PAPER

Occurrence and risk assessment of polycyclic aromatic hydrocarbons in soil from the Tiefa coal mine district, Liaoning, China†

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In order to evaluate soil-associated polycyclic aromatic hydrocarbons (PAHs) pollution from coal mine activities in Tiefa coal mine, Northeast China, 16 PAHs identified as priority pollutants by US Environmental Pollution Agency were determined in mining zone soil (MZS), agricultural soil (AS), local lake bank soil (LBS), a vertical soil profile and three coal gangue samples. The total concentration of 16 PAHs (defined as Σ_{16}PAH, dry weight) in surface soil ranged from 5.1 to 5642.3 ng g^{-1}, with an arithmetic mean of 1118.3 ng g^{-1}. Σ_{16}PAH values at the sites from MZS are significantly higher than those found in AS and LBS. The vertical distribution of PAHs indicated that these compounds can penetrate the deeper layers of the soil, especially the low-rings compounds. A complex of petrogenic origin and pyrolytic sources was found within the study area, as suggested by the isomeric ratios of PAHs. According to principal component analysis (PCA), four factors were identified in the source contribution, including coal combustion, unburned coal particulates, coal gangue and vehicular emissions. The degree of contamination and the PAH toxicity assessment suggested that the soils of the study area have been seriously polluted and pose a high potential health risk.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a set of environmental organic pollutants with a similar structure of two or more fused aromatic rings and are widely known for their carcinogenic and mutagenic impact to human health.[1–5] When considering PAHs the NPLs (national priorities lists) and the US Environmental Protection Agency (EPA) have listed 16 PAHs as priority pollutants because of the greater chance of exposure by humans and their high concentrations in the environment. Seven of these pollutants have been classified as probable human carcinogens by the International Agency for Research on Cancer.[6]

Soil is an excellent repository and transfer deposition sink for PAHs.[7] Semi-volatile organic contaminants such as PAHs are released into the surface soil through dry and wet atmospheric deposition.[8] When PAHs are absorbed by soil organic matter (SOM), they are usually retained for a long time.[9] PAHs stored in soils not only pose potential risks to human beings but also contaminate vegetation, which may be consumed by animals and humans.[10,11]

During the coal mining process, coal dust can also spread to the soil through mining operations and transport activities, thus releasing native PAHs to the environment.[12] Furthermore, large amounts of mining wastes such as coal gangue are produced and stacked around the coal mine in these areas. Through long-term self-ignition, weathering and leaching,[13,5] pollutants may diffuse into the surface soil, permeating the deep soil and so polluting groundwater.[14]

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Environmental impact

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants and are known to be carcinogenic and mutagenic to humans. Crude oil and its combustion products are considered to be the most important anthropogenic sources of previously studied PAHs. However, Walker *et al.*, (2005) has described coal as an unknown or unsuspected source of PAH, and other studies (Ahrens and Morrisey, 2005; Pies *et al.*, 2008) considered unburned coal as a potential source of PAHs in soils. The aim of this study is to explore if mining activities affect the level of PAHs in soil and to assess the potential risk to local residents.

2634 | *J. Environ. Monit.*, 2012, **14**, 2634–2642

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However, there are few data on the levels of PAH contamination in surface soils in the environment surrounding coal mining exploration. The present study aims to investigate the concentration, spatial distribution and composition of 16 PAHs in surface soils of different types (mining zone soil, agricultural soil, lake bank soil) and in soils from a vertical profile. The primary PAH sources and the health risk assessment, as affected by mining activities on PAH emissions, are discussed.

2. Methodology

2.1. Study area and sample collection

The Tiefa coal mine district, with an area of 513.3 km^2, is located at Diaobingshan City in Northeast Liaoning province. The average annual temperature is 8.6 °C, with the highest temperature at 35.8 °C and the lowest at −34.3 °C. The Tiefa coal mine district is one of the most important coal-producing bases in China. The accumulative coal reserves were ascertained as 2.3 bn tons in the Tiefa coal mine area by 2010. The annual production of the Tiefa coal mine is greater than 14 M tons. This coal is mainly used for power generation and industrial boilers. As it is well known, that two serious types of damage are caused by coal mining activities. Firstly, land subsidence and collapse can result in the formation of lakes; secondly, coal waste, such as coal gangues, are dumped. According to a survey, there are twelve spoil tips, with an area of approximately 0.5 km^2 in the Tiefa coal mine area. All the soil samples were collected from the five mining fields in the area, which are shown in Fig. 1. An agricultural area lies approximately 200 m from the collapsed lake. Almost all of the collapsed lakes are located near to spoil tips, at a distance of from 1 to 2 km from the tips. Twenty-six surface soils (0–10 cm) and 6 vertical cutting soil samples (0–150 cm) (Table 1, Fig. 1) were collected from the Tiefa coal mine area. In addition, three coal gangue samples were collected from the spoil tips.

2.2. Extraction and clean-up

Approximately 20 g of soil was air-dried and sieved through a 100-mesh screen, and spiked with surrogates. The organic compounds in each solid sample were extracted by Soxhlet extraction with dichloromethane (DCM) (250 ml) for 48 h. Activated copper pieces were added to remove sulfur.

The sample extracts were condensed, the solvent exchanged to hexane, and further reduced to 1 ml with a vacuum rotary evaporator. The extracts were then subjected to chromatographic separation on a glass column packed with alumina : silica gel (1 : 2 in volume). The fraction containing PAHs was eluted with 70 ml of a mixture of methylene chloride and hexane (3 : 7, v : v). The internal standards of known concentrations were added prior to analysis using a gas chromatograph equipped with a mass spectrometer (GC-MS) for the determination of 16 PAHs: naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Acen), fluorene (Flu), phenanthrene (Phen), anthracene (Anth), fluoranthrene (Flan), pyrene (Pyr), benz[*a*]anthracene (B[*a*]A), chrysene (Chry), benzo[*b*]fluoranthene (B[*b*]F), benzo[*k*]fluoranthene (B[*k*]F), benzo[*a*]pyrene (B[*a*]P), indeno[*1,2,3-cd*]pyrene (IP), dibenzo[*a,h*]anthracene (DB[*ah*]A) and benzo[*g,h,i*]perylene (B[*ghi*]P).
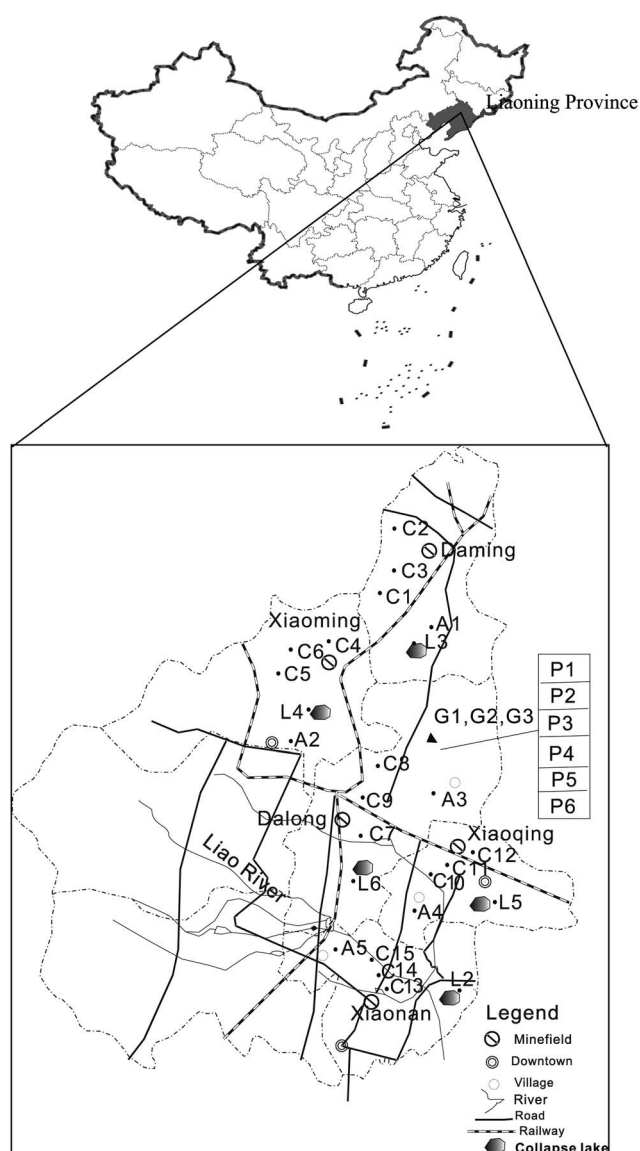

Fig. 1 Sampling location of surface soils in Tiefa coal mine area including five mining fields, Daming, Xiaoming, Dalong, Xiaoqing, Xiaonan. Notes: A: a representative agricultural soil; C: a representative coal mine zone soil; L: a representative lake bank soil; G: a gangue sample from spoil tips; P: representative soil samples from a vertical profile at a 30 cm interval (0–150 cm).

2.3. Analysis

Sample analysis was conducted on a Shimadzu model 2010 GC-MS equipped with an AOC-20i auto injector (Shimadzu, Japan), using negative chemical ionization in the selected ion monitoring model. A 60 m × 0.25 mm inner diameter (0.25 μm film thickness) DB-5 capillary column was used to separate the individual target compound, and detection was made by mass spectrometer. The GC temperature was programmed from an initial temperature of 60 to 200 °C at a ramp of 5 °C min^{-1}, then to 250 °C at 2 °C min^{-1}, and then to 290 °C at 20 °C min^{-1} and then held for 20 min at 290 °C.

The internal calibration method was employed in the quantitative analysis, and PAH identification was performed by

Table 1 Total PAHs concentrations of all samples with TEFs values from the Tiefa coal mining area

Sample	Σ_{16}PAHs (ng g^{-1})	Σ_7PAHs (ng g^{-1})	B[a]P$_{eq}$ (ng g^{-1})	Sample	Σ_{16}PAHs (ng g^{-1})	Σ_7PAHs (ng g^{-1})	B[a]P$_{eq}$ (ng g^{-1})	Sample	Σ_{16}PAHs (ng g^{-1})	Σ_7PAHs (ng g^{-1})
C1[a]	627.0	11.0	1.7	A1[b]	714.3	127.0	26.9	G1[d]	2350.1	697.4
C2	1995.3	843.6	152.1	A2	449.1	30.7	3.1	G2	1678.2	782.4
C3	2394.3	501.3	139.9	A3	1249.2	348.1	85.5	G3	3534.9	1793.3
C4	453.0	ND		A4	56.2	8.5	1.5	Min	1678.2	1793.3
C5	313.2	16.9	1.0	A5	5.1	3.2	0.3	Max	3534.9	697.4
C6	1550.9	317.9	115.7	Min	5.1	3.2	0.3	Mean	2521.1	1091.0
C7	2283.3	1149.0	227.9	Max	1249.2	348.1	85.5	P1[e]	817.8	157.5
C8	778.7	246.2	41.8	Mean	494.8	103.5	23.5	P2	418.5	50.0
C9	5642.3	2143.0	400.4	L1[c]	1093.5	290.2	68.4	P3	400.9	45.9
C10	273.5	35.1	4.2	L2	73.2	31.9	11.1	P4	584.6	77.0
C11	1914.6	226.9	10.5	L3	94.8	35.4	6.5	P5	49.3	11.8
C12	4525.7	2454.6	127.9	L4	201.6	95.7	35.1	P6	159.4	63.0
C13	53.6	3.5	0.3	L5	291.8	69.0	21.4	Min	49.3	11.8
C14	194.4	194.4	36.7	L6	1728.8	195.5	31.3	Max	817.8	157.5
C15	117.3	14.1	1.8	Min	73.2	31.9	6.5	Mean	405.1	67.5
Min	53.6	3.5	0.3	Max	1728.8	290.2	68.4			
Max	5642.3	2143.0	400.4	Mean	580.6	119.6	29.0			
Mean	1541.1	543.8	90.1							

[a] C represents soils from the coal mining field. [b] A represents agriculture soils. [c] L represents lake bank soils. [d] G represents coal gangue samples from spoil tips. [e] P represents soil samples from a vertical profile at a 30 cm interval (0–150 cm); ND: not detected.

comparing the retention time and the ions peak m/z with standards. A mixture of the internal standards 2-fluoro-1,1-biphenyl, p-terphenyl-d_{14}, and dibenzo[a,h]anthracene-d_{14} was added to the sample before injection. 2-Fluoro-1,1-biphenyl was used for Naph, Acy, Acen, Flu; p-terphenyl-d_{14} was used for Phen, Anth, Flan, Pyr, B[a]A, Chry, B[b]F, B[k]F, and B[a]P and dibenzo-[a,h]anthracene-d_{14} was used for IP, DB[ah]A, and B[ghi]P.

2.4. Quality assurance/quality control (QA/QC)

Laboratory blanks, spiked blanks and replicate samples were analyzed along with field samples through the procedures of extraction and cleanup. Seven consecutive spiked blank samples were analyzed and then the standard deviation (SD) was calculated. The detection of the method (MDL) is estimated by the formula MDL = SD $t(n - 1, 0.99)$, $n = 7$, $t = 3.14$.

The recoveries of surrogate standards were kept between 60% and 120% in all of the spiked samples; otherwise, a repeated analysis of the sample was performed.

3. Results and discussion

3.1. Level and profiles in surface soils

The sum of these 16 PAH contents (Σ_{16}PAHs) and 7 PAHs (Σ_7PAHs, B[a]A, B[b]F, B[k]F, B[a]P, I[cd]P, D[ah]A and Chry, identified as carcinogens by IARC) at different sites are listed in Table 1. In general, the Σ_{16}PAHs in the surface soils varied from 5.1 ng g^{-1} (A5) to 5642.3 ng g^{-1} (C9), with an arithmetic mean of 1118.3 ng g^{-1}, whereas the Σ_7PAHs ranged from 3.2 ng g^{-1} (A5) to 2454.6 ng g^{-1} (C12), with an arithmetic mean value of 99.9 ng g^{-1}. These concentrations greatly exceed the level of natural PAH concentrations in soil (1–10 ng g^{-1}), which are primarily derived from plant synthesis and natural fires.[15] This result indicates that the soils from the area of the present study have been significantly affected by anthropogenic activities.

In the agricultural soils, the Σ_{16}PAHs ranged from 5.1 ng g^{-1} (A5) to 1249.2 ng g^{-1} (A3), with a mean of 494.8 ng g^{-1}. A high level of total PAHs was found at site A3 near the pivot of the railway transportation (Table 1), perhaps due to the combined effect of the vehicular traffic and the fly ash during coal transport. The Σ_{16}PAH contents from mining zone soils ranged from 53.6 ng g^{-1} (C13) to 5642.3 ng g^{-1} (C9), with a mean of 1541.1 ng g^{-1}. Similarly, the high concentration site C9, located near the pivot of the railway transportation, and site C13, located in the southernmost part of the Tiefa coal mine, showed a low level of PAHs. Considering that the Xiaonan minefield is a newly explored mining operation, it may be not subjected to long-term contamination. Moreover, because the Liao River flows through this area, as seen from the local geographic environment (Fig. 1), the river flow can transport PAHs to other areas due to the distillation effect. Eventually, this area will exhibit a relatively low concentration of total PAHs. Compared with the mean concentrations of other agriculture soils around the world (Table 2), the Σ_{16}PAH concentrations in present study are higher than that in south Korea (236 ng g^{-1},[17]), Poland (264 ng g^{-1},[18]) and Nanjing, China (178 ng g^{-1},[19]), and similar to that in Guangdong, China (318.2 ± 148.2 ng g^{-1},[20]), although their level is lower than that in Delhi, India (1910 ± 1020 ng g^{-1},[16]).

There are limited studies in the literature reporting contamination from PAHs in soils surrounding coal mining districts,[21,22] and the Tiefa area studied here shows significantly higher contamination than those from Huaibei and Huainan, China (mean value of 840 ng g^{-1}),[21] and the Shilong coal mine, China[22] (mean value of 350 ng g^{-1}). Liaoning province has a temperate continental climate, and the climate, as a whole, is cool and dry. These conditions lead to poor volatilization, photo-oxidation, and biodegradation, thus further causing the high level of PAHs enriched in the soils. Therefore, the Σ_{16}PAHs contents in the soils of the Tiefa coal mine show a high level of pollution from PAHs. The concentrations of Σ_{16}PAHs in the lake bank soils ranged from 73.2 ng g^{-1} (L2) to 1728.8 ng g^{-1} (L6), with an arithmetic

**Table 2** PAH concentration in soils compared to other studies in the world

Sites	Types	Mean concn (ng g^{-1})	Range (ng g^{-1})	PAHs	Ref.
Delhi, India	Agricultural soils	1910 ± 1020	830–3880	16	16
South Korea	Agricultural soils	236	23.3–2834	16	17
Poland	Agricultural soils	264	28–2447	16	18
Nanjing	Agricultural soils	178	21.91–533.84	15	19
Guangdong, China	Agricultural soils	318 ± 148.2	22.1–1256.9	16	20
Tiefa, China	Agricultural soils	494.8	5.1–1249.2	16	This study
Anhui, China	Coal mining zone soils	840	130–3540	16	21
Shilong, China	Coal mining zone soils	350	50–780	78	22
Tiefa, China	Coal mining zone soils	1541.1	53.6–5642.3	16	This study
Saar Rivers, Germany	River bank soils	21360	18 000–197 000	45	23
Tiefa, China	Lake bank soils	580.6	73.2–1728.8	16	This study

mean of 580.6 ng g^{-1}, which is clearly lower than that of the river bank soils (21 360 ng g^{-1}, [23]).

As can be seen in Fig. 2, total PAHs concentrations in the mining zone was significantly higher than both in agricultural soils and lake bank soils. Moreover, the level of Σ_{16}PAHs in agricultural soils is similar to those in lake bank soils, which can be explained by the high levels appearing in the immediate vicinity of these intense mining activities, implying that mining events influence local soil contamination.

The analysis of PAH patterns in different media is useful to ascertain the fate and transport of PAHs and to track contaminant sources.[24] The individual PAH proportions from three types of soil were presented in Fig. 3, which may reflect different sources. Priority PAHs can be separated into three groups according to the number of rings. Low molecular weight PAHs with two and three rings (LMW-PAHs) include Naph, Acy, Acen, Flu, Phen, and Anth; median molecular weight PAHs with four rings (MMW-PAHs) include Flan, Pyr, Chry, and B[a]A; and high molecular weight PAHs (HMW-PAHs) comprising B[b]F, B[k]F, B[a]P, IP, DB[ah]A, and B[ghi]P[25,3]. The highest proportion of LMW-PAHs (54.8%) was found in the agricultural soils, and Phen and Flu were the dominant substances.

MMW-PAHs and HMW-PAHs contributed 25.1% and 20.1% of the 16 total PAHs in the agricultural soils, respectively. It should be noted that the influence of transport of vehicular emissions was taken into account for the high B[ghi]P input to the agricultural soil.[26] In lake bank soils, the dominant compounds were LMW-PAHs (57.9%), followed by MMW-PAHs (27.5%). The lowest proportion was HMW-PAHs (14.5%). Obviously, the abundance of low molecular PAHs in the two kinds of soils suggested a similar source; furthermore, it indicated recent pollution because the predominance of LMW-PAHs in agriculture soils implies that recent pollution might be caused by incomplete combustion of fossil fuel and the burning of agricultural waste.[27] The pattern of the mining zone soils differs slightly from the arable soil and lake bank soils, showing that the dominant compounds with MMW-PAHs (42.7%), followed by LMW-PAHs, accounted for 36.4%, and HMW-PAHs accounted for 20.8% of the total proportion. Low-ring PAHs with high ratio values were also found in agricultural soils from India.[16] The PAH emission profiles from tropical and sub-tropical soils reported by Xu et al.[28] show more than 50% of the total 16 PAHs with two to three-ring PAHs appearing in the soils. Sixteen types of PAHs were also elevated in the coal gangue samples, and their
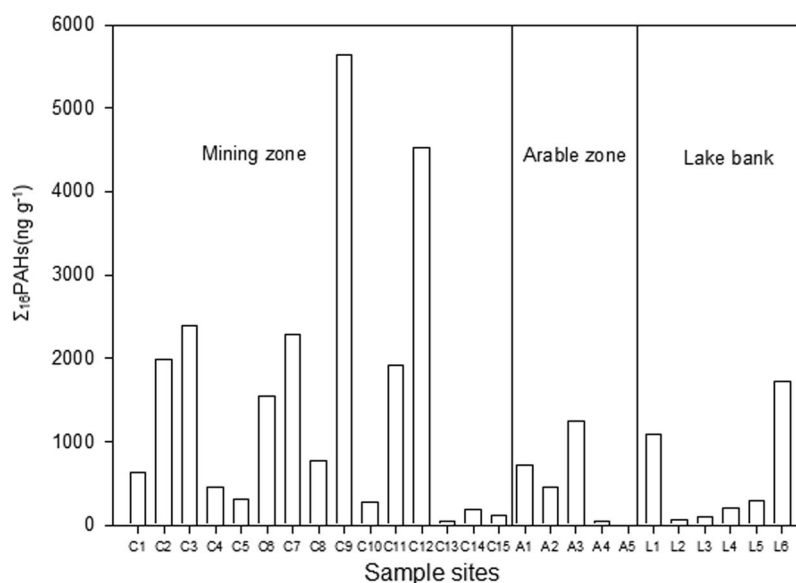
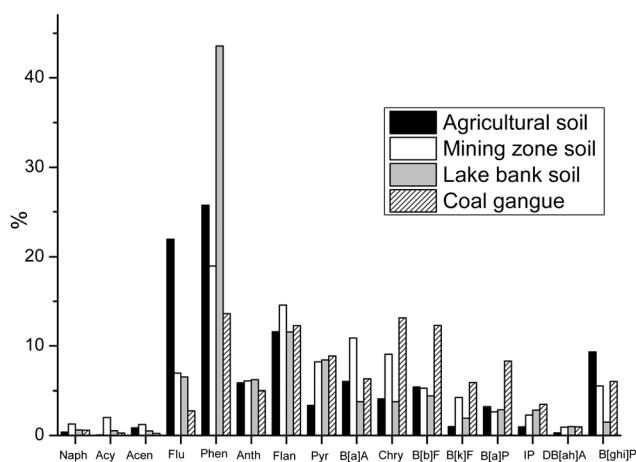**Fig. 2** Concentrations of PAHs of different samples in surface soil from Tiefa coal mine.

Fig. 3 Compare three types of soil with coal gangue in terms of percentage composition of individual PAHs distribution.

concentrations ranged from 1648.2 ng g^{-1} to 3534.9 ng g^{-1}, with a mean of 2521.1 ng g^{-1} (Table 1). To examine whether dumping wastes contribute to the organic contamination of the soils, their PAH patterns were studied. As can be seen from Fig. 3, the 2,3-ring PAHs contributed 22.4%, with a high proportion of Phen at 13.6%; 4-ring PAHs accounted for 40.6%, dominated by Chry and Flan, at 12.3% and 13.2%, respectively; 5,6-ring PAHs accounted for 37.0%, dominated by B[b]F, at 12.3%. Moreover, B[a]P and B[ghi]P accounted for the relatively high proportion in high-weight PAHs of the coal gangue, which cannot be ignored, at 8.3% and 6.0%. Because the PAHs are apt to transfer and because of their photochemical degradation properties, determining their precise source from the environmental media is difficult and complex. Low-weight PAHs are subject to transport and degradation, and high-weight PAHs are prone to rapid deposition, which may be close to the emission source.[29,30] For this reason, both the agricultural soils and lake bank soils had a higher percentage of low molecular weight PAHs than the mining zone soils.

3.2. The variation of PAHs in the soil profiles

The concentrations of Σ_{16}PAH in the soil profile are depicted in Fig. 4. The total content of PAHs showed an obvious decrease with increasing depth. The highest value (817.7 ng g^{-1}) was located at the top of the soil, and the lowest value (49.3 ng g^{-1}) at the interval of 90–120 cm. Photolysis and volatilization processes have proved to be the major courses contributing to the relatively low level in the topsoils.[31,32] The contrary results in this study suggest that the PAHs enriched in soils were not vulnerable to photolysis and volatilization and that the cool and dry climate in north China probably suppressed these effects. Other research indicated that, to some extent, organic matter is effective for PAH adsorption in the soil,[9] and the mobility of PAHs in the depth of the soil is related to the ability of soil enrichment.[33] Fig. 4 shows the distribution of the individual PAHs in the vertical soils. As a whole, most of the single PAH concentrations had a declining trend with increasing depth except that they increased on the interval of 60–90 cm, especially Flan and Pyr. The trend coincides with the total PAH distribution. Fig. 4 shows
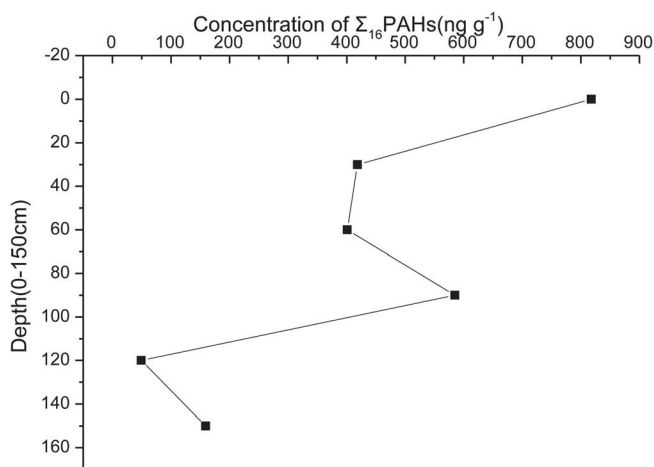
that the concentrations of low molecular weight PAHs, which are dominated by Phen, were significantly higher than the other rings dominated by Pyr. With relatively high solubility and low molecular weight (LMW) activity, 2–3-ring PAHs are prone to be absorbed by the particulate matter in soil and transported down to the deep soil by leaching.[34] As the profile was collected near a spoil tip, it clearly exhibited the extent of horizontal PAH dispersion in the soil. Generally, groundwater is found at an average of 3 meters under the topsoil, which poses a potential risk of contamination in the near future.

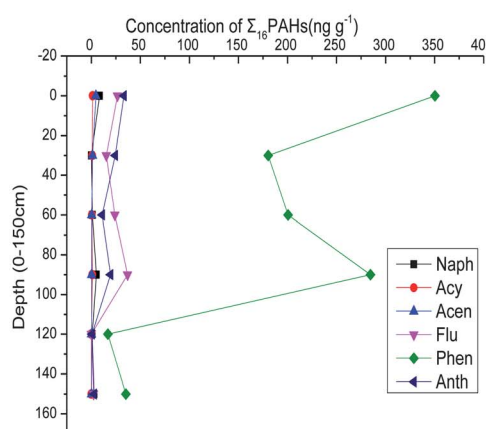### 3.3. Source diagnosis and contribution estimates

Although the composition of the PAHs could be used to reveal some information of their sources, the different PAH emission "fingerprints" can also be diagnosed by the isomeric ratios.[35,36] Five pairs of 16 PAH components (i.e., Anth/(Phen + Anth), Flan/(Pyr + Flan), B[a]A/(Chry + B[a]A), B[b]F/(B[b]F + B[k]F), IP/(B[g,h,i]P + IP)) with the same molecular weight are employed for diagnostic purposes. The ratio of Anth/178 (Anth + Phen) <0.1 suggests a petrogenic origin (crude oil or raw coal), while the ratio >0.1 suggests a pyrolytic origin (incomplete combustion of coal or biomass, natural fire). An Flan/202 (Pyr + Flan) ratio of less than 0.4 implies petrogenic sources, while values between 0.4 and 0.5 imply petroleum (liquid fossil fuel, vehicle and crude oil) combustion, and values greater than 0.5 imply the combustion of coal, grass and wood.[37] Based on the relatively low detection rate of high-ring PAHs in this study, the isomeric ratios of Anth/178 and Flan/202 were used to identify different sources, and the plot is given in Fig. 5. As shown in Fig. 5, the ratios of Anth/178 and Flan/202 ranged from 0 to 0.90 and 0 to 0.92, respectively, in the agricultural soils, 0 to 0.95 and 0 to 0.82 in the residential soils and 0.09 to 0.58 and 0.38 to 0.63 in the lake bank soils. These values were concentrated in the range from 0 to 0.6, suggesting a combination of pyrolytic and petrogenic sources at the Tiefa coal mine.

As a result of open pit mining activities, the soil collected from the study area may be influenced by unburned coal particles, and the effects of coal gangue leaching may give rise to the mobility of the PAHs. Traditional methods usually use isomer ratios to identify the sources of PAHs. However, these "fingerprints" from particulate coal can often be confused with other contaminant sources.[12] Moreover, the occurrence in soils or sediments of PAHs derived from raw coal has hardly been recognized.[38] Although mutual pyrolytic and petrogenic sources have been found in this study area, to some extent, the petrogenic source (unburned coal) was disturbed by invasion from the classes of the pyrolytic source.

SPSS16.0 (Statistical Package for the Social Sciences) was used to perform principal component analysis (PCA) and to identify the primary factors of individual PAH contamination sources in the Tiefa soils. Higher values of factor scores indicate a greater contribution of that factor. A compound score above 0.7 was selected as the level of significant factor. Four factors were extracted with varimax rotation. According to the results presented in Fig. 6, 16 PAHs were separated into four major categories. The accumulation of the variance (84.6%) of the data was explained by four Eigenvectors. The first factor is responsible for 38.3% of the total variance, including Anth (0.809), Flan (0.821), Pyr (0.922), B[a]A (0.925), Chry (0.943), B[b]F (0.906), and B[k]F

2638 | *J. Environ. Monit.*, 2012, **14**, 2634–2642

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(a) Vertical distribution of total 16PAH contents in the soil profile

(b) Low molecular weight PAH
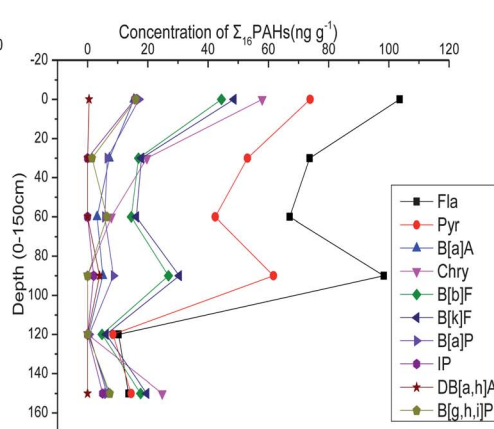
(c) Middle and high molecular weight PAH

Fig. 4 Distribution characteristics of PAHs compounds in the soil profile. (a) Vertical distribution of total 16PAH contents in the soil profile. (b) Low molecular weight PAH. (c) Middle and high molecular weight PAH.
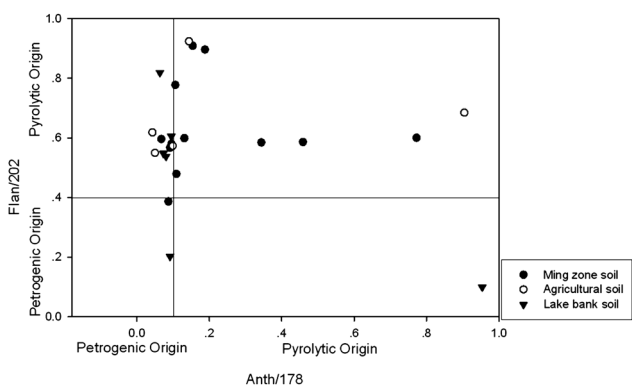

Fig. 5 Relationship of Anth/178 and Flan/202 for various soil samples in Tiefa coal mine to diagnose the source (Anth/178 represents the ratio of anthracene concentration divided by total concentrations of anthracene plus phenanthrene and Flan202 represents the ratio of fluoranthene concentration divided by total concentrations of fluoranthene + pyrene).

(0.755) which are typical emissions from coal combustion processes.[39,40] The second factor accounted for 24.0%, with mainly low molecular weight (LMW) comprising Acen (0.944), Flu (0.819), DB[a,h]A (0.930), and Naph (0.807), which might represent the source of raw coal. Because LMW PAHs are typical

compounds in coal,[41] the dominant substance of naphthalene and its alkylated derivatives have been found in soil derived from coal.[38] The third factor is responsible for 14.2% of the total variance and had a heavy factor loading by Phen (0.869) and B[a]P (0.744). Based on the dump waste throughout the coal mine and a high proportion of Phen and B[a]P has been found in the coal gangue (Fig. 3), it is reasonable to assign factor 3 as the source from coal gangue. The variances of the fourth compound were 8.17%, with high loadings of B[ghi]P (0.721), which were indicators of vehicular sources. Other studies[26,39,40] have identified B[ghi]P as the typical tracer of vehicular sources.

Using a multivariate linear regression (MLR) from PCA factor scores, the equation was calculated as follows: $\Sigma_{16}PAH = 0.824F1 + 0.328F2 + 0.443F3 - 0.064F4$ ($R = 0.993$). The quantitative contributions of the four major sources in the surface soil were an F1 (coal combustion) of 49.7%, F2 (unburned coal) of 19.8%, F3 (coal gangue) of 26.7%, and F4 (vehicular) of 3.9%.

3.4. Risk assessment of PAHs

The criteria of PAH concentrations to be allowed in soils has not yet been regulated in China. Maliszewska-Kordybach (1996)
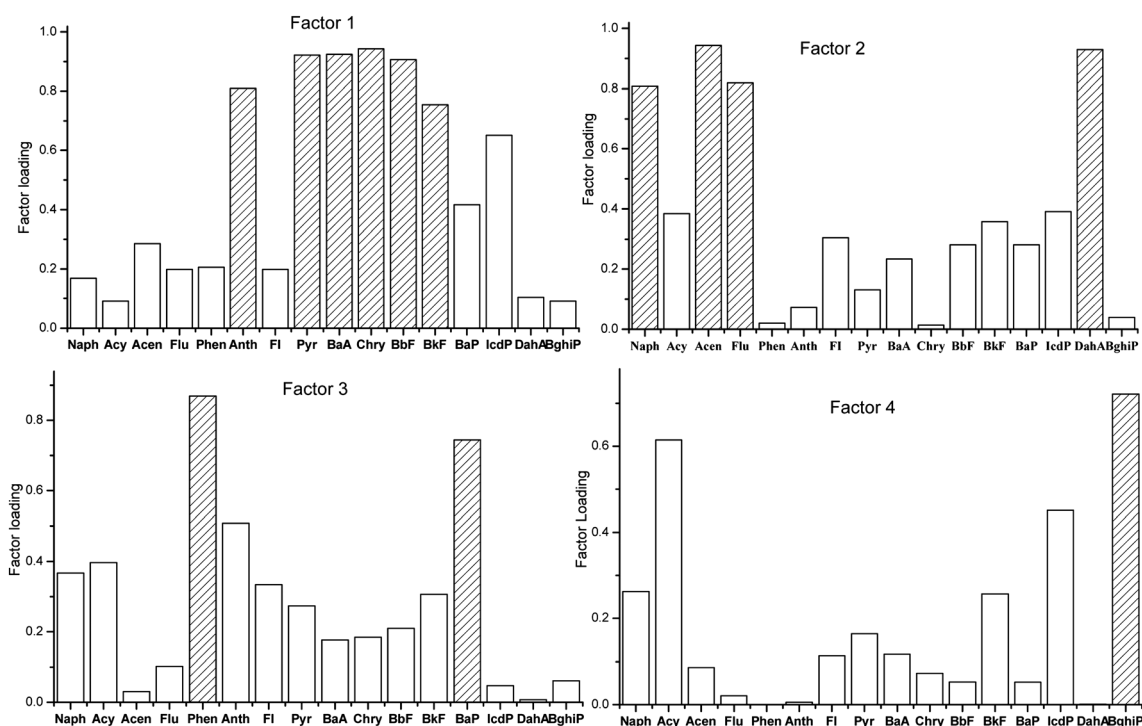
Fig. 6 Factor loadings of PCA based on the measured individual PAHs in surface soil. Factor analysis scores following Varimax rotation Matrix[a] for all PAHs. Notes: dash area represent factor loading >0.7. Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaiser Normalization; [a]Rotation converged in 6 iterations.

suggested a Polish soil contamination classification system based on 16 PAHs as follows:[18] non-contaminated soil (<200 ng g^{-1}), weakly contaminated soil (200–600 ng g^{-1}), contaminated soil (600–1000 ng g^{-1}) and heavily contaminated soil (>1000 ng g^{-1}). According to the criteria, 19.2% of the surface soils were not contaminated including A4, A5, C13, L2, L3; 30.8% were weakly contaminated including A2, C4, C5, C10, C14, C15, L4, L5 and 19.2% were contaminated including A1, A3, C1, C8, L1 and heavily contaminated accounting for 30.8% of the total samples, which were C2, C3, C6, C7, C9, C11, C12, L6. Some studies[42–45] have used the index of toxicity equivalence quantity (TEQ) to evaluate the environmental impact. Different values of toxic equivalency factors (TEFs) create different values of TEQ. Nisbet and Lagoy (1992) proposed the toxic equivalency factors (TEFs) and used them to quantify the carcinogenicity of PAHs relative to B[a]P and to calculate the Benzo[a]pyrene-equivalent concentration (B[a]P$_{eq}$).[46] The total benzo[a]pyrene equivalent concentration (B[a]P$_{eq}$) was calculated as the total B[a]P$_{eq} = \Sigma_i C_i \times TEF_i$, where C_i is the concentration of individual PAHs and TEF$_i$ is the corresponding toxic equivalency factor.[47] According to USEPA, the TEFs for seven PAHs (including B[a]A, B[a]P, B[b]F, B[k]F, IP, DB[ah]A and Chry), which were classified by the International Agency for Research on Cancer,[6] are 0.1, 1, 0.1, 0.01, 0.1, 1 and 0.001, respectively. The total B[a]P$_{eq}$ concentrations of the seven carcinogenic PAHs of surface soils from the Tiefa coal mine are introduced in Table 1. The values from the different sampling sites vary from 0.3 ng g^{-1} (C13, A5) to 400.4 ng g^{-1} (C9). The heavily polluted sampling site C9, located in the Dalong minefield, also posed the highest carcinogenic potency, while the Xiaonan minefield posed the least risk

exposure. The mining zone soils had the highest mean B[a]P$_{eq}$, with a value of 90.1 ng g^{-1}, compared with other soils around the coal mine, which were 23.5 ng g^{-1} by agricultural soil and 29.0 ng g^{-1} by lake bank soil. These values suggested that the higher carcinogenic potency in the mining zone, especially in the Dalong minefield, should be given much more attention. Additionally, a certain quantity of B[a]P$_{eq}$ exposure to agricultural soil could create potential risk through enrichment in the food chain. To some degree, the local residents could be affected by the carcinogenic potency of the high value of B[a]P$_{eq}$.

4. Conclusions

The concentrations of 16 PAHs in surface soils were relative high compared with other studies and the standards of Poland. Because the PAHs found in the mining zone soils were remarkable higher than the other two types of soils, the coal mining activities evidently promoted the PAH contamination level. Coal mining activities not only contaminated the mining zone soils but also affected both the agricultural and lake bank soils surrounding the Tiefa coal mine. The agricultural soils and lake bank soils present similar PAH levels and profiles. Three types of soils were subjected to mutual pyrolytic and petrogenic sources. The PAHs distributed in the topsoil were more highly concentrated than in the deep soil, and the predominance of low molecular weight PAHs tended to move down to deep soil. The PCA results showed that four sources contributed to the PAHs in the study area: coal combustion (49.7%), unburned coal (19.8%), coal gangue (26.7%), and vehicular (3.9%). The dumped spoil tips not only polluted the surrounding surface soil but also

influenced the lower depths of the soil. As a result, groundwater is threatened by the potential risk of PAHs over the long-term. The high value of B[a]P$_{eq}$ and the high proportion of heavily contaminated soils suggests that local residents are exposed to materials in the environment which have a high carcinogenic potential.

Acknowledgements

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