Bull. Environ. Contam. Toxicol. (2006) 76:80–89
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DOI: 10.1007/s00128-005-0892-8

Bulletin of Environmental Contamination and Toxicology

Pilot Study of Polycyclic Aromatic Hydrocarbons in Surface Soils of Guiyang City, People's Republic of China

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Received: 27 May 2005/Accepted: 12 October 2005

Polycyclic aromatic hydrocarbons (PAHs) are a class of well-know toxic and carcinogenic compounds that are widely present in industrial waste, gas, automobile exhaust, coal tars, cigarette smoke and meat products, which constitute the most common ways of exposure of humans to the PAHs (Castillo et al. 2004). PAHs are listed by the US Environmental Protection Agency (USEPA) as priority pollutants.

PAHs are usually identified and quantified by high performance liquid chromatography (HPLC) with UV-visible, fluorimetric or amperometric detection, or, alternatively, by gas chromatography-mass spectrometry or with GC-flame ionization detection. Fluorescence- based methods offer wide linear dynamic ranges, low detection limits and stable responses (Berset et al. 1999; Kayali-Saydi et al. 2000). The extraction of PAHs from solid samples can be carried out by pressurized fluid or accelerated solvent extraction, sonication, soxhelt, or supercritical fluid extraction alone or with modifiers. Some of these procedures require high solvent volumes or as a result, high expensive instrumentation (Schantz et al. 1997; Saim et al.1998; Langenfeld et al. 1993). Therefore, a rapid and accurate method for extraction of PAHs from soil samples is described in this study. This method is only based on sonication extraction with dichloromethane (DCM) and clean-up by silica gel. The determination of PAHs is carried out by HPLC using a program of pairs of extraction and emission wavelength for fluorimetric detection. This method was applied to measure the soil samples of Guiyang city, China. In Guiyang city, coal is widely used for industrial and domestic purposes and the sum of the vehicle is growing, so the PAHs contamination should not be neglected. The PAHs in soil can be accumulated in vegetables and therefore exert a negative impact on human health. However, no data about PAHs in soil of Guiyang city have been reported before. This study reports the PAHs contamination in soil of Guiyang city.

MATERIALS AND METHODS

Independent stock standard solutions (5mg/L) of Naphthalene(Nap), Acenaphthylene(Acy), Acenaphthene(Ace), Fluorene(Fle), phenanthrene(Phe), Anthracene(Ant), Fluoranthene(Fla), Pyrene(Pyr), Benz[a]anthracene(BaA),

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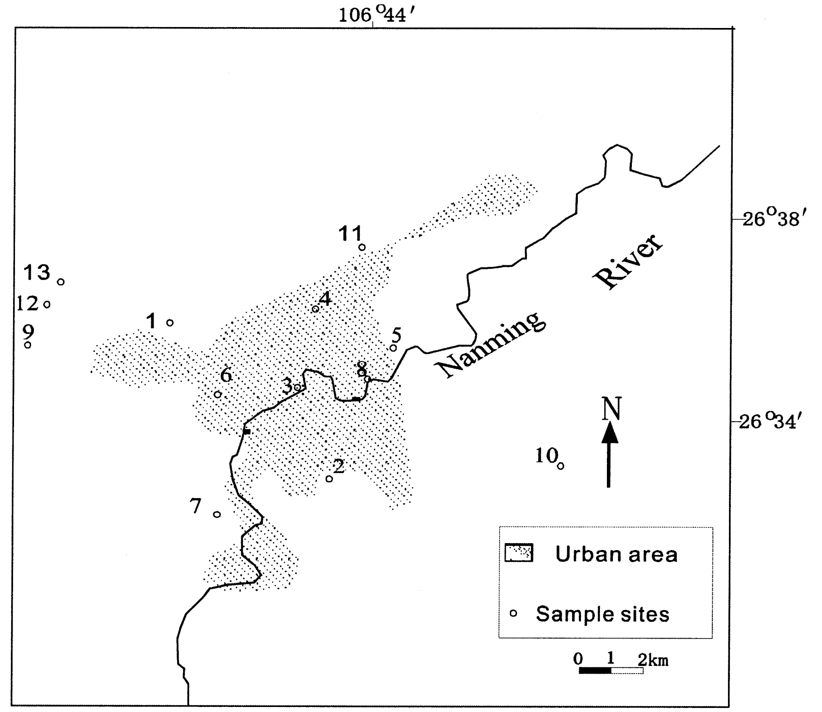

Figure 1. Map showing the sample sites in Guiyang city.

Chrysene(Chr), Benzo[b]fluoranthene(BbFL), Benzo[k]fluoranthene(BkFL), benzo[a]Pyrene(BaP), Dibenzo[a,h]anthracene(DBA), Benzo[g,h,I]perylene(BPE), Indeno[1,2,3-c,d]pyrene(Ipy) were prepared by solving pure solid (purity-99.5 %, Accustandard Incorporation, New Havan, USA) in acetonitrile. Working standard PAH mixtures were prepared by suitable dilution of the stock standard with acetonitrile (each standard mixture solution obtained independently from the individual stock solution). All solutions were stored at 4℃ prior to use. A chromatographic system (HP1100) equipped with a fluorimetric detector (FLD) and a UV detector was used for PAHs determination. The sample loop is 20 μL. The UV detector was used to determine the PAH species (Acy and Ipy) lacking FLD signal. A Waters PAH column (4.6×250mm, 5μm particulate size, made in Germany) was used for separation of PAHs, and the mobile phase is composed of acetonitrile and water. All reagents are of HPLC grade, and Millipore Milli-Q system deionized water (18.2 MΩ•cm) was used in all the processes.

Guiyang City, located southwest of China (east longitude 106°07' to 107°17', and north latitude 26°11' to 27°22'), owns an urban area of 98 square kilometers, a population of 1 million people, and a vehicle quantity of 170,000. Its altitude is 1050 m. Soil samples were collected at eight urban sites and five suburban sites in Guiyang city (Figure 1). The description of sampling sites is shown in Table 1. For all samples, the 0-10 cm depth original surface soil was collected and mixed. Samples were air dried and pulverized to less then 60 mesh (0.3 mm) prior to

Table 1. Description of sampling sites.

Sampling sites	Site description	Land use
1	Urban area	Forest
2	Urban area	Forest
3	Urban area	Grassland
4	Urban area	Grassland
5	Urban area	Grassland
6	Urban area	Forest
7	Urban area	Forest
8	Urban area	Grassland
9	Suburban area, west of Guiyang city	Grassland
10	Suburban area, east of Guiyang city	Grassland
11	Suburban area, north of Guiyang city	Forest
12	Suburban area, west of Guiyang city	Grassland
13	Suburban area, west of Guiyang city	Grassland

further processing. Soil samples (3 g) were extracted ultrasonically with DCM for three times (20 mL × 3), 20 minutes each time. The extractions were combined and filtered through a 0.45 μm glass filter. When the extraction evaporated to approximately dryness, the residue was dissolved in 2 mL hexane, and then added in the silica gel column for cleaning up. The silica gel was previously heated at 130℃ for 16 h and then packed in a column and covered with 1 g of anhydrous Na_2SO_4. An extra 2 mL hexane was added to elute aliphatic hydrocarbons. Following this, 4mL (2mL × 2) DCM was added and the eluant was collected. The eluant was blown to dryness under gentle argon, and redissolved in 2 mL acetonitrile, and then analyzed by HPLC. All the data are expressed as dry weight of soil.

One method blank and two spiked soil samples were measured to ensure the quality of the pretreatment and HPLC analysis. The spiked soil sample was conducted as below: a soil sample was previously extracted with DCM to remove PAHs, and then standard PAHs solution was spiked into the soil and mixed thoroughly. The soil was air-dried and then treated the same as other soil samples. In addition, two duplicates were treated and measured for the batch of experiment to meet the quality control.

RESULTS AND DISCUSSION

Mobile phase composition and detector wavelength are essential for PAHs separation and detection sensitivity respectively. A series of analyses using 16 PAHs standard mixture were run to achieve the optimized mobile phase (Table 2) and fluorimetric wavelength (Table 3). Figure 2 shows the separation of 16 PAHs. Furthermore, linearity (R^2), detection limits, repeatability, reproducibility and recovery of this method are respectively 0.9994, 0.05-0.2 μg/L, 1.2%, 2.3%, and 79-101%. Linearity is calculated according to the results of 2.5, 5, 10, 20, 50, 200μg/L PAHs mixed solutions. Detection limit is the concentration giving a

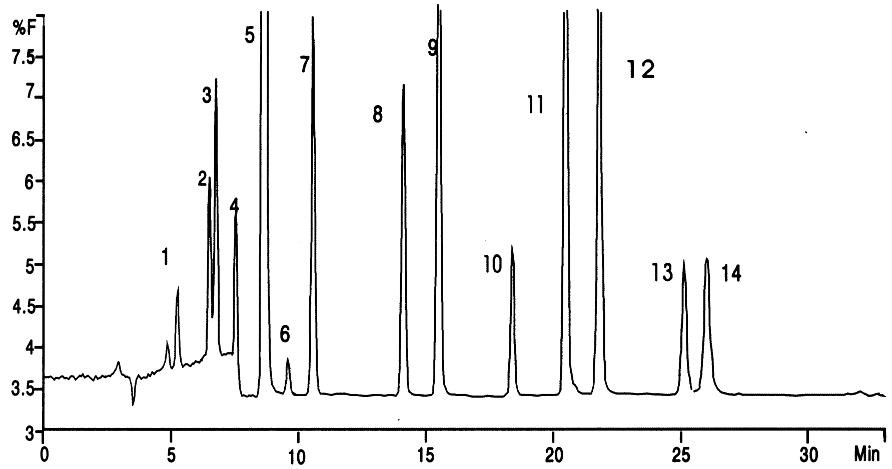

Figure 2. Chromatogram of a standard mixture (10 μg/L) of PAHs.
1. Nap, 2. Ace, 3. Fle, 4. Phe, 5. Ant, 6. Fla, 7. Pyr, 8. BaA, 9. Chr, 10. BbFL, 11. BkFL, 12. BaP, 13. DBA, 14. BPE
Note: Due to the lack of FLD signal for Acy and Ipy, UV detector was used to for determination of these two PAH species. The UV peak of Acy locates between Nap and Ace and UV peak of Ipy locates behind BPE.

Table 2. Mobile phase gradient program.

Time (min)	Acetonitrile (%)	Water(%)
0	70	30
18	100	0
29	100	0
31	70	30

signal three times the standard deviation (N=6) of the blank. Repeatability is determined by calculating the relative standard deviation (RSD) of 6 analyses (10 μg/L each PAH). Reproducibility is determined by calculating the RSD of analyses performed on three different days (3 analyses each day, 10 μg/L each PAH). Recovery is calculated according to the results of PAHs solutions spiked in a soil sample in which PAHs has been removed previously.

The concentrations of 16 priority PAHs in soils are listed in Table 4. The total PAHs concentration in soil varies from 61 to 1560 μg/kg. Urban samples and suburban samples show obviously different PAHs levels. Concentration of 16 PAHs is 247-1560μg/kg for urban soils and 61-511 μg/kg for suburban soils. The PAHs concentration of soils in Guiyang city are not only above the endogenous level (1.0-10 μg/kg), but also obviously higher than the target value set by Dutch government for unpolluted soil (20-50 μg/kg) (Ma and Chu 2004). Consequently, similarly with other cities worldwide, Guiyang city is found suffering a soil PAHs contamination and the causes accounting for this contamination should be addressed. According to the total PAHs level, all the samples can be divided into three grades of contamination: Heavy contamination -- PAHs concentration higher

Table 3. Program of excitation and emission wavelength pairs.

Compounds	Time（min）	λ_{ex}（nm）	λ_{ex}（nm）
Nap, Fle, Ace	0	280	324
Phe, Ant, Fla	7.2	254	402
Pyr, Chr, BaA	10	270	384
BbFL, BkFL, BaP, DBA, BPE	17	286	430

Table 4. Concentrations of individual PAH compound (μg/kg) in soils of Guiyang City.

Site	Nap	Acy	Ace	FLe	Phe	Ant	Fla	Pyr	BaA	Chr	BbFL	BkFL	BaP	DBA	BPE	Ipy	16PAH
1	13.7	11.2	6.9	2.8	58.5	2.8	158	16.0	16.3	95.0	126	42.2	5.8	77.4	16.5	41.9	692
2	12.6	21.9	103	3.4	5.8	4.1	177	22.5	68.6	138	10.6	57.7	76.5	69.0	116	38.4	926
3	4.5	24.6	7.6	1.6	56.3	ND	481	15.3	8.3	28.0	99.0	8.9	1.7	68.8	13.0	7.7	826
4	4.6	17.4	5.1	1.6	60.2	6.0	195	ND	36.2	81.6	92.6	4.4	8.1	40.1	51.6	21.7	626
5	ND	5.2	3.2	2.4	26.9	1.7	41.1	8.3	10.2	42.9	0.5	16.2	18.8	29.2	18.9	21.6	247
6	ND	5.3	6.0	ND	44.5	0.9	91.7	11.0	13.0	42.3	55.5	16.4	ND	21.0	42.9	0.1	351
7	ND	ND	11.8	ND	118	4.7	102	59.9	34.5	100	134	29.7	40.6	49.5	54.5	0.1	739
8	ND	ND	ND	ND	162	22.3	77.3	30.8	182	157	214	124	205	81.7	181	123	1560
9	ND	1.4	ND	1.2	7.9	ND	8.5	8.5	3.1	5.5	9.9	2.6	3.1	7.9	0.9	ND	61.0
10	3.5	12.0	0.9	13.0	33.6	1.1	86.4	45.6	16.5	30.3	37.1	12.8	13.9	12.2	20.2	ND	339
11	9.8	5.2	3.2	13.3	31.3	0.7	55.8	6.5	3.0	28.2	35.8	0.9	13.5	12.1	14.3	ND	234
12	6.1	4.7	5.6	6.1	2.1	ND	16.4	7.8	30.5	51.4	61.3	23.5	3.6	122	170	ND	511
13	ND	3.6	ND	8.5	43.9	0.6	43.9	6.3	8.7	4.2	52.6	1.7	17.7	3.0	49.5	20.2	264
Mean	4.2	8.7	11.8	4.2	50.1	3.5	118	18.4	33.1	61.9	71.5	26.2	31.4	45.7	57.6	21.2	567
Max.	13.7	24.6	103	13.3	162	22.3	481	59.9	182	157	214	124	205	122	181	123	1560
Min.	ND	1.4	ND	1.2	2.1	ND	8.5	ND	3.0	4.2	0.5	0.9	ND	3.0	0.9	ND	61.0

ND: Not detected

than 1000 μg/kg, including sample 8; Medium contamination--PAHs concentration between 500 and1000 μg/kg, including samples 1, 2, 3, 4, 7 and 12; Slight contamination – PAHs concentration below 500 μg/kg, including samples 5, 6, 9, 10, 11 and 13. Sample 8 shows the highest PAHs content (1560 μg/kg), indicating a heavy contamination. This site is in the city center and is adjacent (about 50m) to a former coal-burning chimney, which had been releasing coal-burning air particulates for more than 30 years before it was closed in 2002. It can be implied that coal burning is the dominant PAHs source accounting for the high PAHs content of this site. Medium contamination soils include 5 urban samples (1, 2, 3, 4 and 7) and one suburban sample (12). Sample1, 2, 3, 4 and 7 are in the urban area, and may be subject to the influence of diverse sources, such as traffic exhaust and coal-combustion. Although in suburban area, sample 12 shows a PAHs concentration of as high as 511 μg/kg, owing to that site 12 is close to a coal pyrolysis plant locating about 300 m away. Accordingly, sample 12 can similarly with sample 8, be regarded reflecting a result of predominant coal combustion. Slight contamination soils include four suburban samples (9, 10, 11 and 13) and two urban samples (5 and 6). Samples 9, 10 and 11 are not adjacent to any PAHs sources, implying that these sites may only be affected by gaseous diffusion from PAHs sources far away and consequently show a low level of PAHs. Some distance from site 13, there are some iron works and brick works, where coal is burned for calcination. Site 13 may be affected by coal burning in these works, but its PAHs concentration is still low because these works are about 2 km far away and have a limited impact. The two urban samples (5 and 6) show low PAHs concentrations of 247 μg/kg and 351 μg/kg, possibly due to their distance from PAHs sources and slight influence of contamination. The classification of this study is consistent with that proposed by Maliszewska-Kordybach (1996), which suggested that a soil PAHs concentration of 200 - 600 μg/kg is regarded as a weak contamination, a soil PAHs concentration of 600 - 1000 μg/kg is regarded as a medium contamination, and a soil PAHs concentration of above 1000 μg/kg is regarded as a heavy contamination.

Compared with other studies (Table 5), the soil PAHs concentration in Guiyang city is much higher than that in Bangkok, Western Europe, Switzerland, Kyala Lumpur, and New Orleans, whereas lower than that in Parnu, Kohtla-Jarve, Tallinn, Guangzhou, Beijing, and Tianjing. It can be concluded that the soil in Guiyang city has been contaminated by PAHs at a medium level.

Some PAH ratios were used to differentiate between petrogenic and pyrogenic sources of PAH. Such PAH ratios include Ant/(Ant&Phe), Fla/(Fla&pyr), BaA/BaA&Chr, Ipy/(Ipy+ BPE), Phe/Ant and Fla/Pyr, (Yunker et al. 2002; Wang et al. 2004). However, some researches (Hwang et al. 2003) pointed out that any transformation of PAHs in the environment might influence the diagnostic capabilities of PAH ratios and make the ratios only effective in some specific cases whereas not applicable in most other cases. In this study, the PAH ratios do not show promise for apportionment of PAHs souce, so it was attempted to use the correlation coefficient of the concentration of different PAH ring (2+3-ring, 4-ring, 5-ring, 6-ring) to evaluate the possible PAHs sources. The concentrations of

Table 5. Comparison of PAHs concentrations of soils in Guiyang and other cities.

Location	Concentration (μg/kg)	References
Bangkok, Thailand	12-380	Wilcke et al., 1999
Western Europe	11-200	Atanassova et al., 2004
Switzerland	50-619	Bucheli et al., 2004
Kyala Lumpur, Malaysia	220±110	Omar et al., 2002
New Orleans	731-2927	Mielke et al., 2001
Parnu	7665±4306	Trapido et al., 1999
Kohtla-Jarve	12390±9810	Trapido et al., 1999
Guangzhou, China	42-3077	Chen et al., 2004
Beijing, China	1347±950	Ma et al., 2004
Tianjing, China	1000-21015	Wang et al., 2004
Hangzhong, China	59.71-615.8	Chen et al., 2004
Suburb, Guiyang	61-511	This study
Urban area, Guiyang	247-1560	This study

different ring PAH species include 2-ring, 3-ring, 4-ring, 5-ring and 6-ring are shown in Figure 3.

In all the samples, PAHs are dominantly composed of 4-ring and 5-ring PAH species. It can be seen that sample 8, 12 and 13 show a feature of 4-ring lower than 5-ring, while the other ten samples show a feature of 4-ring higher than 5-ring. It can be inferred that samples 8, 12 and 13 are dominantly affected by one source, and the other ten samples are mostly affected by other source. It was reported that a large proportion of high molecular weight parent PAHs is a typical characteristic of a combustion origin, the enrichment of low molecular weight PAHs is common in fresh fuels (Femandes et al. 1997; Baumard et al. 1998). Taking into account that domestic coal-burning is very common in Guiyang city, any soil samples may be affected more or less by coal-burning. Additionally, the impact of traffic exhaust can also migrate through gaseous diffusion and may affect every sample site. Considering this, PAHs of samples 8, 12 and 13 may dominantly source from coal-combustion, and PAHs of other ten samples may dominantly originate from diffusion of traffic exhaust and coal-combustion. This opinion is consistent with the details of the three sample sites that are affected by coal-combustion sources. The other ten samples are not close to any obvious point source of PAHs and show a feature of 4-ring higher than 5-ring, thus they may reflect an impact of gaseous diffusion and deposition of mixed PAHs sources, such as traffic exhaust and coal-combustion. This opinion can be further supported by the following discussion of correlation coefficient (R^2). The correlation coefficient (R^2) between samples based on different ring PAH concentrations was calculated, and the result is shown in Table 6. According to the correlation

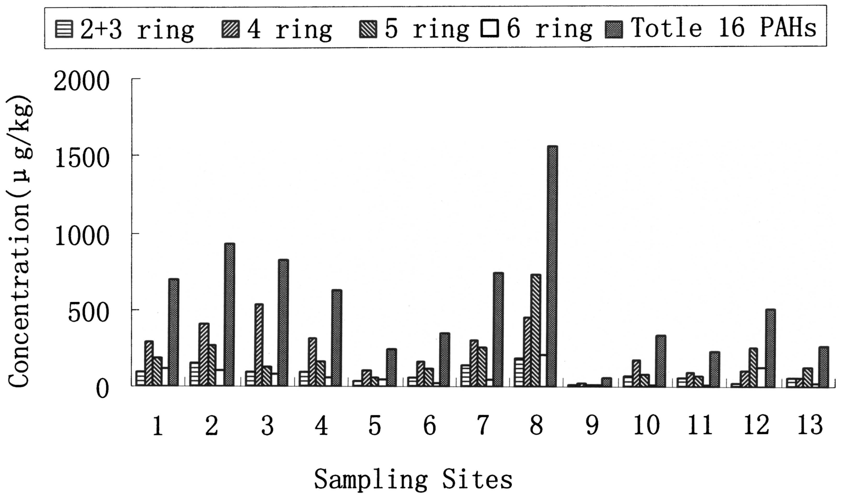

Figure 3. The composition pattern of PAHs by ring size.

coefficient, the samples can be classified as two groups: group Ⅰ – samples 8, 12 and 13 are obviously positively correlated, suggesting that, although these 3 samples show quite different PAHs concentrations, they may have a similar source. Group Ⅱ includes ten samples that also show a positive correlation, with most R^2 values>0.70. Different from group Ⅰ, these ten sampling sites might be co-affected by traffic exhaust and domestic coal burning source, meaning a result of area-source contamination. Group Ⅰ and group Ⅱ show a very poor correlation, with most R^2 values <0.3, indicating two different dominant sources for these two groups of samples. This conclusion is in accord with the discussion above.

Table 6. Correlation coefficient (R^2) matrix between samples based on 2+3-ring, 4-ring, 5-ring and 6-ring PAH concentrations.

	1	2	3	4	5	6	7	8	9	10	11	12
1												
2	0.94											
3	0.83	0.83										
4	0.93	0.98	0.93									
5	0.90	0.81	0.95	0.89								
6	0.85	0.96	0.68	0.90	0.64							
7	0.74	0.88	0.52	0.77	0.48	0.97						
8	0.34	0.34	0.05	0.22	0.09	0.48	0.59					
9	0.93	0.99	0.86	0.99	0.83	0.95	0.86	0.30				
10	0.82	0.95	0.87	0.96	0.76	0.90	0.80	0.19	0.96			
11	0.51	0.74	0.55	0.72	0.39	0.81	0.81	0.20	0.75	0.86		
12	0.11	0.05	0.01	0.01	0.01	0.10	0.16	0.78	0.04	0.01	0.01	
13	0.12	0.19	0.01	0.09	0.01	0.36	0.52	0.83	0.17	0.12	0.27	0.51

Acknowledgments. This research was funded by the Science Innovation Program of the Chinese Academy of Sciences (No. KZCX3-SW-140) and the National Science Foundation of China (No. 40273039). The authors are sincerely thankful to Engineer Ning An for his assistance in the HPLC analysis of PAHs.

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