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Concentration, Distribution and Sources of Polyaromatic Hydrocarbons in Soils from the Karst Tiankengs, South China

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Abstract Polycyclic aromatic hydrocarbons (PAHs) were investigated in the surface soils from Dashiwei and Datuo Karst tiankengs, Guangxi Province, South China. Concentrations of total PAHs ranged from 16.93 ng g^{-1} to 190 ng g^{-1} with a mean of 58.29 ng g^{-1}. In Dashiwei more PAHs were concentrated than in Datuo (mean 74.42 ng $g^{-1} > 42.15$ ng g^{-1}). Dashiwei and Datuo accounted for the majority of all PAHs concentrated in the lower location through increased rates (58% and 37%) from the upper to lower geographical levels, respectively. Dashiwei presented the stronger trapping ability for heavier molecular weights on the tiankeng floor with a concentration increase rate of 167% when compared to that of the lighter molecular weights (which had a concentration increase of rate 6%), which was in contrast to the Datuo with a concentration increase rate of 37% for lighter molecular weights and 31% for heavier molecular weights. In Dashiwei, it was found that the ratio of heavier PAH compound molecular weight resulted in its higher precipitation recording on the tiankeng floor. The differentia between two tiankengs, therefore, are related to their environmental characteristics and the PAHs physiochemical properties. The analytical result from the PAHs indicators suggest that a petrogenic source was dominant in the area studied. Therefore, the karst tiankeng has the potential to act as a geophysical well for PAHs deposition, especially for the heavier molecular weighted PAH.

Keywords PAHs · Karst tiankeng · Trap · South China

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous compounds found in the environment, and are mainly derived from biomass burning, incomplete fossil fuel combustion, petroleum leakage/evaporation, and the early diagenesis of organic matter. Owing to their hydrophobicity and lipophilicity, PAHs may accumulate in organisms and many PAHs are known to be carcinogenic and mutagenic (Aas et al. 2001). Recently, scientists have become increasingly concerned about the distribution and fate of persistent organic pollutants, such as PAHs, in the tropical and subtropical regions of Asia. Due to the high temperatures and heavy rain events that rapidly dissipate PAHs through the atmosphere, soil and aquatic systems from their points of discharge or usage (Yunker Mark et al. 2002).

In the Karst area, due to its special geomorphological characteristics, contamination in the atmosphere is hard to diffuse before being precipitated again. Plentiful runoff and groundwater subsequently scatters pollutants widely. A project supported by China Geological Survey has been developed in order to research the environmental pollutant impacts in the karst area, south-western China as the environmental fragility in karst areas is widely acknowledged. Karst tiankengs, featuring a huge size, well or pit shaped, are generally the youngest karst landforms commonly known as "large collapse dolines". Dashiwei tiankeng group, discovered recently in Guangxi Province, is a group of giant tiankengs ranking among 50 Karst tiankengs recorded in China. As a part of the project, this

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work was to provide original data of PAHs behaviour in the Karst tiankengs as a baseline for further research.

Materials and Methods

Study Area and Sampling

Guangxi Province, lying in the tropical/subtropical zone, spans the Tropic of Cancer which has a distinct monsoonal climate. Formerly considered as one of the areas least industrialized in Southern China, Guangxi has recently founded light and heavy industries, such as oil refineries, fertilizer plants and factories that produce paper, leather and pharmaceuticals. Agricultural production utilizes only 10%–15% of the land owing to lack of surface soil. The region is famous for its scenic karst landscape and extensive subterranean karst aquifer networks.

The Dashiwei tiankeng group is located in Leye country, 456 km from Nanning (capital of Guangxi Province), at longitude of 106°21′49″–106°40′30″ E and latitude 24°51′40″–24°56′06″ N. Among this group Dashiwei and Datuo are two of the largest and most typical tiankengs. Dashiwei is pear-shaped in form, 600 m long, 420 m wide, 1580 m around the perimeter, and 613 m at its maximum depth. Its shaped walls with vertical cliffs surround the advanced secondary forest which covers the valley floor. Datuo is about 290 m deep and 523 m in entrance diameter which has degraded scree slopes round approximately half its perimeters (Zhu et al. 2003).

Nine soil samples were collected with a hand shovel in October 2007 from Dashiwei (Fig. 1) and were marked as number 1–4 (top samples) and 5–9 (bottom samples). The 12 soil samples from Datuo (Fig. 2) were collected in two cross-sectional profiles named AA′ and BB′ and marked 1–12 and calibrated more finely by (Oramah et al. 2008). All soil samples were sealed in polyethylene bags and then properly cooled with ice during transportation to the laboratory where they were stored at −20°C until analyzed.

Analytical Procedures

The PAH analytical procedure and QA/QC follows that described by Mai et al. (2003). Briefly, about 10 g of the sample was spiked with surrogate consisting of naphthalene-d_{8}, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}, then extracted with methylene chloride. Activated copper was added for desulphurization. The extract was concentrated and fractionated using a silica–alumina (2:1) column. The fraction containing PAHs was eluted with 5 mL of hexane and 70 mL of methylene chloride/hexane (3:7). Hexamethylbenzene was added as internal standard and the mixture was reduced to 0.2 mL and subjected to GC-MSD (Agilent 6890N/5975MSD) analysis. The GC was equipped with a HP-5 capillary column (25 m × 0.25 mm id, film thickness 0.25 µm) with helium as carrier gas. The GC operating conditions were: held at 80°C for 5 min, ramped to 290°C at 4°C min^{-1} and held for 30 min. The sample was injected splitless with the injector temperature at 290°C. The MSD was operated in the electron impact (EI) mode at 70 eV and the selected-ion-monitoring (SIM) mode. Procedural blanks, standard-spiked blanks, standard-spiked matrix and parallel samples were analyzed for quality assurance and control. The

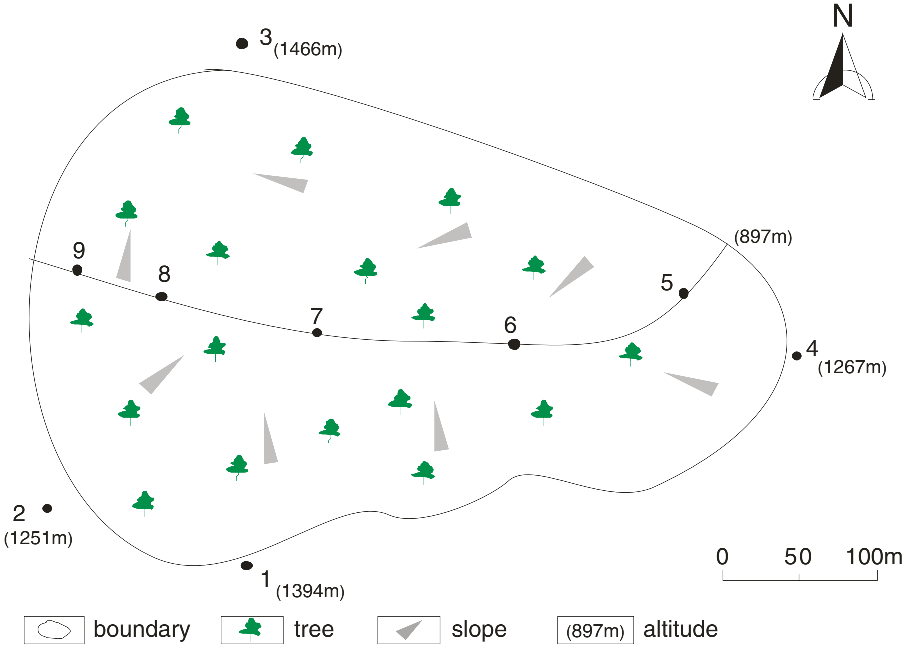
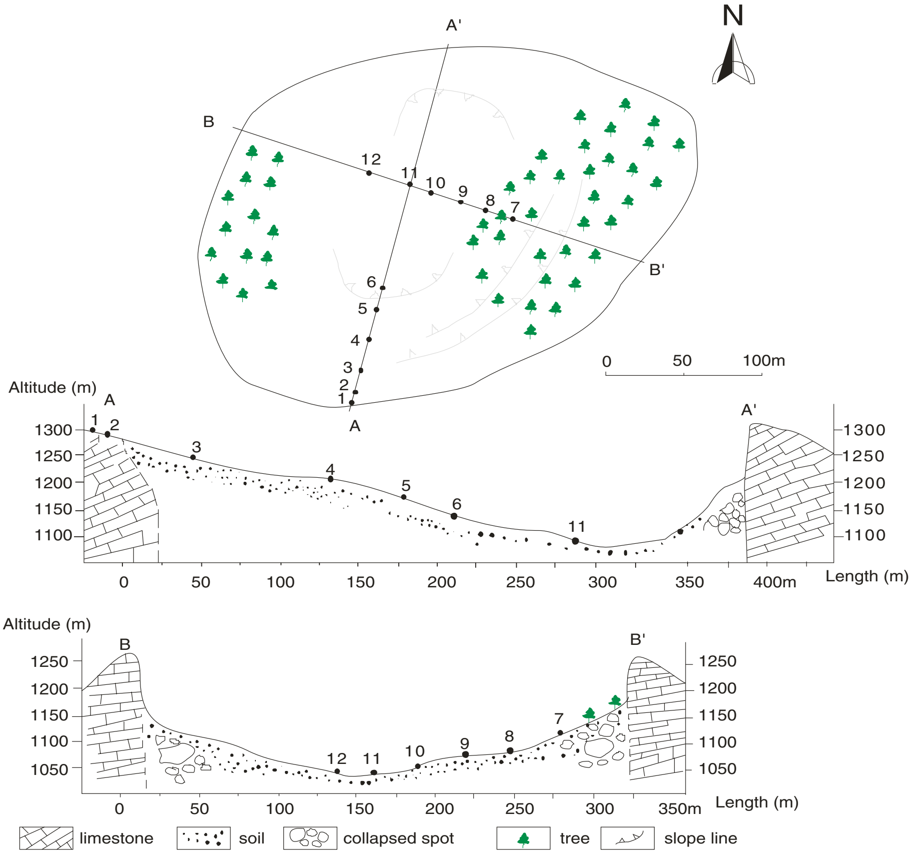


Fig. 1 Sampling sites in Dashiwei tiankeng

Fig. 2 Sampling sites in Datuo tiankeng



recovery was 37.4 ± 11.3% for naphthalene-d$_8$, 69.2 ± 8.8% for acenaphthene-d$_{10}$, 101.4 ± 11.3% for phenanthrene-d$_{10}$, 54.2 ± 12.5% for chrysene-d$_{12}$ and 48.5 ± 10.5% for perylene-d$_{12}$. Procedural blank samples contained no detectable amount of the PAHs targeted. The relative percent analysis difference of paired duplicate samples was <15% (n = 5). Method detection limits for individual PAHs ranged from 0.2 to 2 ng g^{-1}. The 16 USEPA priority PAHs measured were: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluo), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[*1,2,3-cd*]pyrene (Ind), dibenz[*a,h*]anthracene (Dib) and benzo[*ghi*]perylene (BghiP).

Results and Discussion

Concentrations and Compositions of PAHs in Soils from Tiankengs

A summary of PAH concentrations in the soils are shown in Table 1.

Table 1 PAH concentrations in soils from Dashiwei and Datuo tiankengs (ng g^{-1})

PAHs	Dashiwei			Datuo			Netherlands standards
	Mean	Min	Max	Mean	Min	Max	
Nap	10.70	5.13	16.77	7.51	0.99	15.47	15
Acy	0.93	0.44	1.72	0.48	0.10	0.87	–
Ace	0.69	0.41	1.01	0.41	0.10	0.76	–
Flu	4.46	2.29	5.41	2.98	1.24	5.19	–
Phe	16.11	6.66	25.10	9.69	4.03	15.29	50
Ant	4.00	0.36	30.70	1.93	0.27	11.71	50
Fluo	5.85	2.21	10.78	3.71	1.24	6.16	15
Pyr	2.90	1.05	5.70	1.99	1.09	3.11	–
BaA	1.14	0.21	2.99	0.71	0.25	1.36	25
Chr	5.55	0.85	16.60	3.11	0.87	5.76	20
BbF	6.68	0.63	25.40	3.54	0.69	7.07	–
BkF	1.89	0.30	5.70	1.62	0.31	3.38	25
BaP	2.00	0.23	7.81	0.84	0.14	2.14	25
Ind	4.94	0.52	22.60	1.94	ND	4.59	25
Dib	0.71	0.20	0.94	0.35	ND	0.84	–
BghiP	6.09	0.36	41.33	1.31	ND	3.47	20
$\sum$PAHs	74.42	23.40	190.00	42.15	16.93	68.07	50

ND not detected

All 16 United States Environmental Protection Agency (USEPA) priority PAHs were detected in the soil samples, with the exception of Ind, Dib and BghiP, the three heaviest molecular weight compounds, from Datuo (site 3, 4, 10). The total PAH concentrations ranged from 16.90 ng g^{-1} to 190 ng g^{-1} with a mean of 58.29 ng g^{-1}. The lower section of the tiankengs accumulated PAHs indicators from 16.90 to 190 ng g^{-1} (mean 68.21 ng g^{-1}), which spanned one order of magnitude, while in the upper ranged from 23.40 to 88.94 ng g^{-1} (mean 46.33 ng g^{-1}), the increased rate of PAHs concentrations was quite considerable with a percentage of 47. It showed the tiankeng's potential to hold or trap PAHs on the bottom where conditions were relatively humid and enclosed. The highest and lowest PAHs content values were obtained in location 8 of Dashiwei and location 8 of Datuo, respectively. Phe was the most abundant PAH, followed by Nap, BbF, Fluo, Chr, Flu, BghiP, Ind and Ant. Seven other types of PAH compound contributed less than 14% to the total PAHs concentration.

In this study, the PAHs were divided into two groups, light molecular weight PAHs (LMW, 2–3 benzenoid rings) and heavy molecular weight PAHs (HMW, 4–6 benzenoid rings). LMW contents varied from 12.06 to 77.25 ng g^{-1} (mean 34.73 ng g^{-1}), which occurred more frequently than those of HMW varying from 4.35 to 48.15 ng g^{-1} with a mean of 23.59 ng g^{-1}.

Compared with other areas, either being close or similar to the studied area in geomorphology and geography, the total PAHs concentrations in the present study were much lower than those recorded in the vegetable soils of Guangzhou (42-3077 ng g^{-1}), a prosperous city neighboring the studied zone (Chen et al. 2005), and those in remote or pristine Europe as seen in Moscow soils, 59–1350 ng g^{-1} (Wilcke et al. 2005), and comparable to that in the North American Prairie 63-321 ng g^{-1} (Wilcke and Amelung 2000). After consideration of the Karst physiognomy, PAHs concentrations here were comparable to those from the country soils (59.6–506 ng g^{-1}) and lower than those documented on the urban soils with a range of 220–1437 ng g^{-1} in Guiyang city, another famous karst region in China (Hu et al. 2006).

In contrast to the National Environmental Quality standards for Soils of Netherlands (Trapido 1999), Nap concentrations in five studied soil samples (site 1, 3, 4 from Dashiwei and 7, 9 from Datuo) were slightly higher than the criterion (15 ng g^{-1}), BghiP content of site 7 from Dashiwei (26.50 ng g^{-1}) exceeded the criterion (20 ng g^{-1}). For total PAHs level, every sample from Dashiwei overran the criterion (50 ng g^{-1}) except for site 2 (23.4 ng g^{-1}), four samples from Datuo (site 7, 8, 10, 12) were appreciably higher (range from 50.10 to 68.10 ng g^{-1}) than the criterion.

The Comparation of PAHs Concentration and Distribution Between Two Tiankengs

PAHs distribution in the two tiankengs are illustrated as Fig. 3. Dashiwei concentrated more PAHs (23.4–190 ng g^{-1}, mean 74.42 ng g^{-1}) than Datuo (16.90–68.07 ng g^{-1}, mean 42.15 ng g^{-1}). In Dashiwei, PAHs concentrations of the bottom (43.40–190 ng g^{-1}, mean 87.76 ng g^{-1}) were higher than those of the top (23.40–88.94 ng g^{-1}, mean 57.74 ng g^{-1}). Analogously, in Datuo, PAHs levels in the lower soils ranged from 16.90 to 68.10 ng g^{-1} (mean 48.65 ng g^{-1}), were more than those in the upper (29.10–43.04 ng g^{-1}, mean 34.92 ng g^{-1}).

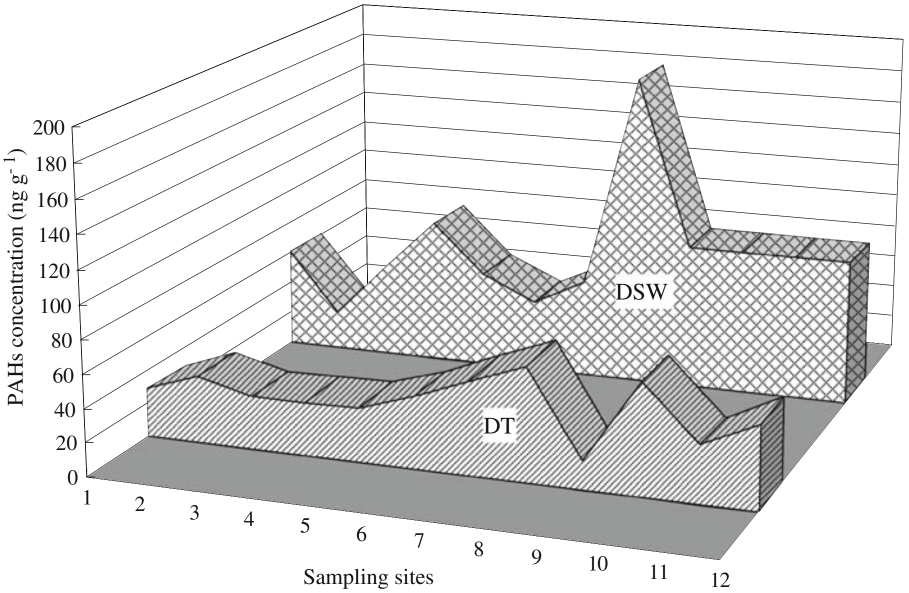


Fig. 3 PAH concentrations in the soils from Dashiwei (DSW) and Datuo (DT) tiankengs (ng g^{-1})

However, the PAHs concentration difference between the top and the bottom from Dashiwei doubled that from Datuo and the increased rates of concentration were 58% in Dashiwei to 37% in Datuo. The results demonstrated that PAHs tended to accumulate on the bottom for either of two tiankengs, but different tiankengs exhibited different accumulative capacity through their different geomorphological characteristcs.

Similar phenomena are represented in the LMW and HMW. In Datuo, the LMW and HMW content in the lower soils (mean 30.85 ng g^{-1} and 17.09 ng g^{-1}) were all higher than those in the upper soil (mean 22.57 ng g^{-1} and 13.07 ng g^{-1}) with an approximative content increase rate of 37% and 0.31% respectively. The proportion of LMW for total PAHs content in the AA′ profile (63%) was quite close to that of BB′ (64%) (Fig. 4). Contrasting Datuo with Dashiwei, the LMW content in the bottom (mean 43.91 ng g^{-1}) was slightly more than those in the top (mean 41.27 ng g^{-1}) with a content increase rate of 6%. However, the HMW in the bottom (43.96 ng g^{-1}) were much greater than those in the top (mean 16.49 ng g^{-1}) with a content increased rate of 167%. The proportion of HMW for total PAHs recorded in the bottom (50%) was significantly greater to that of the upper (28%).

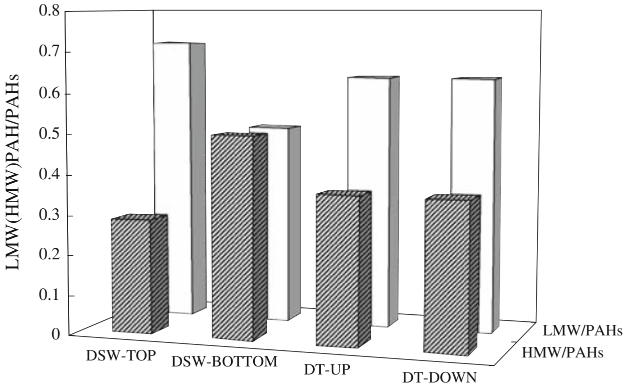


Fig. 4 The concentration ratios between LMW/PAHs and HMW/PAHs Dashiwei (DSW) and Datuo (DT) tiankengs

It was a particularly phenomenon that each PAH compound detected in this study had an increased value on the tiangkeng floor with the exception of Nap, Fluo and Dib (Fig. 5). The concentration increase rate on the 13 PAH compounds (range from 1% to 450%) correlated to their respective molecular weight (range from 152 to 276), i.e., the heavier molecular weight the PAH compound has, the more reliable its bottom presence through precipitation. By this token, Dashiwei demonstrated the stronger trapping ability for HMW on the bottom than LMW. Tiankeng formations, therefore, become environmental Traps for PAHs, especially for HMW in the study area.

Sources of PAHs in the Surface Soils from Dashiwei and Datuo Tiankengs

Some useful indicators, such as the Phe/Ant (PH/AN), BaA/Chr and the ratios of LMW PAHs to the HMW PAHs have been applied to provide information on source recognition (Yunker Mark et al. 2002; Tam et al. 2001; Baumard et al. 1998). In general, PAHs from petrogenic sources contain mostly lighter molecular weight (LMW) and are generated from the geochemical alteration of organic matter from petroleum spills, coal-fired plants and municipal sewage treatment facilities; while PAHs from fossil fuel combustion generally yield an abundance of PAHs with 4–6 benzenoid rings normally termed pyrogenic/pyrolitic sources (Zeng and Vista 1997).

Fig. 5 PAH concentration in the top and bottom soils from Dashiwei (DSW) tiankeng (ng g^{-1})

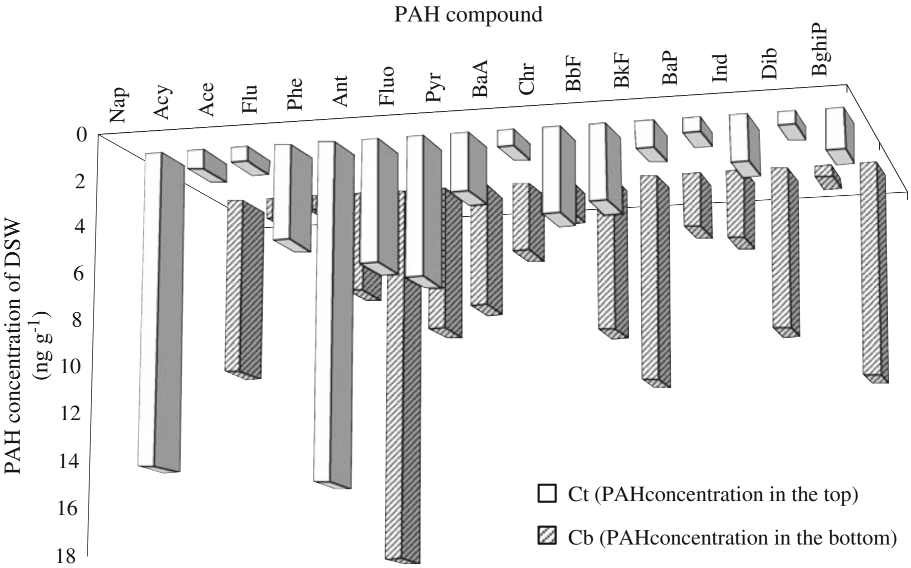


Table 2 The concentration ratios of PAH indicators in the soil samples

Sampling site in Dashiwei	LMW/HMW	BaA/Chr	Phe/Ant	Sampling site in Datuo	LMW/HMW	BaA/Chr	Phe/Ant
1	2.03	0.20	21.56	1	4.58	0.29	20.73
2	4.39	0.24	18.39	2	1.64	0.22	19.24
3	3.56	0.21	22.68	3	1.31	0.23	15.82
4	2.09	0.18	17.88	4	1.83	0.27	19.21
5	1.91	0.22	22.09	5	1.61	0.2	26.23
6	0.82	0.27	32.81	6	1.38	0.24	24.54
7	0.68	0.23	27.01	7	1.51	0.19	35.32
8	1.69	0.18	0.82	8	1.56	0.19	25.41
9	1.68	0.23	24.66	9	2.47	0.27	15.20
				10	2.11	0.28	25.64
				11	1.35	0.23	0.83
				12	1.93	0.23	0.83
Petrogenic	>1	≤0.4	>10	Petrogenic	>1	≤0.4	>10
Pyrogenic	<1	>0.9	<10	Pyrogenic	<1	>0.9	<10

As seen from Table 2, the ratios of the PAHs indicators applied in this study suggest a higher level of LMW PAH, Phe and Chr, which suggested a dominative petrogenic source in this area. As few anthropogenic events are related to petroleum around the studied area, it may derive from the slow maturation of organic matter under geochemical gradient conditions. In addition, atmospheric transportation and deposition might reasonably contribute to the PAHs presence in the Tiankengs.

Conclusion

Analysis of surface soils from the Karst tiankengs, Southern China, have provided useful information for the evaluation of PAH pollution in the Karst area. The 16 USEPA priority PAHs were measured in surface soils from the Dashiwei and Datuo tiankengs, and the similarities and differences on concentration and distribution between the two Karst tiankengs were investigated. Major conclusions are as follows:

1. The total PAH concentrations ranged from 16.90 ng g^{-1} to 190 ng g^{-1} with a mean of 58.29 ng g^{-1}, which were lower than those observed in the urbanized and industrialized locations around the Guangxi Province and those from areas with reasonably small impacts from anthropogenic events.
2. PAH concentrations in the lower section were greater than those in the upper with a considerable increase rate of 47%, indicating that tiankengs tended to accumulate PAHs on the bottom or lower sections.
3. Dashiwei trapped more PAHs than Datuo. Dashiwei and Datuo were accounted for by the majority of PAH concentration in the lower location through increased rates of 58% and 37% from the upper level, respectively. Dashiwei presented the stronger trapping ability for HMW on the bottom with a content increased rate of 167% than LMW (content increased rate 6%). An indication was noted in Dashiwei, that the heavier molecular weight PAH compounds have more precipitation to the bottom. Tiankeng, therefore, acts as a Trap for PAHs, especially for heavy molecular weight PAHs, in the study area.
4. PAH sources can be identified by some indicators. The results implied that a petrogenic source was dominative in this area, but may because be related to the early diagenesis of organic matter and atmosphere contribution.

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