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ORIGINAL PAPER

Contamination, spatial distribution, and source contribution of persistent organic pollutants in the soil of Guiyang city, China: a case study

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Abstract The contamination of persistent organic pollutants (POPs), including dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH), and polycyclic aromatic hydrocarbon (PAH), is the most studied environmental issue. In 2020, a total of sixty soil samples collected from ten locations in Guiyang were analyzed to assess the presence of four DDTs and HCHs and sixteen PAHs. The concentrations of total DDTs, total HCHs and Σ_{16}-PAHs in the soil were between 0.26 and 12.76, 0.23 and 51.80 μg/kg, and 10.02 and 1708.86 μg/kg, respectively. The mean and median concentrations of total DDTs, total HCHs and Σ_{16}PAHs in the soil were 1.04 and 0.26 μg/kg, 4.32 and 0.23 μg/kg, 139.14 and 98.98 μg/kg, respectively. *p*,*p*′-DDT, *p*,*p*′-DDD and γ-HCH the dominant organochloride pollutants in the soil, while 4-ring PAHs were the dominant PAHs, occupying 41.1–53.6% of the total PAHs in the soil. The highest levels of PAHs in the soil were observed in areas of Guiyang with relatively larger population densities and more developed heave industries. Various diagnostic tools were used to identify the potential sources of the POPs in the soil. The data indicated that DDTs and HCHs were from past and recent common inputs and that mixtures of several combustion activities (biomass, coal and petroleum combustion, diesel, gasoline, and vehicular emissions) were the major sources of PAHs in the Guiyang soil. The results provide information for the assessment of the extent of POP pollution in the Guiyang soil and can help authorities establish environmental protection regulations and soil remediation techniques.

Keywords Persistent organic pollutant · Soil · Distribution · Source · Guiyang

Introduction

In recent decades, persistent organic pollutants (POPs) have been the main environmental contaminants that ubiquitously remain in soil and water ecosystems, possibly accumulating in crops and food chains and threatening human health and the environment (Kim et al., 2021). Most POPs are synthetic organochlorines, such as dichlorodiphenyltrichloroethane (DDT)

Guanglong Zhang and Tingting Lan have contributed equally in this paper.

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and hexachlorocyclohexane (HCH), and polycyclic aromatic hydrocarbons (PAHs) derived from nature and fuel combustion (Liu, 2021).

The use of DDT and HCH has contributed substantially to the increase and stable supply of food products after the 1940s; however, due to their long half-lives, both organochlorine pesticides were banned in manufacture and application in mid-1970 in several developed countries (Barber et al., 2005; Takagi, 2020; Weber et al., 2010). Despite the regulatory efforts of authorities and society, organochlorine pesticides continue to threaten the environment and human health, even in the twenty-first century (Kim et al., 2019; Matsumoto et al., 2009). Total DDT is the summation of *o*,*p*'-DDT, *p*,*p*′-DDE, *p*,*p*′-DDD, and *p*,′-DDT; total HCH is mainly the combination of α-HCH, *β*-HCH, *γ*-HCH (lindane, insecticidal property), and δ-HCH (Willett et al., 1998; Zhang et al., 2002). DDT and HCH reached soil and soil–water mixtures due to their large-scale application to plants in crop-growing areas due to rainfall and surface run-off (Bhatt et al., 2009). Thus, there is a necessity for monitoring DDT and HCH pollution in soil to evaluate the potential risk of crop contamination by these organochlorine pesticides.

Another kind of POP is PAH, an important group of organic contaminants commonly found in industrially polluted areas (Warshawsky, 1999). PAHs include naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Flo), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), 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 (IcdP), dibenz[a,h]anthracene (DahA), and benzo[g,h,i]perylene (BghiP) (Wang et al., 2021a, b). Due to their natural and anthropogenic sources, they have been detected in all regions of the world, such as in soil and aquatic environments, have accumulated from the atmosphere to crops and foods and have further impacted human health (Loick et al., 2009). PAHs are known to show acutely toxic effects or possess mutagenic, teratogenic, or carcinogenic properties; as a result, they have been classified as primary pollutants by the U.S. Environmental Protection Agency (Kanaly & Harayama, 2000; Kudłak & Namieśnik, 2008). Because of rapid improvements in the economy and energy consumption, PAH emissions in China have been continuously increasing and reached more than 0.1 megatons in 2007, accounting for approximately 20% of the global total emissions (Bao et al., 2018; Shen et al., 2013). A few studies have reported substantial variation in soil pollution and the distribution and source of PAH contamination in different regions owing to different locations, climates and agricultural production (Ghanavati et al., 2019; Han et al., 2015; Wang et al., 2017). However, information on the status and risk of POPs in the soil in Guiyang City (capital of Guizhou Province, China) is still lacking.

The present study aimed to (1) explore the concentration of POPs (several isomers of DDT and HCH and 16 kinds of U.S. EPA priority PAHs (Saber et al., 2021)) in soil samples collected from Guiyang; (2) illustrate the spatial distribution of the POPs in different locations of Guiyang; and (3) speculate as to the possible sources of the POPs in soil samples from Guiyang.

Materials and methods

Soil sampling and pretreatment

Between April and June 2020, a total of 60 soil samples were collected from the 0–15 cm surface soil layer in ten different areas of Guiyang city, including site 1 (Nanming District), site 2 (Yunyan District), site 3 (Guanshanhu District), site 4 (Huaxi District), site 5 (Wudang District), site 6 (Baiyun District), site 7 (Qingzhen City), site 8 (Kaiyang County), site 9 (Xifeng County) and site 10 (Xiuwen County). The sampling plots and location information are shown in Fig. 1 and Table S1 (Supporting information). Triplicate samples were randomly collected at each sampling site and homogenized into one test sample. All collected soil samples were kept in polyethylene boxes with lids and placed in the dark. In the laboratory, the soil samples were air-dried, sieved through a 1-mm mesh and stored at − 80 °C before analysis.

Extraction and instrumentation

Organochlorine pesticides

According to the approach in the Environmental Protection Standard of China (HJ 921–2017, Ministry

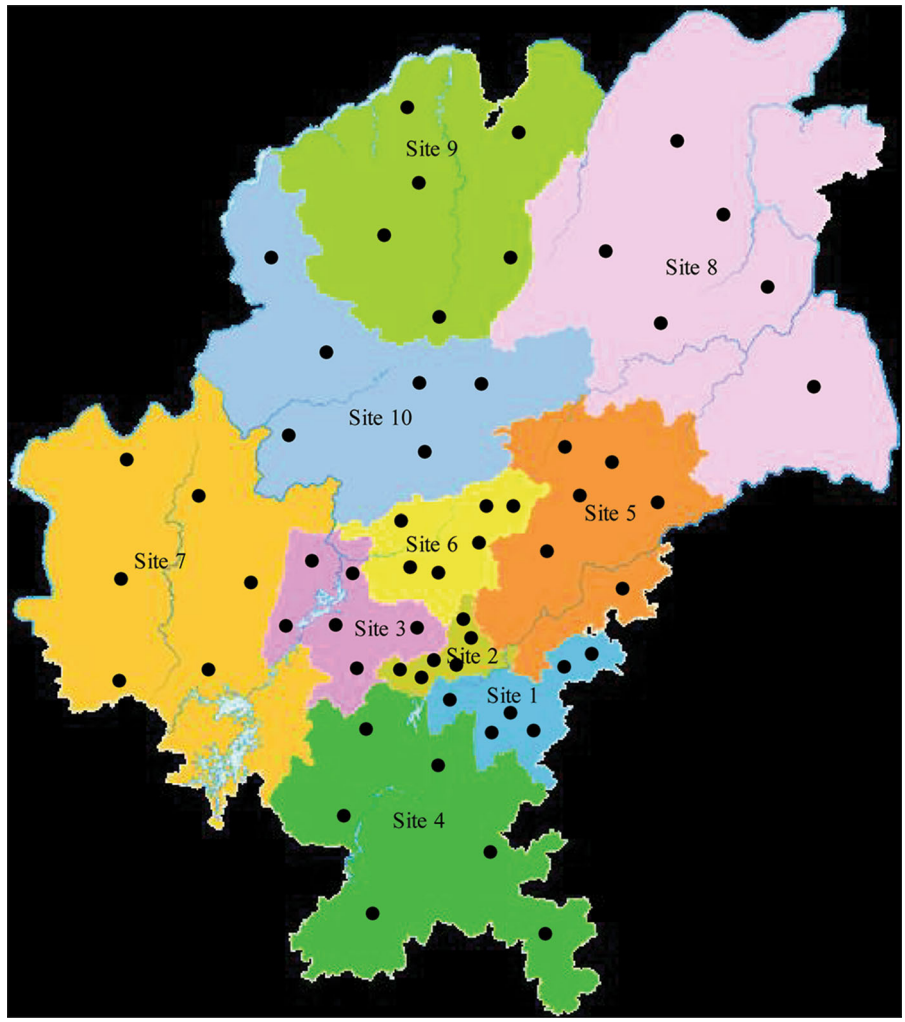

Fig. 1 The geographical locality of sampling sites of soil in Guiyang city, China

of Ecology and Environment, 2018), 10 ± 0.01 g of soil samples were Soxhlet extracted for 16 h with 100 mL of acetone and *n*-hexane mixture (1:1, *v*/*v*). The extracts were concentrated to approximately 1 mL at 45 °C by a rotary evaporator, passed through a magnesium silicate solid-phase extraction (SPE) column, and eluted with 10 mL of acetone and *n*-hexane mixture (1:9, *v*/*v*). The final eluent was evaporated and dissolved in 1 mL of acetone and *n*-hexane mixture (1:9, *v*/*v*). Analysis of DDT and HCH was performed on a Varian 450 gas chromatograph (GC, Varian Medical Systems, Inc., CA, USA) equipped with an electron capture and Agilent DB-5 MS column (30 m × 0.32 mm, 0.25 μm film thickness; Agilent Technologies, CA, USA). The carrier gas and tail gas were both nitrogen (99.999% purity) at flow rates of 2 mL/min and 20 mL/min, respectively. Injector and detector temperatures were set at 220 °C and 280 °C, respectively. The oven temperature was programmed from 100 to 220 °C at 15 °C/min, maintained for 2 min, raised to 260 °C at 5 °C/min, and held for 20 min. One microliter of sample solution was injected in split mode (split ratio, 1:10; flow rate, 60 mL/min).

Polycyclic aromatic hydrocarbons (PAHs)

The extraction and detection methods for PAHs in the soil samples followed the Chinese environmental protection guideline (HJ 805–2016, Ministry of

Ecology and Environment, 2016). Soil samples (20 ± 0.01 g) were Soxhlet extracted for 16 h with 100 mL of acetone and *n*-hexane mixture (1:1, *v*/*v*). The extracts were evaporated to 2 mL and purified by a magnesium silicate SPE column. The eluent was a mixture of dichloromethane and *n*-hexane (1:9, *v*/*v*). After concentration, the residue was dissolved with the internal standard solution. The 16 PAH compounds were detected by a Bruker 450 GC tandem with a 320 MS (Bruker Group Corporation, Wisconsin, USA). An Agilent DB-5 MS column and electron ionization (EI) source were applied. The carrier gas was helium (99.999% purity) at a flow rate of 1 mL/min, and the injector temperature was 280 °C. Oven temperature was programmed from 80 (kept 2 min) to 180 °C at 20 °C/min, held for 5 min, then raised to 290 °C at 10 °C/min, and kept 5 min. Sample solution (1 μL) was injected in the splitless mode. The temperatures of the ion source, interface and quadrupole were 230 °C, 280 °C and 150 °C, respectively. The ionization energy was 70 eV, the mass scanning range was 45–450 amu, the solvent delay time was 5 min, and the scanning mode was full scan mode.

Quality control and data analysis

The external standard method was used to quantify the concentrations of two organochloride pesticides in the soil. The limits of quantification (LOQs) and detection (LODs) for different components of DDT and HCH were determined as the lowest fortified concentrations and calculated as the signal-to-noise (*S*/*N*) of 3, which were in the respective ranges of 0.05–0.09 μg/kg and 0.015–0.027 μg/kg, respectively. The recoveries of individual DDTs and HCHs in the soil were 84.6% (*p*,*p*′-DDE) and 107.2% (*β*-HCH). The relative standard deviations (RSDs) were less than 15%. For the quantification of PAHs in the soil, an internal standard approach was applied. The internal standards included d_8-Nap, d_{10}-Phe, d_{10}-Ace, d_{12}-Chr and d_{12}-perlyene. The LODs and LOQs of sixteen PAHs in the soil were in the ranges of 0.03–0.12 μg/kg and 0.14–0.40 μg/kg, respectively, and the recoveries of individual PAHs ranged from 79.5 (BaP) to 110.6% (Fla) with RSDs < 13%.

The identification of pollution modes and the possible origins of the POPs in the soil samples collected from different locations in Guiyang was conducted by using different ratios of individual POP compounds. Moreover, principal component analysis, Pearson's moment correlation analysis and other statistical analyses were performed by using Microsoft Excel 2010 and IBM SPSS ver. 25.0.

Results

Levels of POPs in the soil samples collected from different locations in Guiyang

For organochloride pollutants (DDTs and HCHs), the concentration of each single component and total amount in the soil samples collected in Guiyang city, China, were determined and are listed in Table S2 (Supporting information). On the one hand, the concentrations in all tested soil samples were 0.09–1.70 μg/kg for *o*,*p*'-DDT, 0.05–3.09 μg/kg for *p*,*p*′-DDE, 0.06–4.21 μg/kg for *p*,*p*′-DDD, and 0.06–3.76 μg/kg for *p*,*p*′-DDT, and the concentrations of total DDTs were 0.26–12.76 μg/kg in the soil samples. On the other hand, the amounts of *α*-HCH, *β*-HCH, *γ*-HCH, *δ*-HCH, and total HCH were 0.06–0.37 μg/kg, 0.05–1.75 μg/kg, 0.06–42.30 μg/kg, 0.06–7.38 μg/kg, and 0.23–51.80 μg/kg, respectively. Compared with the negligible environmental risk from organochloride pollutants, the threat of PAHs to the soil ecosystem of Guiyang should be thoroughly evaluated. The concentrations of 16 PAH compounds in the soil samples were determined separately. Moreover, different combinations of PAHs, including the sum of low molecular weight 2–3 ring (LMW) PAHs, sum of high molecular weight 4–6 ring (HMW) PAHs, sum of seven carcinogenic PAHs (Σ_7PAHs) and sum of sixteen PAHs (Σ_{16}-PAHs), were calculated. All data are shown in Table S3 (Supporting information). The single concentrations of PAHs ranged from 0.14 to 383.94 μg/kg, which indicated that a potential risk may exist in the environment. In accordance with the contamination classification for PAHs (Maliszewska-Kordybach, 1996), twelve soil samples, approximately 20% of the Guiyang soil samples, were contaminated with PAHs, where the concentrations of Σ_{16}PAHs were larger than 200 μg/kg (221.53–1708.86 μg/kg). The remaining forty-eight soil samples were not contaminated with PAHs, whose concentrations were between 10.02 and 197.80 μg/kg.

Spatial distribution of POPs in Guiyang

In Table 1, the amounts of POPs in ten different locations in Guiyang City are illustrated, and the concentrations of DDTs, HCHs and PAHs were different among several areas. The average levels of total DDTs and total HCHs increased in the following ranked sequence: site 6 < site 9 < site 4 < site 7 = site 8 < site 2 < site 10 < site 5 < site 1 < site 3 and site 7 < site 6 < site 4 < site 2 < site 8 < site 9 < site 5 < site 3 < site 10 < site 1. The results of the spatial distribution of organochloride pollutants in the soil from Guiyang showed that the concentrations of DDTs and HCHs in northern and southeastern locations were higher than those in other locations. The levels of PAHs in the soil were also different from those at the ten sampling locations in Guiyang (Table 2). The decreasing order of average concentrations of Σ_{16}PAHs was ranked as: site 7 > site 5 > site 6 > site 4 > site 10 > site 1 > site 8 > site 2 > site 3 > site 9. The average concentrations of Σ_7PAHs also followed the above decreasing order.

Composition profile of POPs in the soil collected from Guiyang

The proportions of different DDTs in the soil among ten locations in Guiyang were not similar (Fig. 2a). For example, the percentage of *o*,*p*'-DDT from site 3 (6.6%) was lower than that from the other locations, including site 1 (19.8%), site 2 (11.0%), site 4 (18.1%), site 5 (25.6%), site 6 (27.8%), site 7 (14.4%), site 8 (14.4%), site 9 (21.3%) and site 10 (8.3%). For HCHs, the composition distribution in the soil samples collected from different locations in Guiyang is illustrated in Fig. 2b. The percentage of γ-HCH (lindane) from site 10 (6.9%) was apparently lower than that from the other nine areas (64.7–97.1%). The composition profile of PAHs in the soil collected from Guiyang was comparable among different locations (Fig. 2c). The 4-ring PAHs occupied the highest proportion (41.1–53.6%) of the total PAHs in all Guiyang soil samples. Moreover, the high molecular weight PAHs (HMW PAHs, 4–6 rings) accounted for the majority (74.4–89.2%) of the total PAHs in the soil from the ten locations. For the individual PAH pollutants, the majority of compounds included Chr (20.3%), Fla (18.1%), BbF (16.0%), Phe (12.2%), and Pyr (8.2%), similar to the distribution data from Xi'an, China (Bao et al., 2018).

Potential source of POPs in the soil collected from Guiyang

Comparatively higher concentrations of *p*,*p*′-DDT than *p*,*p*′-DDE (Table 1) and higher average ratios (1.02–17.90, Table S4, Supporting information) in the soil samples collected from ten locations in Guiyang indicated that DDT contamination might have occurred in recent years. Lindane formulation is mainly used in ecosystems when the ratio of α-HCH/γ-HCH is less than/equal to 1, and a higher ratio (> 1) indicates that the input formulation is technically HCH (Kumar et al., 2021; Malaiyandi & Shah, 1980). In Table S4 (Supporting information), the average isomeric ratios of α-HCH/γ-HCH in different soil samples (0.04–0.67) indicated that the lindane formulation input was the main potential source of HCH pollution in Guiyang. For PAH, the 4-ring PAHs dominated the composition of sixteen PAH compounds, followed by 5-ring and 3-ring PAHs in the soil collected from ten locations in Guiyang (Fig. 2c), which showed mixed pyrogenic sources. HMW PAHs were likely to exist near the emission sources and were indicators of pyrogenic activities at high temperature, such as vehicular emission, coal combustion (coal comb), and biomass combustion, while LMW PAHs were produced by wood combustion (wood comb), petroleum combustion (petroleum comb), gasoline and so on (Khalili et al., 1995; Marr et al., 1999). Eight different diagnostic ratios of PAHs, including Fla/(Fla + Pyr), Flo/(Flo + Pyr), IcdP/(IcdP + BghiP), Ant/(Ant + Phe), BaP/(BaP + Chr), BaA/(BaA + Chr), BaP/BghiP and BbF/BkF, were calculated and conducted to further identify the potential sources of PAHs in Guiyang City (Fig. 3).

Discussion

The risk-screening values of DDT (total DDT) and HCH (total HCH) for soil contamination of agricultural land are both 100 μg/kg, which is the soil environmental quality standard (Ministry of Ecology and Environment and State Administration for Market Regulation, 2018). In our study, the average measured concentrations (DDT: 1.04 μg/kg, and HCH: 4.32 μg/

Table 1 Effect of location on the concentrations of DDTs and HCHs in Guiyang soil

Analyte	Site 1		Site 2		Site 3		Site 4		Site 5		Site 6		Site 7		Site 8		Site 9		Site 10	
	Concentration (μg/kg)																			
	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean
o,*p*'-DDT	1.65	0.35	0.09	0.09	0.64	0.18	0.09	0.09	1.70	0.36	0.19	0.11	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
p,*p*'-DDE	0.05	0.05	0.05	0.05	2.15	0.44	0.56	0.14	3.09	0.56	0.05	0.05	0.05	0.05	0.13	0.06	0.05	0.05	0.10	0.06
p,*p*'-DDD	4.21	0.75	0.60	0.15	2.30	0.43	0.98	0.21	0.69	0.17	0.70	0.17	1.35	0.33	0.06	0.06	0.06	0.06	0.14	0.08
p,*p*'-DDT	1.37	0.62	1.47	0.53	3.76	1.70	0.06	0.06	0.73	0.31	0.06	0.06	0.60	0.15	1.48	0.41	0.45	0.22	2.14	0.87
Total DDT	7.28	1.77	2.21	0.82	8.85	2.75	1.69	0.50	6.21	1.40	1.00	0.39	2.09	0.62	1.76	0.62	0.65	0.42	2.47	1.10
α-HCH	0.37	0.11	0.36	0.11	0.32	0.10	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
β-HCH	0.05	0.05	1.75	0.33	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.75	0.17
γ-HCH	42.30	7.91	3.13	1.96	15.71	5.55	3.96	1.65	24.76	5.71	2.29	1.35	3.59	0.97	3.92	1.96	10.80	4.05	31.82	7.25
δ-HCH	0.44	0.15	1.43	0.29	7.38	1.38	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	5.44	0.96	0.06	0.06	0.53	0.14
Total HCH	43.16	8.22	6.67	2.69	23.46	7.08	4.13	1.82	24.93	5.88	2.46	1.52	3.76	1.14	9.47	3.03	10.97	4.22	33.16	7.62

Table 2 Effect of location on the concentrations of PAHs in Guiyang soil

Analyte	Site 1		Site 2		Site 3		Site 4		Site 5		Site 6		Site 7		Site 8		Site 9		Site 10	
	Concentration (μg/kg)																			
	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean
Nap	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
Acy	0.73	0.51	0.40	0.40	0.60	0.43	1.85	0.69	0.97	0.70	1.01	0.55	1.00	0.59	0.40	0.40	0.40	0.40	0.53	0.44
Ace	0.80	0.50	0.98	0.53	0.87	0.47	2.19	0.88	1.87	0.84	0.81	0.59	2.23	1.05	0.53	0.40	0.37	0.37	0.80	0.48
Flo	6.71	2.74	4.84	1.80	2.29	1.04	5.25	1.37	2.98	1.45	2.97	1.47	6.51	2.07	0.97	0.58	0.71	0.46	1.58	1.12
Phe	44.14	22.98	64.84	19.64	22.36	10.73	46.87	15.66	57.58	27.39	55.64	21.79	172.45	45.93	18.72	10.40	9.13	5.98	20.22	14.48
Ant	2.92	1.09	1.11	0.69	1.94	0.69	3.15	1.57	3.98	1.75	1.35	0.88	15.07	3.53	1.05	0.54	0.80	0.49	1.93	1.03
Fla	36.09	18.65	26.90	16.32	30.32	14.96	95.78	25.52	160.91	54.38	53.53	33.29	383.94	97.27	34.56	18.45	13.52	7.16	44.27	25.35
Pyr	14.39	7.51	10.94	6.61	21.86	7.69	52.34	13.11	60.98	25.38	25.86	14.74	229.90	52.64	17.04	8.40	5.04	2.73	22.32	11.65
BaA	6.21	2.81	5.28	2.59	11.01	3.26	14.64	5.92	22.59	8.55	8.56	4.98	87.24	20.93	12.26	6.95	14.34	3.00	11.13	5.19
Chr	22.91	16.38	30.91	18.10	25.01	15.78	63.63	24.94	188.62	66.45	56.62	33.11	221.38	89.38	36.73	20.89	13.71	9.64	32.24	19.63
BbF	21.06	14.09	19.26	13.23	21.44	14.74	43.19	18.14	117.20	49.70	48.49	29.71	194.70	73.59	28.61	16.17	9.56	7.02	25.72	14.66
BkF	8.88	5.31	7.32	5.06	9.36	5.96	19.89	8.19	24.39	16.45	12.64	10.03	73.66	25.58	12.47	6.97	4.19	2.91	8.71	5.30
BaP	6.72	2.92	4.91	2.23	9.34	3.10	20.42	5.58	20.96	7.95	11.97	4.36	80.01	19.08	13.75	4.29	1.66	1.16	8.90	4.59
DahA	7.37	4.29	2.45	2.01	5.44	3.13	3.35	2.50	14.24	6.30	7.77	4.32	19.80	7.48	3.30	2.06	1.92	1.41	7.55	3.23
IcdP	11.25	5.29	5.41	3.18	6.56	4.37	11.52	3.91	30.32	12.88	17.58	7.79	124.53	31.54	7.82	3.50	2.24	1.38	8.78	4.29
BghiP	9.29	4.83	4.10	2.47	5.42	3.23	8.97	3.58	28.74	11.22	12.29	5.93	94.99	24.28	7.97	3.10	2.53	1.19	6.36	3.53
LMW PAHs	50.84	28.22	72.55	23.46	28.46	13.77	55.61	20.57	66.26	32.53	60.70	25.67	197.66	53.56	21.85	12.72	11.49	8.10	25.01	17.95
HMW PAHs	136.30	82.05	106.29	71.79	145.29	76.21	326.99	111.39	644.02	259.27	225.34	148.25	1510.15	441.77	169.78	90.78	60.84	37.58	171.92	97.42
ΣPAH_7	76.53	51.07	65.72	46.40	87.69	50.33	169.90	69.18	393.39	168.29	156.30	94.30	801.32	267.58	110.21	60.83	40.40	26.51	97.60	56.89
ΣPAH_{16}	174.06	110.27	177.20	95.25	173.75	89.98	353.24	131.96	710.28	291.80	276.14	173.92	1707.81	495.32	191.63	103.50	69.52	45.68	196.93	115.36

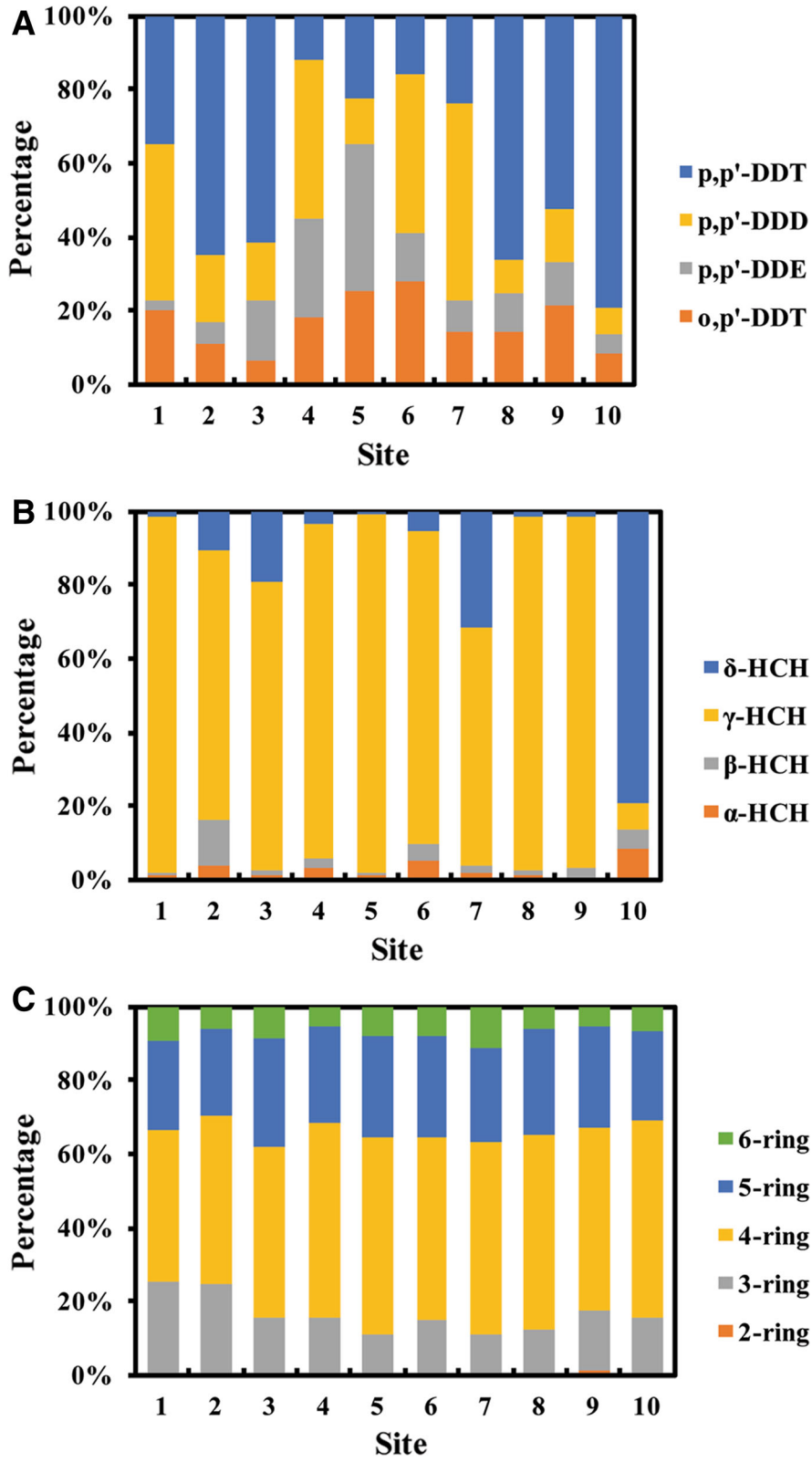

Fig. 2 Composition profile plot of POPs in soil samples collected from ten sites including site 1 (Nanming district), site 2 (Yunyan district), site 3 (Guanshanhu district), site 4 (Huaxi district), site 5 (Wudang district), site 6 (Baiyun district), site 7 (Qingzhen city), site 8 (Kaiyang county), site 9 (Xifeng county) and site 10 (Xiuwen county) in Guiyang city, China

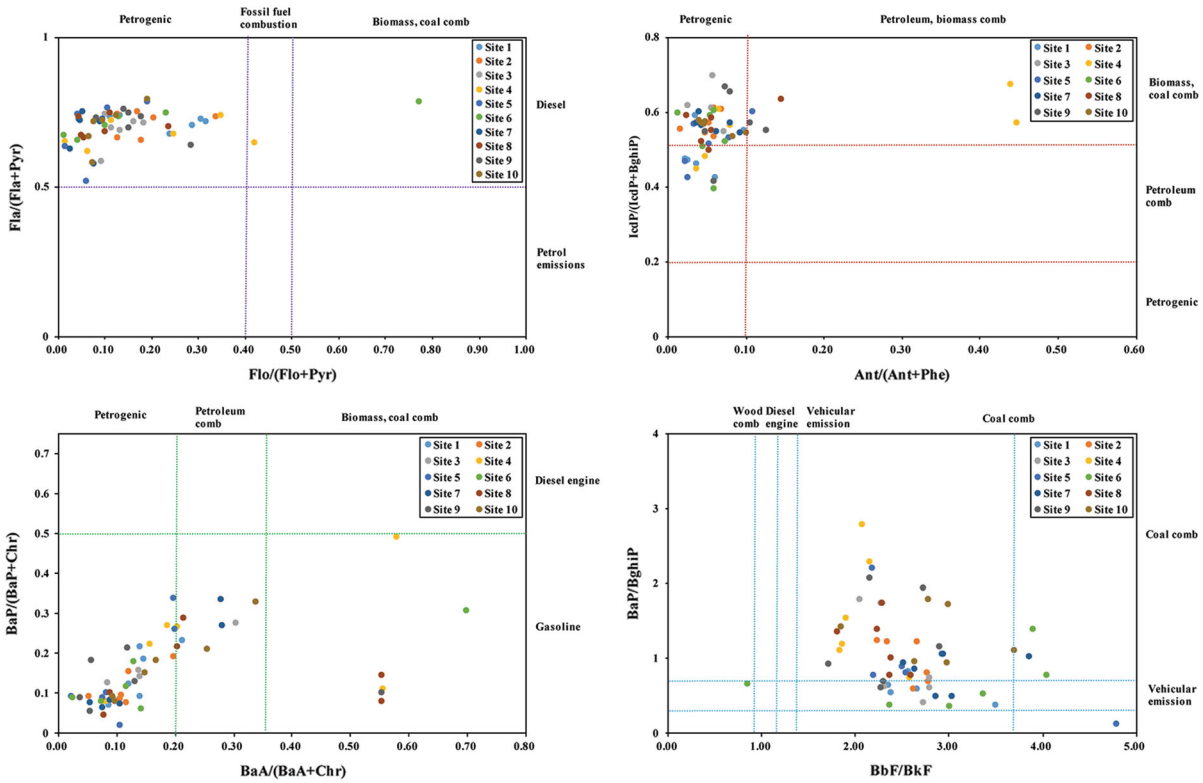

Fig. 3 Cross-plots for the isomeric ratios of Fla/(Fla + Pyr) versus Flo/(Flo + Pyr), IcdP/(IcdP + BghiP) versus Ant/(Ant + Phe), BaP/(BaP + Chr) versus BaA/(BaA + Chr) and BaP/BghiP versus BbF/BkF of PAHs in soil from Guiyang city, China

kg) are largely lower than the limit values. The data indicated that the soil contamination risk of these two organochloride pesticides in Guiyang could be negligible, which may have been contributed by the rigorous environmental protection policy set by the government and the improved environmental protection consciousness held by the public (Ni & Wang, 2012; Peng & Deng, 2020). Furthermore, the levels of PAHs were relatively lower than those in some developing megacities in China, such as Beijing (924–44,495 μg/kg, Zhang et al., 2016), Shanghai (83–7220 μg/kg), Nanjing (59–18,000 μg/kg, Wang et al., 2015a, b), and Xi'an (149–5770 μg/kg, Bao et al., 2018). As the capital city of Guizhou, a southwestern province in China, Guiyang has been built as an eco-civilized city in the last several years, and environmental protection will always be the most crucial priority in the future construction of this developing city. Furthermore, the concentrations of Σ_{16}PAHs in the soil were positively influenced by population density and the development of heavy industries (Nam et al., 1999).

The data of DDTs and HCHs significantly ($p < 0.05$) indicated that these five areas were identified as the primary source of DDTs and HCHs in Guiyang. Site 1 (Nanming District) and site 3 (Guanshanhu District) were two main urban areas in Guiyang city, and the relatively high amounts of organochloride pesticides may be attributed to the high population destiny and economic prosperity. For site 5 (Wudang District), site 9 (Xifeng County) and site 10 (Xiuwen County), the previous applications of agrochemicals and agricultural-oriented development may have contributed to the residues of DDTs and HCHs. The PAH amounts at site 7 were significantly ($p < 0.05$) higher than those in the other areas, demonstrating that site 7 may have been the main original source of PAHs in Guiyang city. Site 7, Qingzhen City, is the major industrial area in Guiyang, whose aluminum manufacturing industry has been developed rapidly in recent years. Similar results have been found in Urumqi (Chen et al., 2013) and Xi'an (Bao et al., 2018), where higher levels of PAHs in the soil were found in industrial areas. Moreover, site 5

(Wudang District) and site 6 (Baiyun District), where the second and third highest concentrations of PAHs in the soil were detected, were used as industrial zones in Guiyang in the last decade. The spatial distribution of Σ_{16}PAHs and Σ_7PAHs in the Guiyang soil indicated that the western and northeastern areas presented relatively higher concentrations of PAHs than other areas. Therefore, more concern should be exhibited regarding the relatively more serious pollution in these areas.

The percentage of *p*,*p*'-DDE from site 1 (2.8%), *p*,*p*'-DDD from site 10 (6.9%), and *p*,*p*'-DDT from site 4 (12.0%) were much lower than that from the other sites. Different industrial and agricultural distributions and environments may have contributed to the different proportions in different areas (Megharaj et al., 2000; Wang et al., 2021a, b). Except for site 10, γ-HCH in site 1-site 9 accounted for the largest portion in the soil samples, which was similar to previous studies conducted in other cities (Kumar et al., 2021; Martijn et al., 1993). Moreover, the Pearson's moment correlation coefficient data (Table 3) demonstrated that the correlations between *o*,*p*'-DDT and α-HCH and between *p*,*p*'-DDT and δ-HCH were significant ($p < 0.05$). Other significant correlations ($p < 0.01$) were also observed among *o*,*p*'-DDT, *p*,*p*'-DDE and *p*,*p*'-DDT; between *p*,*p*'-DDE and *p*,*p*'-DDD; among *p*,*p*'-DDT, α-HCH and γ-HCH; and between α-HCH and β-HCH. These correlations among individual target DDTs and HCHs showed that these organochloride pollutants in Guiyang City originated from common sources.

The composition profile of PAHs in the soil collected from Guiyang was similar to previous reports conducted in Beijing (Li et al., 2006), Hong Kong (Chung et al., 2007), Harbin (Ma et al., 2009), Taizhou (Hu et al., 2015), Nanjing (Cai et al., 2017) and Xi'an (Bao et al., 2018). The possible reason for this was that HMW PAHs more easily accumulated in the soil samples that were close to the emission sources of pollutants and were more likely to persist in the soil environment (Liu et al., 2011). The Pearson's moment correlation data between individual target PAHs are shown in Table 4. Almost all correlation coefficients among different PAHs (except Acy) illustrated a significant intercorrelation ($p < 0.01$). Ace and Flo were moderately correlated with other PAH compounds (correlation coefficient > 0.4). Phe, Ant and all individual HMW PAH compounds were significantly ($p < 0.01$) correlated with one another (correlation coefficient > 0.7). However, there was an insignificant correlation between Acy and other PAHs (except Ace). The results suggested that the sources of various PAHs were different from others.

According to a previous report (Aislabie et al., 1997; Pozo et al., 2017), *p*,*p*′-DDT could degrade to *p*,*p*′-DDE, and their ratio was widely applied to identify the potential source of DDTs in the environment. When the isomeric ratio of *p*,*p*′-DDT/*p*,*p*′-DDE is larger than 1, the DDT has recently been released into the environment. Otherwise, a ratio < 1 indicates an historical application of DDT (Kumar et al., 2021; Tavares et al., 1999). For HCHs, the ratio of α-HCH/γ-HCH has always been used to deduce the potential source of HCH pollutants in the soil ecosystem

Table 3 Pearson's correlation coefficient among individual target DDTs and HCHs

Analyte	*o*,*p*'-DDT	*p*,*p*'-DDE	*p*,*p*'-DDD	*p*,*p*'-DDT	α-HCH	β-HCH	γ-HCH	δ-HCH
o,*p*'-DDT	1.000	0.547**	0.046	0.366**	0.256*	− 0.031	0.043	0.021
p,*p*'-DDE		1.000	0.726**	0.052	− 0.050	− 0.037	− 0.038	− 0.020
p,*p*'-DDD			1.000	0.061	0.002	0.054	− 0.067	− 0.012
p,*p*'-DDT				1.000	0.450**	0.115	0.380**	0.330*
α-HCH					1.000	0.534**	0.008	0.056
β-HCH						1.000	− 0.011	0.125
γ-HCH							1.000	− 0.011
δ-HCH								1.000

*Correlation is significant at the 0.05 level (2-tailed)

**Correlation is significant at the 0.01 level (2-tailed)

Table 4 Pearson's correlation coefficient among individual target PAHs

Analyte	Acy	Ace	Flo	Phe	Ant	Fla	Pyr	BaA	Chr	BbF	BkF	BaP	DahA	IcdP	BghiP
Acy	1.000	0.811**	0.236	0.309*	0.490**	0.275*	0.308*	0.263*	0.256*	0.293*	0.283*	0.253	0.464**	0.339**	0.346**
Ace		1.000	0.457**	0.587**	0.752**	0.571**	0.617**	0.568**	0.479**	0.544**	0.573**	0.615**	0.663**	0.621**	0.621**
Flo			1.000	0.776**	0.611**	0.540**	0.521**	0.492**	0.495**	0.496**	0.485**	0.481**	0.547**	0.548**	0.568**
Phe				1.000	0.864**	0.889**	0.879**	0.840**	0.785**	0.826**	0.830**	0.822**	0.763**	0.884**	0.893**
Ant					1.000	0.903**	0.943**	0.909**	0.691**	0.778**	0.833**	0.918**	0.803**	0.943**	0.941**
Fla						1.000	0.983**	0.946**	0.865**	0.912**	0.926**	0.903**	0.761**	0.955**	0.963**
Pyr							1.000	0.961**	0.785**	0.862**	0.915**	0.953**	0.785**	0.968**	0.968**
BaA								1.000	0.780**	0.845**	0.892**	0.930**	0.740**	0.948**	0.952**
Chr									1.000	0.976**	0.898**	0.692**	0.700**	0.819**	0.843**
BbF										1.000	0.960**	0.791**	0.798**	0.902**	0.915**
BkF											1.000	0.887**	0.823**	0.933**	0.937**
BaP												1.000	0.762**	0.930**	0.922**
DahA													1.000	0.849**	0.843**
IcdP														1.000	0.996**
BghiP															1.000

*Correlation is significant at the 0.05 level (2-tailed)

**Correlation is significant at the 0.01 level (2-tailed)

(Chakraborty et al., 2016; Kata et al., 2015). Potential sources of organochloride pesticides in Guiyang were from ongoing application and the long-range atmospheric transport tendencies of DDT and HCH under a subtropical humid climate, which were similar to the results from some previous studies (Kata et al., 2015; Mitra et al., 2019). The potential sources of PAHs in the environment can be determined by using several diagnostic ratios of different PAH homologs and PAHs with different molecular weights (Dickhut et al., 2000; Khalili et al., 1995; Kumar et al., 2021; Ravindra et al., 2008; Simcik et al., 1999; Yunker et al., 2002). The diagnostic ratio data demonstrated that the potential sources were mixtures of several combustion activities. For example, Fla/(Fla + Pyr) was 0.52–0.79 indicating diesel as a potential source (Khalili et al., 1995); Flo/(Flo + Pyr) was 0.01–0.35 (except two samples) indicating a petrogenic source (Yunker et al., 2002); IcdP/(IcdP + BghiP) was 0.39–0.70, Ant/(Ant + Phe) was 0.01–0.45 and BaA/(BaA + Chr) was 0.02–0.70 indicating petrogenic, biomass, coal and petroleum comb sources, respectively; BaP/(BaP + Chr) was 0.02–0.49 indicating a gasoline source (Simcik et al., 1999); BaP/BghiP was 0.10–2.77 and BbF/BkF was 1.72–4.81 (except for one sample) indicating vehicular emission and coal comb sources, respectively (Dickhut et al., 2000).

Conclusions

The concentrations of POPs, including DDTs, HCHs and PAHs, were measured in soil samples collected from different locations in Guiyang city, China. Then, the spatial distribution and possible sources of the POPs were further assessed. The relatively lower levels of DDTs and HCHs ($<<100$ μg/kg) in the Guiyang soil indicated negligible soil contamination risk due to rigorous environmental protection policies and social consciousness. In addition, 20% of the soil samples were polluted by PAHs because of Σ16PAH concentrations >200 μg/kg, which were positively affected by population density and heavy industrial development. Different locations presented different amounts of POPs in the soil, and the highest levels of PAHs in the soil were observed in the major industrial area (sites 5–7) in Guiyang. The dominance of *p*,*p*′-DDT, *p*,*p*′-DDD and γ-HCH and the correlation and isomeric ratio between DDT and HCH analytes demonstrated the historical and recent input of organochloride pollutants from common sources. A composition profile and correlation analysis of PAHs suggested that 4-ring PAHs accounted for the majority of the total PAHs in the soil, and Chr, Fla, BbF, Phe, and Pyr were the major compounds of individual PAH analytes. The diagnostic ratio results among PAHs illustrated that the potential sources were mixed pyrogenic sources, including diesel, petrogenic, biomass, coal and petroleum comb, gasoline, and vehicular emissions.

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Declarations

Data availability All data in this study are available upon request.

Conflict of interest The authors have no conflict of interest to declare.

Ethical approval No applicable.

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