 3 × 3 in. NaI(Tl) γ-ray spectrometric system with excel 8 % energy resolution (^{137}Cs 661.6 keV). The detector, maintained in a vertical position in a lead cylindrical shield of 10.5 cm thickness and 38 cm height, was coupled to a 1,024 microcomputer multi-channel pulse height analyzer and the system was calibrated for the γ-energy range 50 keV–3.2 MeV [19]. The activity of ^{232}Th was determined by 238.6–2614 keV gamma rays emitted from ^{212}Pb and ^{208}Tl, respectively. The activity of ^{226}Ra was measured by 609.3 and 1,764.5 keV gamma rays emitted from ^{214}Bi, whereas ^{40}K activity was measured directly through its gamma ray energy peak of 1,460.8 keV [20]. The standard sources for ^{226}Ra and ^{232}Th (in secular equilibrium with ^{228}Th) were prepared using known activity contents and

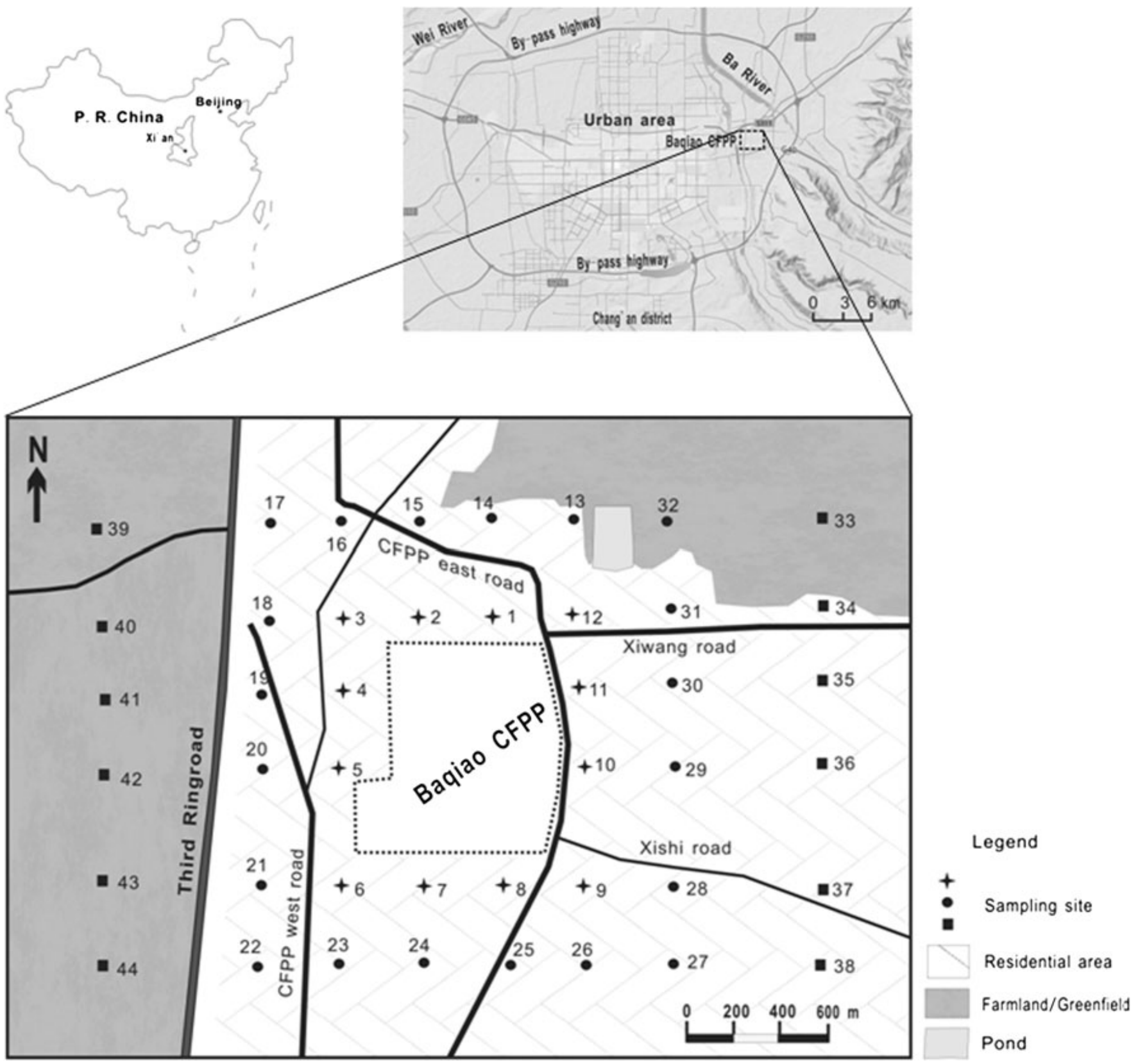

Fig. 1 Location of Baqiao CFPP and the sampling site of soil

mixing with the matrix material of phthalic acid powder [19]. In order to avoid the loss of gaseous daughter products of ^{226}Ra and ^{232}Th which may lead to disturbance in radioactive equilibrium, the prepared standard sources were kept in sealed cylindrical polyethylene plastic containers (7.0 cm height and 6.5 cm diameter). Analar grade potassium chloride (KCl) of a known amount of the same geometry was used as the standard source of ^{40}K. All samples were counted for 300 min. Each sample was counted four times before an average was calculated.

The concentrations of Co, Cr, Cu, Mn, Ni, Pb, Zn and V in soil samples were measured by X-ray fluorescence spectrometry (XRF, PANalytical PW2403 apparatus) [18]. Standard samples (GSD-12 and GSS1) and duplicate samples were analyzed simultaneously to provide quality control [18]. The analyzed precision, measured as relative standard deviation, was routinely 3–5 %. The accuracy of the analyses was checked using standard and duplicate samples. The quality control gave good precision (SD $<$5 %).

Results and discussion

Heavy metal concentration and contamination assessment

The descriptive statistical results of Cu, Cr, Co, Mn, Ni, Pb, Zn and V concentrations in soil around Baqiao CFPP, as well as background values for Shaanxi soil [21], are given in Table 1. Table 1 shows that the concentration of Cu, Cr, Co, Mn, Ni, Pb, Zn and V ranges from 20.4 to 531.8, 78.2 to 149.1, 13.0 to 24.0, 495.7 to 741.5, 20.1 to 36.2, 19.3 to 204.7, 51.6 to 315.8 and 64.8 to 105.9 mg kg^{-1} with an arithmetic mean of 40.3, 99.1, 18.0, 626.4, 30.3, 39.7, 124.7 and 82.5 mg kg^{-1}, respectively. The geometric means for Cu, Pb and Zn are less than their arithmetic means, while the geometric means for Cr, Co, Mn, Ni and V are close to their arithmetic means. The arithmetic means, geometric means and medians of Cu, Pb, Zn, Co and Cr in soil around Baqiao CFPP are higher than, while the mean concentration of Mn, Ni and V are close to their corresponding background values of Shaanxi soil, respectively. The mean concentrations of the studied heavy metals in soil around Baqiao CFPP divided by the corresponding background value of Shaanxi soil descend in the order of Cu > Pb > Zn > Co > Cr > V > Mn > Ni. The maximum concentrations of Cu, Cr, Co, Mn, Ni, Pb, Zn and V are 24.9, 2.4, 2.3, 1.3, 1.3, 9.6, 4.6 and 1.6 times the corresponding background values of Shaanxi soil, respectively. Figure 2 shows that the mean values of the studied heavy metals in soil samples collected from the southwest and northeast of Baqiao CFPP are higher than which in soil samples from the northwest and southeast of Baqiao CFPP, the mean concentrations of heavy metals in soil samples collected at 100 m are greater than those at 400 m, especially for Cu, Pb and Zn. The standard deviations and coefficient of variations (CVs) can reflect the degree of dispersion distribution of heavy metals and the effect of human activities on heavy metals concentrations in the study area [22]. The CVs of Cu, Pb, Zn, Co and Cr are relatively higher, especially for Cu, Pb and Zn, which are 193, 81 and 49 %, respectively. The maximum concentrations, CVs and standard deviations of heavy metals (Table 1) show that the contents of Cu, Pb and Zn in soil around Baqiao CFPP were intensively affected by human activities, such as coal combustion for energy production.

Kurtosis values of all studied heavy metals except Co are bigger than zero which indicates that the distributions of these heavy metals are steeper than normal. The skewness values of Cu, Cr, Pb and Zn are greater than unit which shows these heavy metals positively skew towards lower concentrations [18, 23].

To assess the heavy metal contamination levels of soil, the pollution load index (*PLI*) of heavy metals is calculated according to Suresh et al. [22]. The *PLI* is defined as

$$PLI = \sqrt[n]{\prod_{i=1}^{n} C_i/B_i} \quad (1)$$

where C_i is the concentration of heavy metal i, B_i is the background value of heavy metal i. In the study, B_i is the background value of heavy metal i in Shaanxi soil [21]. The *PLI* gives an assessment of the overall toxicity status for a sample and also it is a result of the contribution of the studied heavy metals [22]. The calculated *PLI* values of heavy metals in surrounding soil of Baqiao CFPP range from 1.05 to 3.10 with an average of 1.33 indicating the studied soil are polluted with heavy metals [22].

Natural radioactivity and radiological hazard

The statistic results of natural radionuclides concentrations in soil around Baqiao CFPP are showed in Table 2. It can be seen in Table 2 that the activity concentration ranges for ^{226}Ra, ^{232}Th and ^{40}K are 27.6–48.8 Bq kg^{-1} with an average 36.1 Bq kg^{-1}, 44.4–61.4 Bq kg^{-1} with an average of 51.1 Bq kg^{-1} and 640.2–992.2 Bq kg^{-1} with an average of 733.9 Bq kg^{-1}, respectively. The total activity concentration of three radionuclides (^{226}Ra, ^{232}Th and ^{40}K) in the studied soil ranges from 719.9 to 1,090.7 Bq kg^{-1} with an average of 820.2 Bq kg^{-1}. The concentration of ^{40}K accounts for ~85.5–96.4 % of the total gamma activity of the soil samples, which indicates that the specific activity due to ^{40}K is the largest contributor to the total activity for all soil samples. The following correlation analysis results also confirm this. In all soil samples, the natural activity concentration is of the order ^{226}Ra < ^{232}Th < ^{40}K. The activity concentrations of ^{226}Ra and ^{232}Th in the studied soil samples are lower than that in fly ash samples from Baqiao CFPP (60.5–31.8 and 61.5–164.6 Bq kg^{-1}, respectively), while ^{40}K concentration in the soil is higher than that in fly ash samples from Baqiao CFPP (155.9–316.1 Bq kg^{-1}) [24]. All the mean values of ^{226}Ra and ^{232}Th concentrations in soil samples collected from the

Table 1 Heavy metal concentrations in surrounding soil of Baqiao CFPP and other countries (mg kg^{-1})

Element	Cu	Cr	Co	Mn	Ni	Pb	Zn	V
Min	20.4	78.2	13.0	495.7	20.1	19.3	51.6	64.8
Max	531.8	149.1	24.0	741.5	36.2	204.7	315.8	105.9
Mean	40.3	99.1	18.0	626.4	30.3	39.7	124.7	82.5
SD	78.0	16.2	3.6	46.3	3.0	32.2	61.2	8.4
Median	26.4	94.3	17.3	626.6	30.6	26.4	82.6	82.9
Geomean	29.8	98.0	17.8	624.7	30.1	30.9	91.6	82.2
Skewness	6.4	1.2	0.5	−0.3	−0.9	5.6	4.6	0.8
Kurtosis	41.3	1.4	−0.6	1.7	2.6	34.1	25.3	17.2
CV (%)	193	16	20	7	10	81	49	10
SBV[a]	21.4	62.5	10.6	557	28.8	21.4	69.4	66.9

SD standard deviation, *CV* coefficient of variation

[a] Background values of Shaanxi soil [21]

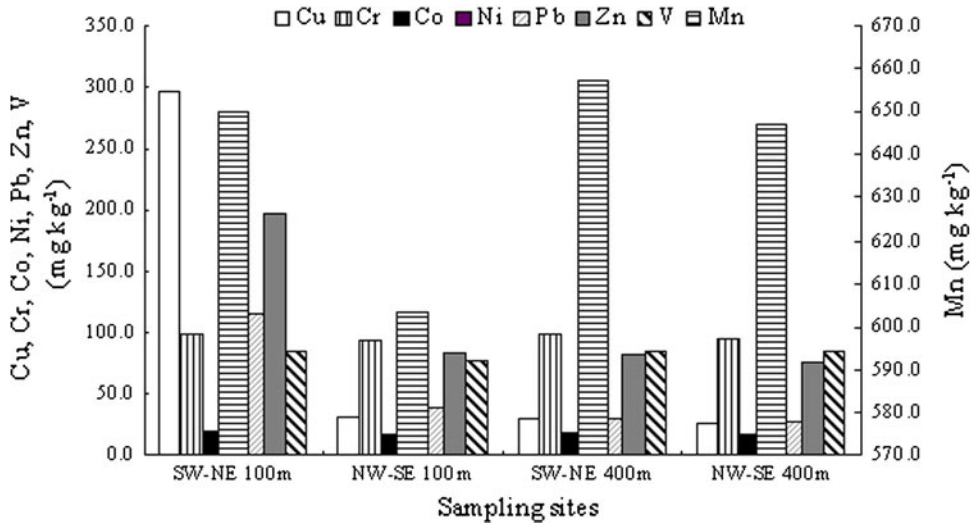

Fig. 2 The mean concentrations of heavy metals in soil samples collected at different directions and distances

surrounding environment of Baqiao CFPP are slightly higher than the average values of Shaanxi soil (34.8 and 47.3 Bq kg^{-1}, respectively) [25] and the worldwide population-weighted average values in soil (32 and 45 Bq kg^{-1}, respectively) [26] and close to the average values in soil of China (37.6 and 54.6 Bq kg^{-1}, respectively) [27], while the average value of ^{40}K in Baqiao CFPP soil is higher than the average concentration for Shaanxi soil (606.1 Bq kg^{-1}) [25], Chinese soil (584 Bq kg^{-1}) [27] and the worldwide population-weighted average value in soil (420 Bq kg^{-1}) [26]. Figure 3 indicates that the mean values of ^{226}Ra and ^{232}Th in soil samples collected from the southwest and northeast of Baqiao CFPP are higher than which in soil samples from the northwest and southeast of Baqiao CFPP, while the mean value of ^{40}K in the southwest and northeast of Baqiao CFPP is lower than which in the northwest and southeast. It can be found in Fig. 3, the mean concentrations of ^{226}Ra and ^{232}Th in soil samples collected at 100 m are greater than those at 400 m, whereas ^{40}K is contrary. These may be related with the wind direction and the deposition of fly ash.

To represent the activities due to ^{226}Ra, ^{232}Th and ^{40}K by a single quantity that takes into account the radiation hazard associated with them, the common radium equivalent activity (Ra_{eq}) was calculated as [28, 29]

$$Ra_{eq} = C_{Ra} + 1.43C_{Th} + 0.077C_K \quad (2)$$

where C_{Ra}, C_{Th} and C_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in Bq kg^{-1}, respectively. Table 2 indicates that the Ra_{eq} in soil round Baqiao CFPP ranges from 148.4 to 199.1 Bq kg^{-1} with an average of 165.7 Bq kg^{-1}, which is lower than the recommended limit of 370 Bq kg^{-1} [26]. For evaluating the external exposure from naturally occurring radionuclides, the outdoor air-absorbed dose rates due to terrestrial gamma rays at 1 m above the ground were calculated from ^{226}Ra, ^{232}Th and ^{40}K concentration values using the formula [30]

$$D(\text{nGy h}^{-1}) = 0.461C_{Ra} + 0.623C_{Th} + 0.0414C_K \quad (3)$$

where C_{Ra}, C_{Th}, and C_K are the activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in Bq kg^{-1}, respectively. The calculated results show that the air absorbed dose rates range from 70.6 to 95.6 nGy h^{-1} with mean value of 78.9 nGy h^{-1} (Table 2), which is higher than the population-weighted average value of global primordial radiation of 59 nGy h^{-1} [26], the average value of natural gamma radiation dose rate of China (62.0 nGy h^{-1}) [26] and the

Table 2 Natural radioactivity, radium equivalent activity in Bq kg^{-1}, air absorbed dose rate (D) in nGy h^{-1} and annual effective dose rate (E) in mSv $year^{-1}$ in soil around Baqiao CFPP

	^{226}Ra	^{232}Th	^{40}K	Total	Ra_{eq}	D	E
Min	27.6	44.4	640.2	719.9	148.4	70.6	0.087
Max	48.8	61.4	992.2	1090.7	199.1	95.6	0.117
Mean	36.1	51.1	733.9	820.2	165.7	78.9	0.097
SD	4.3	4.2	63.5	66.3	11.7	5.5	0.007
Median	35.9	50.5	726.1	813.3	165.2	78.6	0.096
Geomean	35.8	51.0	731.5	817.9	165.3	78.7	0.096
Skew	0.6	0.7	2.3	2.3	0.9	1.0	0.986
Kurt	0.1	7.7	−1.2	0.7	0.1	7.8	0.879
CV(%)	12.0	8.2	8.7	8.1	7.0	7.0	7.0

SD standard deviation, *CV* coefficient of variation

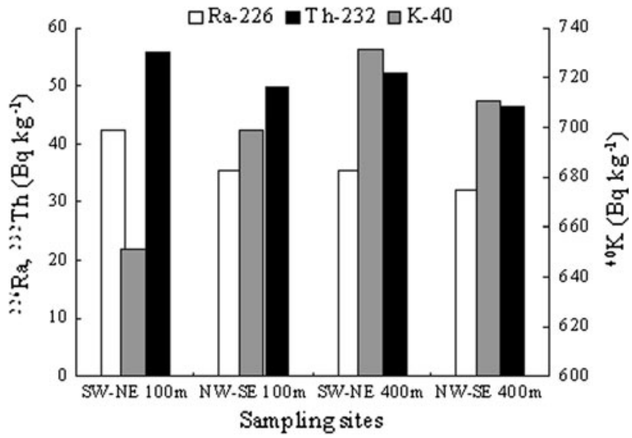

Fig. 3 The concentration variation of ^{226}Ra, ^{232}Th and ^{40}K in soil samples collected at different directions and distances

average natural gamma radiation dose rate of Xi'an (69.0 nGy h^{-1}) [31].

To estimate the annual effective dose equivalent (E) received by the local residents due to natural radioactivity in soil, the conversion coefficient Q (0.7 Sv Gy^{-1}) from the absorbed dose in air to the effective dose and the outdoor occupancy factor O_f (0.2) proposed by UNSCEAR [26] were used. E was calculated using the following formula

$$E = D \times T \times Q \times Of \times 10^{-6} \quad (4)$$

where E is the effective dose equivalent in mSv $year^{-1}$, T is time in hours in 1 year, i.e., 8,760 h, and D is the air absorbed dose rate. The mean annual effective dose equivalent was 0.097 ± 0.007 mSv $year^{-1}$ (Table 2), which is slightly higher than the external worldwide average annual effective dose (i.e., 0.07 mSv $year^{-1}$) [26] and the mean Xi'an outdoor annual effective dose rate of 0.087 mSv $year^{-1}$ [31].

Multivariate statistical results

Multivariate statistical analysis (Pearson's correlation analysis, Cluster analysis and Factor analysis) has been carried out to find out the interrelation among the parameters obtained from natural radionuclides and heavy metals.

Pearson's correlation analysis

The parameters such as concentrations of ^{226}Ra, ^{232}Th and ^{40}K, total activity concentration of radionuclides, air absorbed dose rate, the concentration of the studied heavy metals and the calculated *PLI* values of heavy metals are taken for analysis. Obtained Pearson's correlation coefficients among all analyzed parameters are presented in Table 3. Air absorbed dose rate (D) is significantly positive with ^{40}K, ^{232}Th and ^{226}Ra and the correlation coefficients of D with ^{40}K, ^{232}Th and ^{226}Ra decrease in the order of ^{232}Th > ^{40}K > ^{226}Ra indicating that the air absorbed dose rate mainly controlled by ^{232}Th and ^{40}K. The relative contributions of ^{40}K, ^{232}Th and ^{226}Ra to D also confirm this point. Figure 4 shows the relative contributions of ^{40}K, ^{232}Th and ^{226}Ra to D for all soil samples. The average relative contributions to D due to ^{40}K, ^{232}Th and ^{226}Ra are 38.6, 40.4 and 21.0 %, respectively. The activity concentrations of ^{226}Ra and ^{232}Th in fly ash of Baqiao CFPP are higher than the average values of Shaanxi soil, while ^{40}K concentration in fly ash of Baqiao CFPP is lower than the average value of Shaanxi soil [24]. The discharging and depositing of fly ash to the surrounding environment will enhance ^{226}Ra and ^{232}Th concentrations and dilute ^{40}K concentration in surrounding soil of CFPP. Good positive correlation coefficients among ^{226}Ra, ^{232}Th and *PLI* of heavy metals, and negative correlation between ^{40}K and *PLI* of heavy metals indicate that natural radioactivity level and heavy metals contamination of soil around Baqiao CFPP was possibly affected by the CFPP.

A significantly positive correlation at $P < 0.01$ was found between the elemental pairs Cu–Pb (0.956), Cu–Zn (0.901), Co–Pb (0.434), Co–Zn (0.403) and Pb–Zn (0.959). Mn, Ni and V have significantly positive correlations at $P < 0.01$, and are not correlated with other heavy metals. The correlations among Cr and other heavy metals are not significant. Cu, Co, Pb and Zn are significantly positively correlated with *PLI* of heavy metals at $P < 0.01$ which shows that the heavy metals contamination of soil around Baqiao CFPP mainly caused by Cu, Co, Pb and Zn. High correlation coefficient between the heavy metals means their common sources, mutual dependence and identical behavior during the transport [22].

Cluster analysis

Hierarchical cluster analysis is a statistical method for finding relatively homogeneous clusters of cases based on measured characteristics. It starts with each case in a separate cluster and then combines the clusters sequentially, reducing the number of clusters at each step until only one cluster is left [32]. Hierarchical agglomerative cluster analysis is carried out on the normalized data by means of the complete linkage (furthest neighbor), average linkage (between and within groups) and Ward's methods, using Euclidean distances as a measure of relation [32]. In the study, hierarchical clustering by applying Ward's method was performed on the standardized data set. The variables taken for this analysis are same as Pearson's correlation analysis. The cluster analysis result is shown in Fig. 5 as a dendrogram. Figure 5 displays four clusters: (1) ^{226}Ra–^{232}Th–^{40}K–Total-*D*; (2) Pb–Zn–Cu–*PLI*–Co; (3) Cr and (4) Mn–Ni–V. It is observed, however, that cluster 1, 2 and 3 join together at a relatively higher level, possibly implying a common source.

Table 3 Pearson correlation matrix among the variables

	^{40}K	^{232}Th	^{226}Ra	Total	*D*	Cu	Cr	Co	Mn	Ni	Pb	Zn	V	*PLI*
^{40}K		0.023	0.337	0.000	0.000	0.142	0.378	0.071	0.554	0.611	0.190	0.265	0.771	0.290
^{232}Th	0.350^{a}		0.000	0.015	0.000	0.019	0.228	0.037	0.103	0.009	0.089	0.069	0.001	0.017
^{226}Ra	0.152	0.586^{b}		0.214	0.000	0.002	0.399	0.347	0.075	0.013	0.014	0.010	0.073	0.005
Total	0.983^{b}	0.372^{a}	0.196		0.000	0.292	0.368	0.26	0.694	0.526	0.353	0.449	0.808	0.487
D	0.790^{b}	0.856^{b}	0.713^{b}	0.718^{b}		0.142	0.492	0.026	0.087	0.064	0.299	0.221	0.038	0.113
Cu	−0.230	0.361^{a}	0.467^{b}	−0.167	0.230		0.495	0.039	0.117	0.078	0.000	0.000	0.593	0.000
Cr	−0.140	0.190	−0.134	0.143	0.109	0.108		0.113	0.468	0.443	0.312	0.245	0.142	0.117
Co	0.282	0.323^{a}	0.149	0.344^{a}	0.342^{a}	0.320^{a}	0.248		0.338	0.028	0.004	0.008	0.227	0.004
Mn	0.094	0.255	0.278	0.063	0.267	0.246	−0.115	−0.152		0.000	0.268	0.138	0.000	0.086
Ni	−0.081	0.398^{b}	0.380^{a}	−0.101	0.288	0.275	−0.122	−0.339^{a}	0.777^{b}		0.410	0.264	0.000	0.107
Pb	−0.206	0.266	0.377^{a}	−0.147	0.164	0.956^{b}	0.160	0.434^{b}	0.175	0.131		0.000	0.896	0.000
Zn	−0.176	0.284	0.393^{a}	−0.120	0.193	0.901^{b}	0.183	0.403^{b}	0.233	0.176	0.959^{b}		0.933	0.000
V	−0.046	0.509^{b}	0.280	−0.039	0.322^{a}	0.085	−0.231	−0.191	0.592^{b}	0.519^{b}	−0.021	0.013		0.520
PLI	−0.167	0.367^{a}	0.424^{b}	−0.110	0.248	0.946^{b}	0.245	0.435^{b}	0.268	0.252	0.975^{b}	0.973^{b}	0.102	

The left lower part is correlation coefficient; the right upper part is significant level

Total total activity concentration of radionuclides, *D* air absorbed dose rate, *PLI* Pollution load index

[a] Correlation is significant at $P < 0.05$ (two-tailed)

[b] Correlation is significant at $P < 0.01$ (two-tailed)

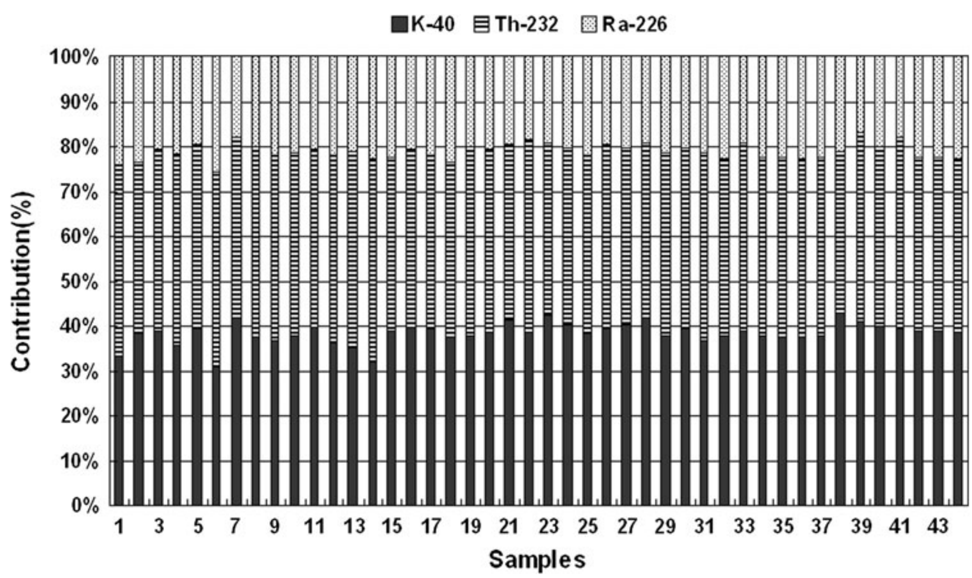

Fig. 4 Relative contributions to *D* owing to ^{40}K, ^{232}Th and ^{226}Ra for the samples

Factor analysis

Factor analysis (FA) is a statistical approach that can be utilized to analyze inter-relationships among a large number of variables and to describe these variables in terms of their common underlying dimensions (factors). The statistical approach tries to find a way of condensing the information contained in a number of original variables into a smaller set of dimensions (factors) with a minimal loss of information [32]. FA was carried out on the data set to assess the relationship by applying varimax rotation with Kaiser normalization. By extracting the eigenvalues and eigenvectors from the correlation matrix, the number of significant factors and the percent of variance explained by each of them were calculated.

Table 4 shows the results of the factor loadings with a varimax rotation, as well as the eigenvalues and communalities. The results indicate that there were four eigenvalues higher than one and that these four factors explain 84.4 % of the total variance. The first factor explains 31.8 % of the total variance and mainly characterized by high positive loading of concentrations of Cu, Co, Pb, Zn and *PLI* (Table 4). Factor 2, dominated by ^{232}Th, ^{226}Ra, ^{40}K, total activity concentrations of

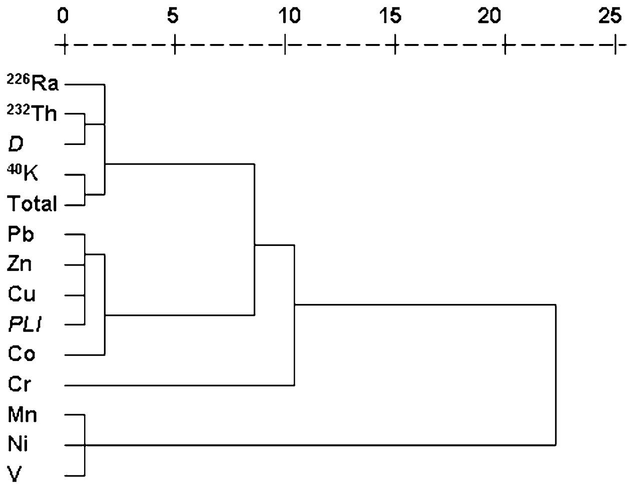

Fig. 5 Dendrogram results from Ward method of hierarchical cluster analysis

radionuclides (Total) and the air absorbed dose rate (*D*), accounts for 23.3 % of the total variance. Factor 3 is loaded primarily by Mn, Ni and V, accounting for 17.0 % of the total variance. Factor 4 accounts for 12.3 % of total variance and shows a positive loading of Cr. The relations among the analyzed parameters based on the first three factors are illustrated in Fig. 6 in three-dimensional space. Results of cluster and factor analyses are well matched with the Pearson's Correlation analysis.

From the overall statistical analyses and the concentrations of heavy metals and the natural radionuclides, Cu, Pb, Zn, Co and the natural radionuclides (^{226}Ra, ^{232}Th and ^{40}K) in the studied soil samples mainly related with CFPP. The variation coefficients of Mn, Ni and V in the studied soil samples are relatively low indicating the smaller diversity of their concentrations in the studied area and suggesting a natural factor controlling their spatial distribution. The positive correlations among Mn, Ni and V in correlation analysis, factor analysis and cluster analysis indicate that these three elements have a common source. The concentrations of Mn, Ni and V in the most of studied soil samples are close to and in a few soil samples are slightly higher than the corresponding background values of Shaanxi soil showing they are mainly controlled by natural factors. The concentration of Cr in the studied soil samples is 1.3–2.4 times the background value of Shaanxi soil indicating it was controlled mainly by anthropogenic activities. Cr is positively correlated with Cu, Pb, Zn and Co, and negatively correlated with Mn, Ni and V, whereas all correlation coefficients are small. It was clustered together with Cu, Pb, Zn, Co and natural radionuclides at a relatively higher level. These show that Cr in the studied soil mainly originates from other anthropogenic activities and partly originates from CFPP.

Table 4 Rotated factor loading of the variables

Variables	Factor				Communalities
	1	2	3	4	
^{40}K	−0.202	0.929	−0.052	−0.048	0.91
^{232}Th	0.304	0.779	0.284	0.350	0.81
^{226}Ra	0.412	0.609	0.293	0.172	0.81
Total	−0.136	0.943	−0.077	−0.045	0.92
D	0.197	0.876	0.289	0.301	0.97
Cu	0.943	−0.046	0.183	0.084	0.93
Cr	0.187	0.105	−0.302	0.799	0.76
Co	0.723	0.278	−0.349	−0.083	0.71
Mn	0.167	0.110	0.792	−0.042	0.87
Ni	0.100	−0.047	0.868	0.349	0.89
Pb	0.985	−0.040	0.033	0.001	0.97
Zn	0.964	−0.018	0.073	0.031	0.94
V	−0.050	−0.009	0.879	0.286	0.87
PLI	0.976	0.006	0.098	0.133	0.98
Eigenvalue	4.452	3.264	2.378	1.726	
% of variance explained	31.8	23.3	17.0	12.3	
% of cumulative	31.8	55.1	72.1	84.4	

Extraction method: principal component analysis. Rotation method: varimax with Kaiser normalization. Rotation converged in 6 iterations

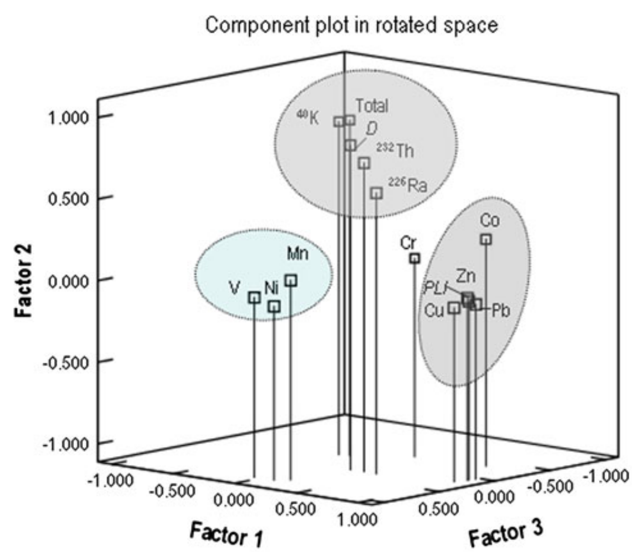

Fig. 6 PCA results in the three-dimensional space: plot of loading of the first three factors

Conclusions

The concentrations of natural radionuclides and heavy metals in soil around Baqiao CFPP of China and their environmental impact have been studied in this work. The mean concentrations of Cu, Pb, Zn, Co and Cr in the studied soil samples are higher than their corresponding background values of Shaanxi soil, while the mean concentrations of Mn, Ni and V are close to the corresponding background values of Shaanxi soil. The contamination assessment results of heavy metals indicate that the soil around Baqiao CFPP was polluted with heavy metals. The mean concentrations of ^{226}Ra, ^{232}Th and ^{40}K in the studied soil samples are slightly higher than the average values of Shaanxi soil. The air absorbed dose rate and the annual effective dose equivalent received by the local residents due to natural radioactivity in soil are slightly higher than the average of Shaanxi. The multivariate statistical analysis results show that Mn, Ni and V in soil around Baqiao CFPP were mainly controlled by natural factors (i.e., local soil type, soil-forming factors), while the natural radionuclides and Cu, Pb, Zn and Co in the studied soils were mainly controlled by CFPP. Cr in the studied soil mainly originates from other anthropogenic activities and part from CFPP.

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