

## Distribution and health-risk of polycyclic aromatic hydrocarbons in soils at a coking plant†

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Nineteen soil samples were collected in and around Songshan coking plant in Guangdong province of China and analyzed for eighteen polycyclic aromatic hydrocarbons (PAHs) by gas chromatography-mass spectrometry (GC-MS). The total concentration of PAHs ranged from 2.36 to 1146.39 mg kg<sup>-1</sup> dry weight, varying significantly among the sampling sites, most individual PAHs were correlated with each other. A cluster analysis was performed to examine the correlation of PAH distribution, five groups were observed with sample types in the coking plant. 2–3 ring PAHs were predominant in group I and II, while 4–5 ring PAHs showed great abundance in group III, IV and V, which contributed to the distance from the emission sources in the coking plant and the behaviors of particle-bound and gaseous PAHs. The ratios of Flu : (Flu + Pyr), BaA : (BaA + Chr), InP : (InP + BgP) and Ant : (Ant + Phen) ratios were 0.51–0.87, 0.16–0.89, 0.47–0.68 and 0.03–0.60, respectively. The total index of all studied soils was > 6, indicating that the source of the PAHs in coking plant soils were from the pyrolysis processes. Health risk assessments were carried out by dermal PAH exposure data to quantify cancer risk. The resultant lifetime exposure levels due to TEQ<sub>BaP</sub> desorbed onto skin for workers ranged from 2.25 × 10<sup>-7</sup> to 7.86 × 10<sup>-5</sup> mg kg<sup>-1</sup> per day, and the estimated cancer risks were between 8.45 × 10<sup>-6</sup> and 2.94 × 10<sup>-3</sup>, indicating that the dermal exposures of PAHs to coking workers might be acceptable in most soil sites.

### Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of diverse organic compounds made up of two or more fused aromatic rings with carbon and hydrogen atoms. They are ubiquitous

environmental pollutants generated primarily during the incomplete combustion of organic materials. PAHs can be generated from many anthropogenic activities, such as heat and power generation from coal and other fossil fuels, coal production, petroleum refining, coal and oil shale conversion, and chemical manufacturing.<sup>1</sup> In principle, PAH formation and emission mechanisms followed two processes, including pyrolysis and pyrosynthesis.<sup>2–4</sup> Coking processes have been recognized as the major source of PAHs, in which secondary reactions (like aromatization/cyclation reactions) take place in an oxygen-absent atmosphere.<sup>5,6</sup>

Once discharged into the atmosphere, PAHs may be widely dispersed through air and they may accumulate in soils.<sup>7–9</sup> Due to their non-polarity and hydrophobicity, PAHs in the air bind with particles and are finally deposited into soils, thus soils become

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### Environmental impact

Coking plants are considered the major source of polycyclic aromatic hydrocarbons in China and their occurrence in the soils could threaten the workers' health. This manuscript studied the measurement and health-risk of PAHs in a representative coking plant of China. In this paper we focused on the soil in and around the coking plant, which is the first study on the toxic chemicals in industrial areas around the world. The distribution, composition profile and diagnostic ratios of PAHs were studied roundly, which provide further understanding of PAHs in the coking areas. To our knowledge, our study into the health-risk of PAHs in coking plant soil was the first report of its kind around the world.

their long-term repository and a steady indicator of environmental pollution.<sup>10</sup> Soils from many sites, especially industrial areas such as oil refineries, coking plants, manufactured gas plants and areas of coal tar spillage, are high in contamination by PAHs, with concentrations varying by several orders of magnitude.<sup>11–14</sup> According to the research of Khodadoust *et al.*,<sup>15</sup> the concentrations of PAHs in the manufactured gas plants can reach 10 000–30 000 mg kg<sup>-1</sup>. Due to the long-term activities associated with working in industries, workers may be exposed, directly and indirectly, to PAHs accumulated in soils in these areas.

PAHs species occurring in the environment are in the form of complex mixtures with widely varying toxic potencies.<sup>16</sup> They may create toxicity in organisms, by interfering with cellular membrane function and the coupled enzyme system. The metabolites of PAHs may bind to DNA, which can cause biochemical disruptions and cell damage in organisms.<sup>16,17</sup> Several PAHs species have been classified into probable (2A) or possible (2B) human carcinogens by the International Agency for Research on Cancer.<sup>18</sup> Therefore, to help the industries to optimize the distribution of the production equipment and to renovate the contaminated soils in the future, it is important to know not only the PAHs distribution, but also the corresponding health risks for worker exposed to these compounds.

In this study, the spatial distribution, composition profiles and diagnostic ratios of soil PAHs were characterized at Songshan coking plant in Guangdong province, China. Meanwhile, the workers' dermal PAH exposure levels were assessed and their resultant risks to health were estimated.

## Materials and methods

### Study area

The study area is located in the South of Shaoguan city in Guangdong province, China. This area has been occupied by the Songshan coking plant since 1966, covering  $19.1 \times 10^6$  m<sup>2</sup>. The factory is one of the subsidiaries of Shaoguan Steel Company and produces  $1.32 \times 10^6$  t of coke per year, with 734 people working in this plant. Around the coking plant, there are three living areas (Eastern district, Western district and Hongqi district), with the distance to the study area of about 1000, 1500 and 3000 m, respectively. The total population living in these areas is about 30 000.

### Sampling and pretreatment

The soil type in the study area is red soil which consists of natural soil and filling material, with sand content of 25–80%, a silt content of 5–15%, pH of 4.6–5.6, water holding capacity of 15–40% (dry wt basis), and a total organic carbon content (TOC) of 0.08–4.1%. Aggregate particle size distribution, pH, water holding capacity, and total organic carbon were determined for each individual soil sample as described in Bengtsson and Torneman.<sup>19</sup>

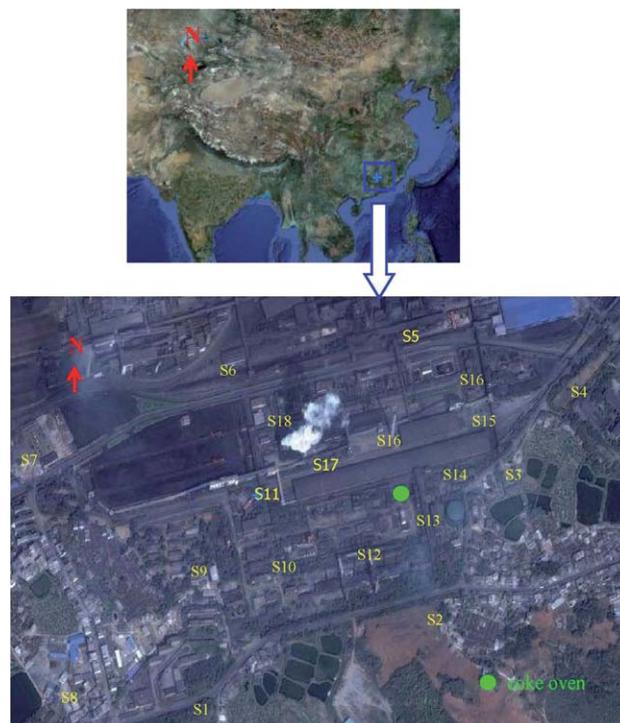
Surface soils (0–5 cm soil layer) were collected from different locations in and around Songshan coking plant in May 2010. The samples were packed with aluminium foil and placed in polythene bags, transported to the laboratory and stored at  $-20$  °C before analysis. At each sampling site, soil from 5 spots within

a distance of 50 cm was collected. In the laboratory, the soil collected from five spots were mixed thoroughly to make a composite sample after freeze-drying and removal of twigs and stones. After homogenization, the soil samples were sieved through a 2 mm sieve. Representative samples were obtained after quartering.

The sampling sites are shown in Fig. 1. Samples were taken from 19 sampling sites, of which 8 sites (S1–S8) were chosen around the coking plant, whilst the other 11 sites (S9–S19) were in the coking plant.

### Chemicals, standards and materials

Reference PAHs (18 compounds, each at 2000 µg mL<sup>-1</sup>) including naphthalene (Naph), 1-methylnaphthalene (1-Me-Naph), 2-methylnaphthalene (2-Me-Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fle), phenanthrene (Phen), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (Inp), dibenzo[*a,h*]anthracene (DBA), benzo[*g,h,i*]perylene (BgP), and deuterated surrogate (each at 4000 µg mL<sup>-1</sup>) containing naphthene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12 were obtained from Suplco (USA), and internal standards of hexamethylbenzene were obtained from Aldrich Co. (Aldrich Co., USA). They were diluted to the concentrations of working standards for capillary GC analyses. All solvents used for sample processing and analysis (dichloromethane, hexane, acetone and methanol) were HPLC grade from Merck (Darmstadt, Germany). Deionized water was produced by a Milli-Q system (Millipore Co., USA).



**Fig. 1** Locations of the sampling sites in and around Songshan coking plant.

## Extraction and analyses of PAHs in samples

Freeze dried soils (0.5 g) were spiked with 20  $\mu\text{L}$  80  $\mu\text{g mL}^{-1}$  surrogate standards and Soxhlet extracted with 200 mL dichloromethane for 48 h in a water bath maintained at 46 °C. The extract of soil samples were passed through a 1 : 2 alumina/silica gel glass column with 1 g anhydrous sodium sulfate overlying the silica gel for clean-up and fraction. First, 15 mL of hexane was applied to remove aliphatic hydrocarbons. Then, the eluents containing PAHs were collected by eluting 70 mL of dichloromethane : hexane (3 : 7, V : V), and were concentrated to 0.5 mL under a gentle purified  $\text{N}_2$  stream. 5  $\mu\text{L}$  internal standards (100  $\mu\text{g mL}^{-1}$ ) were added to the sample prior to GC-MS analysis.

PAHs were analyzed using a GC-MS (Shimadzu, QP2010 Plus) with a 30 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu\text{m}$  film thickness DB-5 MS column (J&W Scientific, USA) in selected ion mode (SIM). The GC-MS conditions for sample analysis were as follows: the injection port, interface line and ion source temperature were maintained at 280, 290 and 250 °C, respectively; the column temperature was programmed from 60 °C to 310 °C at 5 °C  $\text{min}^{-1}$  and hold for 10 min; helium was the carrier gas at a flow of 1.2 mL  $\text{min}^{-1}$  and a linear velocity of 42.4 cm  $\text{s}^{-1}$ . The ionization was carried out in the electron impacted by mode at 70 eV. 1  $\mu\text{L}$  volume of each sample was injected by manual in the split mode, the split ratio was 10 : 1.

## Quality control and quality assurance

Quantification was performed using a seven-point calibration curve established using hexane-based internal standards for each individual PAH. The  $R^2$  values of the PAH calibration curves were all greater than 0.99. The detection limits of the method ranged from 0.06 to 16.56 mg  $\text{kg}^{-1}$  for soil samples. The average recoveries were 62.9  $\pm$  11.7% for naphthalene-d8, 85.9  $\pm$  9.5% for acenaphthene-d10, 91.9  $\pm$  10.4% for phenanthrene-d10, 87.6  $\pm$  6.5% for chrysene-d12 and 90.6  $\pm$  9.6% for perylene-d12.

## Results and discussion

### Distribution and concentration of PAHs in coking plant soils

PAHs were determined in all soil samples, the total concentrations of the 18 PAHs ( $\sum$  PAHs) and the concentration of each individual PAH in the collected soils are summarized in Table 1. The values of  $\sum$  PAHs ranged from 2.36 to 1146.39 mg  $\text{kg}^{-1}$  of dry matrix. The wide range of PAH concentrations found in the soil samples indicated heterogeneous levels of contamination in the investigated area. The heterogeneity of the levels found in the coking plant can be interpreted on the base of the spatial heterogeneity of the pedologic conditions and the location of soils relative to the coke oven.

As shown in Table 1, the higher concentrations of  $\sum$  PAHs of soil samples were found in the stations located either in the northwest (S5, S6 and S18) or under the coke oven (S13 and S14). The  $\sum$  PAHs concentrations were highest in the soil of S18 (1146.4 mg  $\text{kg}^{-1}$ ), which was located near the regulation tank of the coking wastewater treatment plant. The contact with coking wastewater and/or sludge from the wastewater treatment plant could be another reason for the higher concentration of PAHs in

this site. The lower concentrations were found in S1, S2 and S9 (< 5 mg  $\text{kg}^{-1}$ ), located in the south of the coke oven. This spatial distribution of PAHs can be attributed to prevailing wind directions in the sampling area where the prevailing wind direction was from southeast to northwest. Besides the location of soils, the size and organic carbons content of soils could influence the content of PAHs. According to the study of Li,<sup>14</sup> most of PAHs occurred in the 250–500  $\mu\text{m}$  size fraction of soils from a coking plant, and total PAH concentration displayed strong positive linear relationship with organic carbon.

In the coking plant, most individual PAHs were correlated with each other. Significant correlations were found among high molecular weight PAHs (4–6 rings), except DBA in some cases (Table 2). Most individual PAHs displayed better correlation with total PAHs concentration, with correlation coefficient approaching or exceeding 0.9. The stronger correlation among high molecular PAHs could contribute to the sorption by soil organic matter,<sup>20</sup> which inhibited degradation and leaching of these compounds.<sup>21</sup> The correlation of total PAHs with Chr, BbF and BaP exceeded 0.99 for most samples, indicating these compounds could be used to estimate the total PAH concentrations.

The background levels of PAH for soils without the influence of anthropogenic activities are estimated less than 0.1 mg  $\text{kg}^{-1}$ .<sup>22</sup> In the present study, PAH concentration in all of the studied soil samples were higher than the estimated background level. According to the concentration of PAH in the soil, it could be classed as either weekly contaminated (0.2–0.6 mg  $\text{kg}^{-1}$ ), contaminated (0.6–1.0 mg  $\text{kg}^{-1}$ ) or heavily contaminated (1.0 mg  $\text{kg}^{-1}$ ) soil.<sup>23</sup> These values were derived from the results of determination of PAH content of soils, as well as from an estimation of the risk of human exposure and the average intake rates.<sup>17,24–27</sup> Considering our results, the total concentrations measured in all of the coking plant soils, especially these closest to coke oven, were higher than 1.0 mg  $\text{kg}^{-1}$ , indicating that the soils in the studied area had been highly contaminated by the production of coke.

### Composition profiles of soil PAHs

A cluster analysis was performed using SPSS 17.0 software (SPSS Inc., USA) to examine the correlation of PAH distribution in the coking plant (Fig. 2). As shown in the dendrogram from the cluster analysis (Fig. 2(a)), five groups are observed with sample types. Group I and group II have similar profiles, and were characterized by the dominance of Naph, 1-Me-Naph, Phen and Flu, with proportion to total concentration of 6.5–35.7%, 7.3–14.4%, 8.3–22.0% and 7.0–12.9%, respectively. The average percentage of low molecular weight (2–3 rings) to total PAHs of group II ranged from 60.4% to 78.6%, while low molecular weight PAHs to total PAHs varied between 40.3% and 50.7% in group I. The composition of group III and IV was mainly 4–5 ring PAHs, with the percentage to total PAHs ranging from 46.9% to 76.3%. For individual PAHs, Flu was the dominant compound (8.3%–24.7%), followed by Pyr (7.7%–18.4%), BbF (5.8%–10.6%) and BaP (5.1%–11.5%). In group V, 3–5 ring PAHs were the dominant compounds, contributing 76.1% to total PAHs, of which Ace was the most abundant (9.9%), followed by BbF (7.0%) and DBA (7.3%). Compared with group III

**Table 1** Concentration (mg kg<sup>-1</sup>) of single polycyclic aromatic hydrocarbons (mean of three analyses) in studied soil samples

Compounds	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17	S18	S19
Naph	0.20	0.30	2.33	4.55	7.09	14.77	2.04	1.91	0.33	0.51	0.87	1.28	6.95	88.31	0.59	0.08	0.26	9.42	11.45
1-Me-Naph	0.19	0.29	3.95	6.80	8.00	22.80	3.15	0.58	0.15	0.36	0.95	0.44	3.67	35.62	0.19	0.05	0.10	12.44	4.34
2-Me-Naph	0.10	0.14	2.11	3.13	5.66	12.25	1.76	0.25	0.07	0.14	0.71	0.18	1.58	12.63	0.09	0.03	0.05	7.01	1.66
Acy	0.05	0.08	0.90	1.03	9.06	13.22	0.99	0.06	0.06	0.16	0.33	0.19	1.32	1.54	0.11	0.09	0.05	6.19	0.98
Ace	0.03	0.05	0.73	0.55	5.95	35.34	0.77	0.07	0.06	0.33	1.09	0.27	3.01	15.71	0.15	0.02	0.05	44.13	0.13
Fle	0.07	0.11	1.10	1.66	8.06	17.59	1.08	0.13	0.09	0.26	0.83	0.34	2.63	2.63	0.17	0.05	0.07	27.50	1.22
Phen	0.28	0.42	3.19	5.56	12.90	12.66	2.59	1.75	0.45	0.89	1.02	2.47	12.84	36.47	0.80	0.37	0.42	82.29	4.29
Ant	0.05	0.08	0.99	1.25	19.69	13.23	1.06	0.05	0.08	0.19	0.33	0.37	1.73	1.31	0.14	0.07	0.06	16.97	0.69
Flu	0.27	0.40	2.94	3.58	19.80	18.30	2.20	1.03	0.47	1.76	1.51	3.07	14.94	28.66	1.32	0.73	0.69	283.70	3.44
Pyr	0.12	0.18	2.32	2.81	18.71	16.71	1.84	0.15	0.32	1.44	1.15	2.14	10.03	17.57	0.89	0.65	0.51	211.35	2.31
BaA	0.09	0.13	1.89	2.32	15.10	20.25	1.79	0.09	0.23	1.18	0.80	1.10	6.19	1.42	0.62	0.38	0.33	101.84	0.99
Chr	0.17	0.26	2.16	2.84	13.24	25.70	1.86	0.47	0.30	1.16	0.90	1.38	7.57	2.12	0.68	0.57	0.38	70.37	1.49
BbF	0.27	0.27	2.22	2.89	16.42	25.11	2.10	0.44	0.29	1.58	0.86	1.30	8.03	1.14	0.65	0.58	0.46	69.91	1.16
BkF	0.12	0.18	1.72	2.11	14.16	24.63	1.69	0.27	0.21	1.16	0.73	0.96	5.95	0.68	0.47	0.52	0.31	55.95	0.85
BaP	0.19	0.29	1.71	1.56	21.36	23.01	1.61	0.39	0.27	1.90	0.76	1.09	6.53	0.65	0.58	0.52	0.43	69.73	0.71
DBA	0.07	0.10	1.08	1.30	10.82	25.85	1.20	0.07	0.05	0.34	0.30	0.21	1.47	0.12	0.12	0.31	0.08	11.95	0.21
InP	0.12	0.19	1.93	2.41	18.60	18.77	2.07	0.16	0.21	1.65	0.63	1.00	5.63	0.29	0.46	0.58	0.34	35.97	0.74
BgP	0.06	0.09	1.57	1.98	13.62	16.34	1.49	0.08	0.22	1.49	1.19	0.98	5.85	0.33	0.44	0.60	0.33	29.68	0.83
Total PAHs	2.36	3.54	34.86	48.31	238.23	356.52	31.28	7.94	3.85	16.50	14.99	18.76	105.90	247.21	8.46	6.29	4.91	1146.40	37.47

and IV, a higher proportion of low molecular weight PAHs were found in group I, II and V. Although different emission sources and/or the input of other sources (*e.g.* petroleum sources) may lead to the variation of proportions for low molecular weight PAHs, it was believed that this gradient among the five groups mainly resulted from their distance from the emission sources of the coking plant. This was explained by the difference in the behaviors of particle-bound and gaseous PAHs, with particles being deposited closer to the source. On the other hand, according to their physical and chemical characteristics (low molecular weight, high vapor pressure, *etc.*), 2–3 ringed PAHs were mainly in gaseous form and they could be transported to long distances.<sup>17</sup> The phenomenon of the changing profiles in soil samples at different distances from the source was also described by other studies,<sup>28,29</sup> and they contributed it to the deposition of particles and the compounds' atmospheric transport potential.

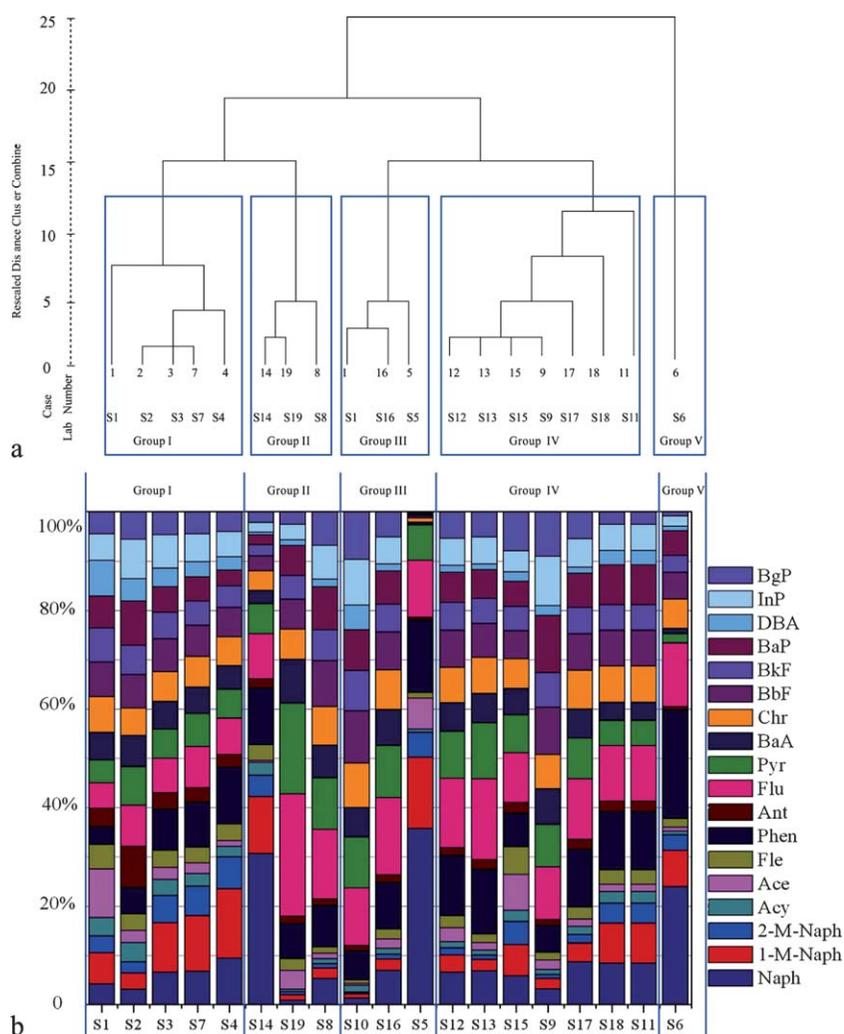
### Diagnostic ratios

In order to characterize the diagnostic ratios of PAHs in the coking plant soils and to assess the influence of the anthropogenic activity to the soil pollution, some indexes were calculated by ratios of concentrations of some PAHs. For example, the abundance ratios of low molecular weight (2–3 rings) hydrocarbons to high molecular weight (4–6 rings) hydrocarbons, Ant : (Ant + Phen), Flu : (Flu + Pyr), BaA : (BaA + Chr) and InP : (InP + BgP) were applied to distinguish the petrogenic and pyrolytic sources of PAHs in environment.<sup>30–33</sup> An Ant : (Ant + Phen) ratio < 0.1 is often considered as an indication of petroleum source whereas the ratio > 0.1 indicates that combustion is a dominant source of PAHs.<sup>34</sup> The Flu : (Flu + Pyr) ratio of < 0.4 is defined as the source of petroleum, while > 0.5 denotes combustion.<sup>30,34</sup> The BaA : (BaA + Chr) ratio < 0.2 usually

**Table 2** Correlation coefficient matrix for PAHs in coking soil ( $n = 19$ )<sup>a</sup>

	Naph	1-Me-Naph	2-Me-Naph	Acy	Ace	Fle	Phen	Ant	Flu	Pyr	BaA	Chr	BbF	BkF	BaP	DBA	InP	BgP	Total PAHs
Naph	1																		
1-Me-Naph	0.761	1																	
2-Me-Naph	0.714	<b>0.984</b>	1																
Acy	<b>0.622</b>	<b>0.856</b>	<b>0.921</b>	1															
Ace	0.485	0.711	0.719	0.598	1														
Fle	0.497	0.674	0.704	0.609	<b>0.964</b>	1													
Phen	<b>0.244</b>	0.273	0.290	0.207	<b>0.700</b>	<b>0.802</b>	1												
Ant	<b>0.446</b>	0.580	0.683	0.794	<b>0.586</b>	<b>0.714</b>	<b>0.467</b>	1											
Flu	0.153	0.188	0.203	0.132	<b>0.642</b>	<b>0.730</b>	<b>0.979</b>	<b>0.375</b>	1										
Pyr	0.162	0.202	0.218	0.147	<b>0.654</b>	<b>0.747</b>	<b>0.982</b>	<b>0.398</b>	<b>0.999</b>	1									
BaA	<b>0.235</b>	0.305	0.329	0.247	<b>0.761</b>	<b>0.848</b>	<b>0.986</b>	<b>0.503</b>	<b>0.978</b>	<b>0.984</b>	1								
Chr	<b>0.345</b>	0.452	0.475	0.380	<b>0.874</b>	<b>0.941</b>	<b>0.950</b>	<b>0.590</b>	<b>0.910</b>	<b>0.920</b>	<b>0.974</b>	1							
BbF	0.346	0.452	0.482	0.398	<b>0.862</b>	<b>0.941</b>	<b>0.949</b>	<b>0.628</b>	<b>0.903</b>	<b>0.915</b>	<b>0.972</b>	<b>0.998</b>	1						
BkF	0.388	0.519	0.551	0.466	<b>0.905</b>	<b>0.972</b>	<b>0.912</b>	<b>0.665</b>	<b>0.858</b>	<b>0.872</b>	<b>0.944</b>	<b>0.992</b>	<b>0.994</b>	1					
BaP	0.329	0.429	0.471	0.411	<b>0.828</b>	<b>0.928</b>	<b>0.940</b>	<b>0.680</b>	<b>0.895</b>	<b>0.908</b>	<b>0.965</b>	<b>0.984</b>	<b>0.993</b>	<b>0.986</b>	1				
DBA	<b>0.602</b>	<b>0.910</b>	<b>0.945</b>	<b>0.953</b>	0.712	0.666	0.229	0.670	0.159	0.174	0.280	0.426	0.433	0.508	0.427	1			
InP	0.446	0.583	0.643	0.618	<b>0.838</b>	<b>0.946</b>	<b>0.809</b>	<b>0.850</b>	<b>0.722</b>	<b>0.742</b>	<b>0.839</b>	<b>0.910</b>	<b>0.931</b>	<b>0.948</b>	<b>0.949</b>	<b>0.602</b>	1		
BgP	0.469	0.605	0.657	0.614	<b>0.873</b>	<b>0.964</b>	<b>0.820</b>	<b>0.813</b>	<b>0.731</b>	<b>0.750</b>	<b>0.848</b>	<b>0.927</b>	<b>0.943</b>	<b>0.962</b>	<b>0.951</b>	<b>0.615</b>	<b>0.995</b>	1	
Total PAHs	0.323	0.412	0.439	0.351	<b>0.836</b>	<b>0.920</b>	<b>0.967</b>	<b>0.592</b>	<b>0.931</b>	<b>0.941</b>	<b>0.986</b>	<b>0.997</b>	<b>0.997</b>	<b>0.984</b>	<b>0.991</b>	0.386	<b>0.906</b>	<b>0.917</b>	1

<sup>a</sup> Coefficients significant at the 0.05 level are italicized, coefficients significant at the 0.01 are bold-faced.



**Fig. 2** The characteristic of PAH distributions in coking plant: (a) the dendrogram from the cluster analysis. (b) the fraction of PAHs in coking plant soils.

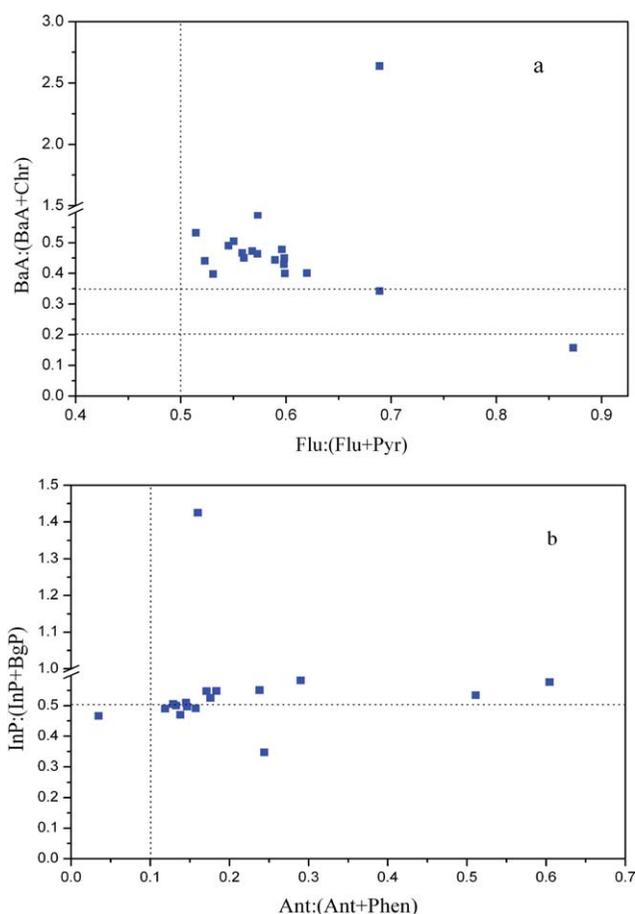
indicates the petroleum source, and the value of 0.2–0.35 implies either petroleum or combustion.<sup>34</sup> The BaA : (BaA + Chr) ratio of  $> 0.35$  is the characteristic of combustion. InP : (InP + BgP) ratio of  $< 0.2$  is suggested the discharge of petroleum input, and ratio of  $> 0.5$  indicates wood and coal combustion, while between 0.2 and 0.5 is considered as the source of fuel petrochemical fuel combustion.<sup>34</sup>

Considering that these soil samples were collected around and in the coking plant, the source of PAHs pollution in the soil under investigation came mainly from the coking processes and/or correlative production processes. The values of isomeric ratios for the different samples of the soils investigated in the present study are listed in Fig. 3. The Flu : (Flu + Pyr) ratio ranged from 0.51 to 0.87, while the BaA : (BaA + Chr) and InP : (InP + BgP) ratios ranged between 0.16 to 0.89, and 0.47 to 0.68, respectively. Only the BaA : (BaA + Chr) ratio of S1, S2 and S8 were found  $< 0.35$ , while InP : (InP + BgP) ratios of S4, S9, S11 and S14 presented the values smaller than 0.5. The Ant : (Ant + Phen) ratio for soils varied from 0.03 to 0.60, only S8 and S13 were below 0.1. The highest ratios were observed in the downwind location, with the ratios of 0.60 for S5 and 0.51 for S6, respectively. The Ant : (Ant + Phen) ratio of  $< 0.1$  was only found in S8 and S14.

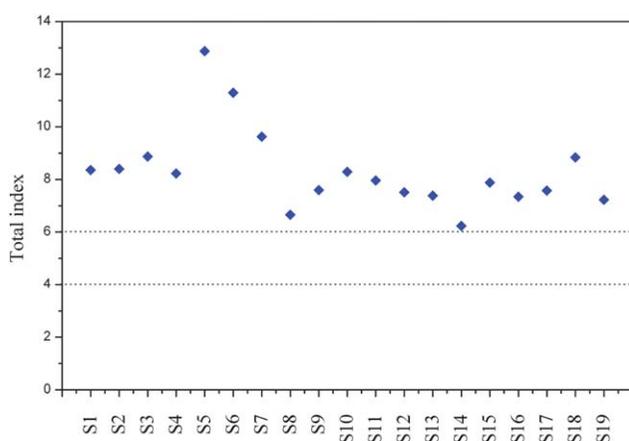
According to the results of our study, the values of these ratios were not in agreement among them in some cases. As the source of PAHs in a matrix could be different and occasional, the total index as the sum of single indices respectively normalized for the limit value (low temperature source-high temperature source) was reported to characterize the source of PAHs: Total index =  $\text{Ant}/(\text{Ant} + \text{Phen})/0.1 + \text{Flu}/(\text{Flu} + \text{Pyr})/0.4 + \text{BaA}/(\text{BaA} + \text{Chr})/0.2 + \text{InP}/(\text{InP} + \text{BgP})/0.2$ .<sup>17,34</sup> Orecchio considered PAHs originating by high temperature processes (combustion) when the total index was  $> 4$ , while lower values indicated low temperature source (petroleum product).<sup>17</sup> The total indexes of the investigated soils from the coking plant were  $> 6$  (Fig. 4), confirming that the PAHs in the studied area were from the pyrolysis of coal.

#### Toxic potency assessment of PAHs in soils

Several PAHs have been classified into probable or possible human carcinogens by IARC,<sup>18</sup> and the carcinogenic potency associated with exposure of a given PAH compound could be obtained by calculating its BaP toxic equivalent concentration (TEQ<sub>BaP</sub>) according to toxic equivalent factor (TEF).<sup>35</sup> The list of TEF<sub>BaP</sub> compiled by Tsai *et al.* was adopted in this study



**Fig. 3** Plot of the isomeric ratios: (a) Flu : (Flu + Pyr) vs. BaA : (BaA + Chr), (b) Ant : (Ant + Phen) vs. InP : (InP + BgP).



**Fig. 4** The total indexes of PAHs in coking plant soils.

(Table 3).<sup>36</sup> To assess the carcinogenic potencies associated with the total PAHs concentrations in the coking plant soils, sum of each individual  $TEQ_{BaP}$  was calculated in the present study (Table 4). The calculated total  $TEQ_{BaP}$  concentrations at different sampling site varied from  $0.32 \text{ mg kg}^{-1}$  (S1) to  $109.97 \text{ mg kg}^{-1}$  (S18). Significant good correlation between the concentration of BaP and total  $TEQ_{BaP}$  was found ( $R^2 = 0.96$ )

**Table 3** Toxic equivalency factors ( $TEF_{BaP}$  and  $TEF_{TCDD}$ )

Compounds	$TEF_{BaP}$	$TEF_{TCDD}$
Naph	0.001	
Acy	0.001	
Ace	0.001	
Fle	0.001	
Phen	0.001	
Ant	0.01	
Flu	0.001	
Pyr	0.001	
BaA	0.1	0.000025
Chr	0.01	0.00020
BbF	0.1	0.00253
BkF	0.1	0.00478
BaP	1	0.000354
DBA	1	0.00203
InP	0.1	0.0011
BgP	0.01	

(Fig. 5 (a)), which was consistent with other studies,<sup>29</sup> indicating that BaP could be the target to assess the toxic of the studied area. It was also reported that PAHs had dioxin-like toxicity. The equivalent concentrations of  $TEQ_{TCDD}$  could be calculated based on the values of  $TEF_{TCDD}$  with respect to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), which were determined by Willet *et al.*<sup>37</sup> In our study, the  $TEQ_{TCDD}$  values ranged from  $0.0014$  to  $0.55 \text{ mg kg}^{-1}$  (Table 4), and the highest value was found at S18, with the lowest value at S1, which was consistent with distribution of  $TEQ_{BaP}$ . Furthermore, a good linear correlation between  $TEQ_{TCDD}$  and  $TEQ_{BaP}$  ( $R^2 = 0.98$ ) was found (Fig. 5 (b)), confirming that  $TEQ_{BaP}$  and  $TEQ_{TCDD}$  presented a consistent assessment of soil PAHs.<sup>29</sup>

Health risk assessments were carried out by dermal PAHs exposure data in order to quantify cancer risk using the following equation:

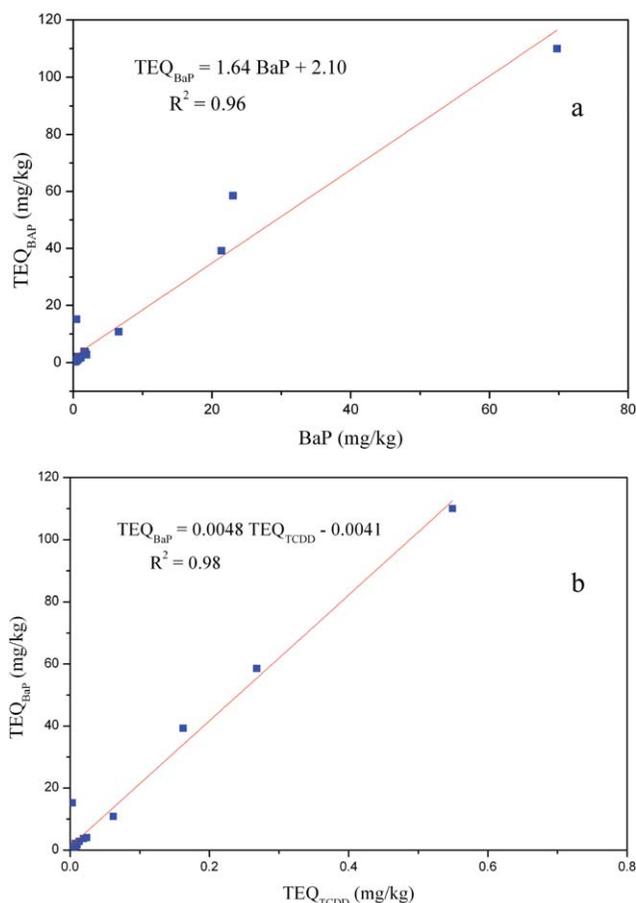
$$DE = (C \times AB \times SA \times EV \times AFd \times EF \times ED) / (BW \times AT)$$

where C is the daily exposure level for dermal contact ( $\text{mg kg}^{-1}$ ), AB is the dermal adsorption fraction, SA is the dermal surface area exposed ( $\text{cm}^2$ ), EV is the event frequency (events per day), AFd is the particle-to-skin adherence factor ( $\text{mg cm}^{-2}$  per event), EF is the exposure frequency (days per year), ED is the exposure duration (years), BW is the body weight (kg), and AT is the average time for carcinogenesis to occur (days).

In this study, the total concentration of  $TEQ_{BaP}$  was applied as the daily exposure level. According to the US EPA,<sup>38</sup> a maximum of 20% of PAHs adsorbed to soils was thought to desorb onto the skin in 24 h. Based on the previous studies,<sup>39–41</sup>  $3067 \text{ cm}^2$  for SA, 1 event per day for EV and  $1 \text{ mg cm}^{-2}$  per event were used in our study. Assuming that workers in the coking plant experienced 25 years employment (8 h per day, 5 days per week, 50 weeks per year) during life span of 70 years, the resultant lifetime exposure levels due to  $TEQ_{BaP}$  desorbed onto skin for workers ranged from  $2.25 \times 10^{-7}$  to  $7.86 \times 10^{-5} \text{ mg kg}^{-1}$  per day (Table 4). In this study, the unite risk of  $37.47 \text{ (mg kg}^{-1} \text{ per day)}$  recommended by Hussain *et al.* for BaP was adopted to estimate the lifetime skin cancer risk posed by the dermal PAHs exposures.<sup>39</sup> As shown in Table 4, the resultant lifetime skin cancer risks of soils in the coking plant were between  $8.45 \times 10^{-6}$  and  $2.94 \times 10^{-3}$ . The highest value was found

**Table 4** The calculated total TEQ<sub>BaP</sub>, total TEQ<sub>TCDD</sub> concentrations and cancer risk estimates from exposure to PAHs via dermal PAHs exposure in coking plant soil

Site	TEQ <sub>BaP</sub> mg kg <sup>-1</sup>	TEQ <sub>TCDD</sub> mg kg <sup>-1</sup>	Exposure level mg kg <sup>-1</sup> per day	Cancer risk
S1	0.316	0.00140	$2.25 \times 10^{-7}$	$8.45 \times 10^{-6}$
S2	0.473	0.00211	$3.38 \times 10^{-7}$	$1.27 \times 10^{-5}$
S3	3.645	0.01923	$2.60 \times 10^{-6}$	$9.76 \times 10^{-5}$
S4	3.953	0.02387	$2.82 \times 10^{-6}$	$1.06 \times 10^{-4}$
S5	39.215	0.16222	$2.80 \times 10^{-5}$	$1.05 \times 10^{-3}$
S6	58.546	0.26815	$4.18 \times 10^{-5}$	$1.57 \times 10^{-3}$
S7	3.648	0.01907	$2.61 \times 10^{-6}$	$9.77 \times 10^{-5}$
S8	0.590	0.00295	$4.22 \times 10^{-7}$	$1.58 \times 10^{-5}$
S9	0.420	0.00220	$3.00 \times 10^{-7}$	$1.13 \times 10^{-5}$
S10	2.835	0.01299	$2.03 \times 10^{-6}$	$7.59 \times 10^{-5}$
S11	1.402	0.00746	$1.00 \times 10^{-6}$	$3.75 \times 10^{-5}$
S12	1.783	0.01009	$1.27 \times 10^{-6}$	$4.77 \times 10^{-5}$
S13	10.840	0.06193	$7.75 \times 10^{-6}$	$2.90 \times 10^{-4}$
S14	2.143	0.00739	$1.53 \times 10^{-6}$	$5.74 \times 10^{-5}$
S15	21.632	0.00499	$6.69 \times 10^{-7}$	$2.51 \times 10^{-5}$
S16	1.064	0.00575	$7.61 \times 10^{-7}$	$2.85 \times 10^{-5}$
S17	15.198	0.00341	$1.09 \times 10^{-5}$	$4.07 \times 10^{-4}$
S18	109.972	0.54943	$7.86 \times 10^{-5}$	$2.94 \times 10^{-3}$
S19	1.446	0.00879	$1.03 \times 10^{-6}$	$3.87 \times 10^{-5}$

**Fig. 5** Correlations of (a) BaP vs. TEQ<sub>BaP</sub> and (b) TEQ<sub>BaP</sub> vs. TEQ<sub>TCDD</sub>.

at S18, followed by S6 ( $1.57 \times 10^{-3}$ ) and S5 ( $1.05 \times 10^{-3}$ ), and the cancer risks of these sites were higher than the significant risk level of  $10^{-3}$  that was defined by a 1980 US Supreme Court.<sup>42</sup> However, it should be noticed that 8 h of one day was applied as the exposure

time in our study, which was higher than the real exposure time of the coking workers. With lower cancer risks ( $8.45 \times 10^{-6}$  to  $4.07 \times 10^{-4}$ ), the dermal exposures of PAHs to coking workers might be acceptable at other soil sites.

## Conclusions

Surveys were carried out in a coking plant to determine the concentrations, composition profiles and diagnostic ratios of PAHs in soils of Songshan coking plant and investigate health-risk for workers to these compounds. The concentrations of PAHs in coking plant were between 2.36 and 1146.39 mg kg<sup>-1</sup>, varying significantly among the sampling sites, and most individual PAHs were correlated with each other. According to a cluster analysis, five groups were observed with sample types in the coking plant. 2–3 ringed PAHs were predominant in groups I and II, while 4–5 ringed PAHs showed great abundance in groups III, IV and V, which contributed to the distance from the emission sources in the coking plant. The source of PAHs in the soils was from the pyrolysis process, with Flu : (Flu + Pyr), BaA : (BaA + Chr), InP : (InP + BgP) and Ant : (Ant + Phen) ratios were 0.51–0.87, 0.16–0.89, 0.47–0.68 and 0.03–0.60, respectively. The resultant lifetime exposure levels due to TEQ<sub>BaP</sub> desorbed onto skin for workers ranged from  $2.25 \times 10^{-7}$  to  $7.86 \times 10^{-5}$  mg kg<sup>-1</sup> per day, and the estimated cancer risks were between  $8.45 \times 10^{-6}$  and  $2.94 \times 10^{-3}$ . Excluding S5, S6 and S18 which had higher cancer risk, the dermal exposures of PAHs to coking workers might be acceptable in other soil sites.

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