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ORIGINAL PAPER

Contamination characteristics of alkyl polycyclic aromatic hydrocarbons in dust and topsoil collected from Huaibei Coalfield, China

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Abstract Alkyl polycyclic aromatic hydrocarbons (APAHs) are more toxic and persistent than their parent compounds. In this study, the concentrations of polycyclic aromatic compounds (PACs) in dust, topsoil and coal gangue from Huaibei Coal mine, China were analyzed by gas chromatography-mass spectrometry, confirming APAHs were the dominant pollutants. The mean concentrations of APAHs were substantially higher than those of 16 PAHs in both dust and topsoil. The mean concentration of APAHs in dust was 9197 μg kg^{-1}, accounting for 80% of the total mean concentration of PACs. The mean concentration of APAHs in topsoil was 2835 μg kg^{-1}, accounting for 77% of the mean concentration of PACs. Alkyl naphthalenes and alkyl phenanthrenes were the primary pollutants in APAHs. Their mean concentrations in dust and topsoil were 7782 μg kg^{-1} and 2333 μg kg^{-1}, respectively. This accounted for 85% and 82% of the concentration of APAHs, respectively. Additionally, low-molecular-weight APAHs dominated the PACs of the coal mine, exhibiting petrogenic characteristics; distribution of C1-C4 NAP and C1-C4 PHE exhibited "bell shape" pattern indicated as petrogenic source. Source identification indicated that the PACs were mainly derived from petrogenic sources and vehicle emissions, followed by biomass and coal burning. Fingerprinting information of dust and topsoil were consistent with coal gangue, indicating that PACs are most likely derived from coal gangue. Coalfields comparable to our study area are widely distributed in China. Therefore, investigating PAC pollution derived from coal gangue warrants further attention.

Keywords Polycyclic aromatic compounds (PACs) · Dust · Topsoil · Petrogenic source · Coal gangue · Low-molecular-weight APAHs

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an important group of persistent organic pollutants

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(POPs) that are of global concern (Durant et al., 1996). In 1976, among the PAHs in the environment, the United States Environmental Protection Agency (EPA) listed 16 of them (16 PAHs) as priority pollutants (Wilcke, 2000; Yang et al., 2007). The environmental pollution of 16 parent PAHs was extensively investigated (Liang et al., 2019, 2020; Wang et al., 2009, 2017). Additionally, alkyl polycyclic aromatic hydrocarbons (APAHs) in environmental samples have attracted attention recently (Hong et al., 2016; Lian et al., 2009; Zhang et al., 2005). The APAHs occupy a considerable proportion among the polycyclic aromatic compounds (PACs, comprising 16 PAHs and APAHs). For example, Colavecchia et al. (2004) analyzed total PACs in Athabasca sediment samples and found that APAHs accounted for approximately 93–99% of all PACs. The concentrations of APAHs in aquatic organisms from oil-contaminated areas is considerably higher than that of non-alkyl PAHs (Hose, 1999). Studies have shown that compared to PAHs, the toxicity of APAHs increases the mortality and malformation rates in biological embryos to a greater extent (Mu et al., 2014; Ramachandran et al., 2004; Vidal et al., 2011; Wirgin & Waldman, 2004). APAHs have been detected in food sources in energy-mining areas, after passing through the food chain (Golzadeh et al., 2021). Therefore, APAHs in the environment should be assessed, in addition to the 16 PAHs.

Petroleum source is considered the main source of APAHs in the environment (Abdel-Shafy & Mansour, 2016). However, recent studies on raw coal have suggested that in addition to inherently containing 16 PAHs (Huang et al., 2016), certain amounts of APAHs are present, with an abundance of alkyl naphthalenes (ANAPs) and alkyl phenanthrenes (APHEs) (Matthias et al., 1984; Sun et al., 2017). Studies on PAHs in coal gangue (Li et al., 2019), a waste generated from coal production, have also reported the presence of APAHs and 16 PAHs. Therefore, in addition to 16 PAHs, APAHs may be readily detected in the environment of coal mining areas affected by coal and coal gangue. China has the greatest coal production worldwide. As a typical example of coal-related environments, soil in coal mining areas has accumulated pollutants over a prolonged period, resulting in environmental release of these pollutants. Owing to the production and consumption of coal in China, the coal mining areas overlap with intensive human activities. However, studies on PACs in coal mining areas in China, which are typically polluted with environmental organic pollutants, have been relatively limited, with few focusing on APAHs (Casal et al., 2014).

This study qualitatively and quantitatively analyzed PACs in dust and topsoil from three typical mining areas using gas chromatography-mass spectrometry. The pollution level and composition characteristics of PACs were analyzed. Applying principal component analysis (PCA) and positive matrix factorization (PMF), we determined PAC sources. A new potential PACs pollution source—coal gangue was proposed using source identification and fingerprinting information. This can provide a groundwork for subsequent environmental and health research in coal mining area.

Materials and methods

Sample collection

The Huaibei coalfield, an important coal-producing area in China, is in the northern portion of Anhui Province, China (116°23′–117°02′ E, 33°16′–34°14′ N). In 2016, it presented an annual output of 45.00 million tons of raw coal and 14.35 million tons of cleaned coal. Three typical mining areas belonging to the Huaibei coalfield were considered, including Tongting mining area (a), Suntuan mining area (b), and Liuqiao mining area (c). A total of 62 dust, 74 topsoil and 6 coal gangue samples were collected (Fig. 1). At each mining area, samples collected from the area of least anticipated impacts to the more highly impacted areas. Dust samples were collected from the top 2 mm (approximately) of the ground surface after cleaning the sample location with a soft brush. Topsoil samples were collected from the top 10 cm of the ground surface with a shovel. Three parallel samples were collected within a sample plot of 5.0 m^2 before being evenly composited and cleared of impurities such as plant debris and stones. The composite samples were subsequently wrapped in aluminum foil and sealed within polyethylene sample bags. Then, samples were maintained at cool temperature for transport to the laboratory to be prepped for analysis.

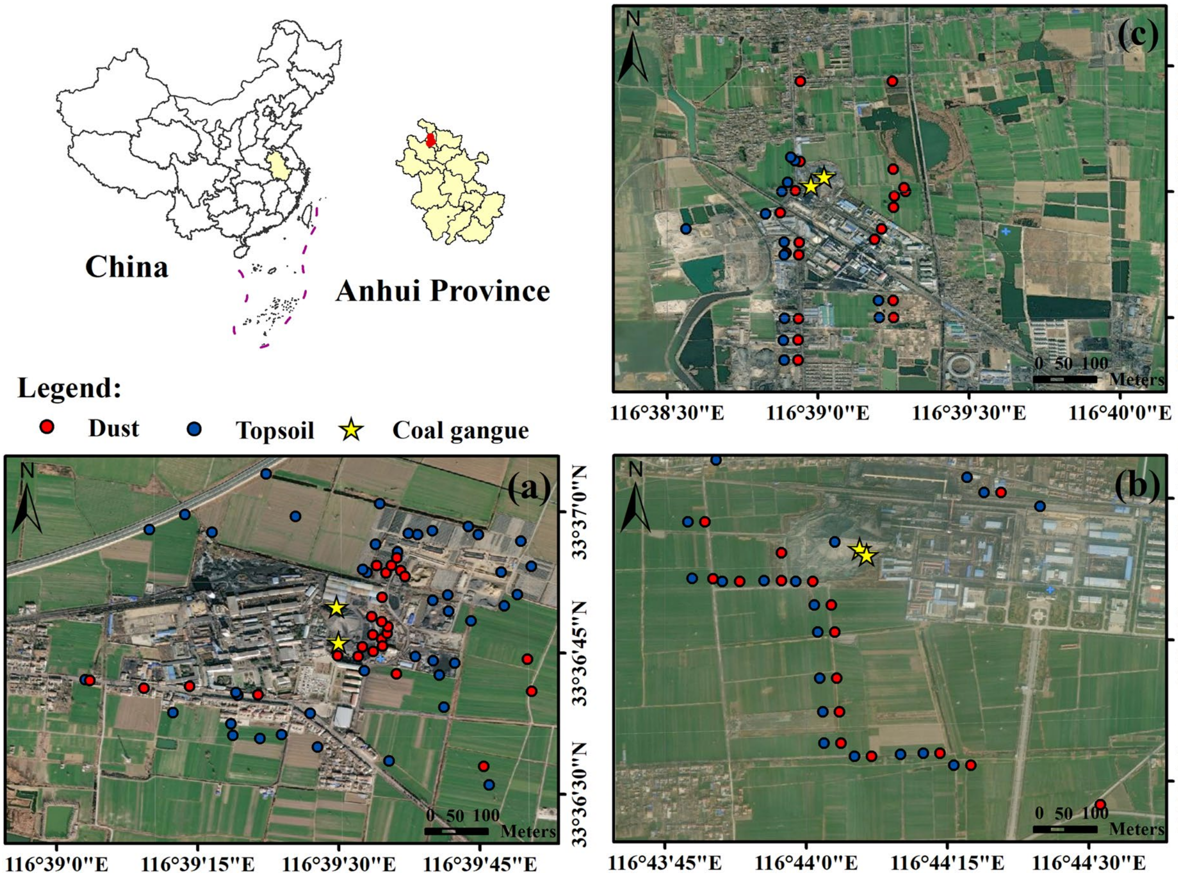

Fig. 1 Geographical locations of the research areas and the distribution of sampling sites **a** Tongting mining area; **b** Suntuan mining area; **c** Liuqiao mining area

Chemicals and reagents

Standard were purchased from AccuStandard (USA). The standard mixture of 16 EPA-priority PAHs included naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), 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), Indene [1, 2, 3-cd] pyrene, dibenzo [a, h] anthracene (DBA), and benzo [g,h,i] perylene (BgP). APAH standard solutions included 1-methylnaphthalene (1-M-NAP), 1,2-dimethylnaphthalene (1,2-D-NAP), 2-methylanthracene (2-M-ANT), 3,6-dimethylphenanthrene (3,6-D-PHE), 1-methylpyrene (1-M-PYR), and 7-methylbenzo [a] pyrene (7-M-BaP). Deuterium-labeled standards included naphthalene-d8 (NAP-d8), acenaphthene-d10 (ACE-d10), phenanthrene-d10 (PHE-d10), chrysene-d12 (CHR-d10), and perylene-d12 (PER-d12) and were used as internal standards.

All reagents applied were high-performance liquid chromatography (HPLC)-grade. Dichloromethane (DCM) and n-hexane (HEX) were purchased from Thermo Fisher (USA). Anhydrous sodium sulfate (Aladdin, China) was dried at 800 °C for 4 h and then placed in an oven at 60 °C before use. All glassware in contact with the samples was rigorously cleaned before and between use to avoid contamination.

Sample pretreatment

The pretreatment steps used have been described and verified previously (Qian et al., 2021). First, 2 g of sample and 2 g of anhydrous sodium sulfate were successively transferred into a 10-mL glass tube and treated with 4.9 mL DCM and 100 μL NAP-d8 (20 μg/mL). The tightly sealed tube was placed in the sample rack of an ultrasonic cleaning tank and ultrasonicated for 5 h, during which the ultrasonic cell temperature was maintained below 20 °C. Thereafter, the supernatant of the spiral glass tube was transferred into a 2-mL centrifuge tube with a rubber head dropper, vortexed for 1 min, and then centrifuged at 14,000 rpm for 10 min. After centrifugation, the supernatant was filtered using a syringe filter (pore size 0.22 μm). Thereafter, 100 μL of the filtrate was transferred into the inner tube of the sample bottle and 100 μL of 400 ng/mL internal standard (ACE-d10, PHE-d10, CHR-d12, PER-d12) was added to the filtrate before the mixture was vortexed for approximately 30 s.

Chemical analysis

The compounds were quantified using gas chromatography-tandem mass spectrometry (Waters, Xevo TQ-GC) with full scan mode. The gas chromatograph was equipped with a DB-5MS column (length, 30 m; internal diameter, 0.25 mm; film thickness, 0.25 mm). Helium was used as the carrier gas with a constant flow rate of 1.0 mL/min. The injection mode was splitless and the injection volume was 1.0 μL. The inlet temperature was set at 280 °C. The initial oven temperature was 70 °C for 1 min, increased to 180 ℃ at a rate of 15 °C/min with a 2-min hold time, increased to 230 °C at a rate of 10 °C/min with a 0.5-min hold time, increased to 250 °C at a rate of 5 °C/min with a 2-min hold time, and finally, increased to 300 °C at a rate of 8 °C/min with a 5-min hold time. Mass spectrometry was performed using an electron bombardment ionization source (electron impact: 70 eV) at an ion source temperature of 250 °C, interface temperature of 280 °C, and acquisition range of 50–550 aum, with solvent delay set to 4.0 min.

Quality control

MassLynx V4.2 (Waters, USA) was used to study the target compounds qualitatively and quantitatively. Strict quality control (QC) was performed, 5% QC samples and 10% blank of total samples were adapted to conformed the radically of the analysis. The carryover showed no detectable PAH contamination. The standard deviation of the sample duplicates was $<$ 15%. The recoveries of the samples ranged from 78.1 to 129%.

Results and discussion

PAC concentrations in dust

In addition to 16 PAHs, abundant APAHs were identified, especially alkyl naphthalenes (ANAPs) and alkyl phenanthrenes (APHEs) (Fig. S1). Based on the quantitative results of 62 analyzed dust samples, the mean concentration of PACs was 11,462 μg kg^{-1} (380–59,129 μg kg^{-1}, $n = 62$). The mean concentration of APAHs was 9197 μg kg^{-1}, which was 4.1 times that of 16 PAHs (2266 μg kg^{-1}), and higher than the concentration ranges of APAHs observed in the dust (1600–9000 μg kg^{-1}) of Shanghai urban area (Lian et al., 2009) and road dust (2483–7886 μg kg^{-1}) of Xi 'an urban area (Wei et al., 2015) (Table S1). In addition, the abundance of homologs of ANAPs and APHEs was the largest in dust, with a mean concentration of 7782 μg kg^{-1}, accounting for approximately 85% of the mean of APAH concentrations and 68% of the mean of PAC concentrations (Table S2). This is consistent with findings for the PAHs studied from dustfall in Shanghai, China, wherein ANAPs and APHEs were the two main contributors, accounting for more than 50% of the total contribution of APAHs (Lian et al., 2009).

Dust in three mining areas exhibited different PAC concentrations: Tongting (15,922 μg kg^{-1}) $>$ Suntuan (10,881 μg kg^{-1}) $>$ Liuqiao (6130 μg kg^{-1}). APAHs also have the same sequence: Tongting (13,551 μg kg^{-1}) $>$ Suntuan (8799 μg kg^{-1}) $>$ Liuqiao (3854 μg kg^{-1}), as well as 16 PAHs: Tongting (2372 μg kg^{-1}) $>$ Suntuan (2082 μg kg^{-1}) $>$ Liuqiao (2276 μg kg^{-1}) (Table 1). This difference was probably related to the amount and chemical composition of coal gangue. There was a large gangue dump in Tongting mining area, and the pile of gangue around the Tongting mining area is more common than the other two mining areas. Laumann et al. (2011) showed that APAHs are abundant in coals of different sources and ranks. Coal gangue is the rock associated with coal, mainly composed of organic compounds and clay minerals, and may be rich in APAHs. Weathering causes the structure of coal gangue to depolymerize, loosen, and granulate, which makes the PACs

Table 1 Concentrations of 16PAHs, ANAPs + APHEs, APAHs, and PACs in the dust of three typical mining areas (μg kg^{-1})

Samples	16 PAHs	ANAPs + APHEs	APAHs	PACs	Samples	16 PAHs	ANAPs + APHEs	APAHs	PACs
Tongting mining area (a)									
AC-1	1196	4296	5271	6466	CC-3	2197	9647	11,055	13,252
AC-2	2381	9146	10,737	13,117	CC-4	2652	13,716	15,466	18,118
AC-3	1325	4891	5962	7287	CC-5	2402	12,720	14,467	16,869
AC-4	1383	4361	5657	7040	CC-6	2067	13,059	14,676	16,743
BC-1	5613	35,918	40,948	46,560	CC-7	2523	13,026	15,002	17,525
BC-2	634	2925	4134	4769	CC-8	1657	7592	8633	10,290
BC-3	2565	11,935	13,740	16,305	CC-9	4048	22,016	25,091	29,138
BC-4	25	327	355	380	CC-10	1829	8864	10,002	11,831
BC-5	1982	8562	10,108	12,090	CC-11	1897	9623	10,770	12,667
BC-6	2259	10,131	11,688	13,947	CC-12	8427	44,184	50,702	59,129
BC-7	3052	15,195	16,994	20,046	CC-13	1244	6122	6879	8123
CC-1	2810	13,573	15,197	18,006	CC-14	2070	10,606	11,939	14,009
CC-2	1556	6393	7215	8771	CC-15	1870	8345	9629	11,499
Mean	2372	11,814	13,551	15,922					
Suntuan mining area (b)									
STC-01	1225	4411	5489	6714	STC-09	1257	4670	5652	6909
STC-02	2663	8298	9683	12,346	STC-10	2524	10,364	12,153	14,677
STC-03	658	2849	3429	4087	STC-11	4022	22,616	25,433	29,455
STC-04	863	3133	3858	4721	STC-12	2724	10,727	12,320	15,044
STC-05	1993	7392	8668	10,661	STC-13	1687	6714	7654	9341
STC-06	5714	12,678	16,301	22,015	STC-14	1294	4252	5019	6313
STC-07	993	3746	4654	5647	STC-15	1643	2633	3207	4850
STC-08	1743	6472	7632	9375	STC-19	2309	8385	9637	11,946
Mean	2082	7459	8799	10,881					
Liuqiao mining area (c)									
LQC-1	2514	2012	2589	5102	LQC-11	839	1508	2276	3115
LQC-2	2116	1681	2642	4758	LQC-12	1067	1184	1636	2703
LQC-3	2109	1575	2455	4564	LQC-13	843	822	1234	2077
LQC-4	1889	2014	2842	4731	LQC-14	2262	3908	5038	7299
LQC-5	3547	5012	7058	10,604	LQC-15	6019	3204	4306	10,325
LQC-6	851	1387	1969	2820	LQC-16	1729	2468	3614	5343
LQC-7	4258	5263	7332	11,590	LQC-17	1845	3009	4062	5907
LQC-8	4615	4999	7125	11,740	LQC-18	1284	2020	2912	4196
LQC-9	2066	3405	4670	6736	LQC-19	2153	2776	3772	5925
LQC-10	2235	5410	6440	8675	LQC-20	1274	2293	3106	4380
Mean	2276	2797	3854	6130					

ANAPs + APHEs: Sum of C1-C4 NAP and C1-C4 PHE

PACs: Sum of 16PAHs and APAHs

Mean: Mean concentration of each mine

in the coal gangue easier to dissociate. During the weathering process, PACs would escape into the surrounding environment, resulting in severe PAC contamination in nearby dust and topsoil.

PAC concentrations in topsoil

The mean concentration of PACs in 74 topsoil samples of the Huaibei coalfield was 3660 μg kg^{-1}

(121–18,438 μg kg^{-1}, $n=74$), which was lower than that contained in the dust sampled from this area. The mean concentration of APAHs (2835 μg kg^{-1}) was 3.4 times the mean concentration of 16 PAHs (825 μg kg^{-1}) and considerably higher than those of the Yangtze River Delta (5–696 μg kg^{-1}) and the roadside urban area of Xi'an (232–819 μg kg^{-1}) (Chen et al., 2017; Wei et al., 2015) (Table S1). Additionally, the mean value of the combined ANAP and APHE concentrations was 2333 μg kg^{-1}, accounting for approximately 82% of the mean concentration of APAHs and 64% of the mean concentration of PACs (Table S2).

The mean concentrations of PACs in three mining areas decreased in the order of Suntuan (7166 μg kg^{-1}) > Liuqiao (4681 μg kg^{-1}) > Tongting (1759 μg kg^{-1}), as well as APAHs: Suntuan (5927 μg kg^{-1}) > Liuqiao (2815 μg kg^{-1}) > Tongting (1443 μg kg^{-1}) (Table 2). The PAC concentrations of dust in Tongting mining area was higher than that in topsoil. It may be because the topsoil from Tongting were most in farmland. In addition to the topsoil disturbances caused by agricultural activities, crops can absorb PACs from the topsoil, and thus, reduce their concentrations (Wang et al., 2010). Concurrently, concentrations of APAHs and 16 PAHs also followed the aforementioned trend noted for concentration of PACs.

Studies on 16 PAHs in soil are quite common, but lacking of research on APAHs, particularly in coal mining areas. Several investigations on 16PAHs and APAHs from the literature are summarized in Tables S1. As for 16 PAHs, the mean concentration of 16PAHs in coal mining area was 260–1541 μg kg^{-1}, and in agricultural soils was ranged from 252 to 847 μg kg^{-1}, which were significantly lower than those in coal mining areas in this work. Coal gangue dump are ubiquitous in Huaibei coalfield, spontaneous weathering and the release of coal gangue were probably the main reasons for the high PACs in coal mining areas. Previous studies on coal gangue mainly focus on heavy metals (Hua et al., 2018; Ouyang et al., 2022), and there are few reports of PAC pollution. Therefore, PAC pollution derived from coal gangue should be paid further attention.

Compositional profile of APAHs in dust and topsoil

APAHs are major contributors to PACs in the Huaibei coalfield and account for 60–85% of PACs (Table S2), which is higher than the proportion of APAHs in Shanghai dust (20–50%) (Lian et al., 2009). The mean of combined ANAP and APHE content accounted for 68–87% of the corresponding APAHs (Table S2), which contributed substantially to the APAH content. Proportions of other PAHs, in descending order, were C1-PYR, C1-CHR, C1-FLA, 7-M-BaP, C1-FLU, and 2-M-ANT, which accounted for 2.3% to 10%, 2.1% to 6.0%, 2.4% to 5.3%, 1.1% to 5.2%, and 1.0% to 2.0% of APAH content, respectively (Fig. S2).

PAHs are divided according to the number of rings: 2–3 rings represent the low ring, the middle ring contains 4 rings, and the high ring contains 5–6 rings. This study divided APAHs into four groups according to the number of carbon atoms, as follows: APAHs-2R (2 rings; Cn-NAP), APAHs-3R (3 rings; C1-FLU, Cn-PHE, and C1-ANT), APAHs-4R (4 rings; C1-FLA, C1-PYR, and C1-CHR), and APAHs-5R (5 rings; C1-BaP). As shown in Figure S3, APAHs in the dust and topsoil of various mining areas in Huaibei are mainly low-ring. Moreover, ∑low-ring PAHs accounted for 74–90% of APAHs, ∑middle-ring APAHs accounted for 9.0–21% of APAHs, while ∑high-ring APAHs had the lowest contribution rate and accounted for 1.0–5.0%. In general, low-molecular-weight APAHs dominated the dust and topsoil of the Huaibei coalfield, implying that as the number of carbon atoms increases, the percentage contribution of the monomer groups to APAHs decreases. This is consistent with previous studies on soils from the Yangtze River Delta and Ruhr Area, Germany (Chen et al., 2017; Hindersmann & Achten, 2018; Li et al., 2016).

Spatial distribution of APAHs in dust and topsoil

Based on the inverse distance weighted spatial interpolation method, the spatial distribution of PACs, APAHs, APAHs-2R, and APAHs-3R in dust and topsoil in mining area (a) are shown in Figs. 2 and 3. According to the pollution levels evaluated by Maliszewska-Kordybach (1996), the soil pollution status was divided into four levels: no pollution (16 PAHs < 200 μg kg^{-1}), light pollution (200 μg $kg^{-1} \leq$ 16 PAHs < 600 μg kg^{-1}), moderate

Table 2 Concentrations of 16PAHs, ANAPs + APHEs, APAHs, and PACs in the topsoil of three typical mining areas (μg kg^{-1})

Samples	16 PAHs	ANAPs + APHEs	APAHs	PACs	Samples	16 PAHs	ANAPs + APHEs	APAHs	PACs
Tongting mining area (a)									
A1	90	376	612	701	E3	778	1925	2179	2957
A2	25	248	311	336	E5	1950	8008	9326	11,276
A3	83	313	383	466	F1	265	790	913	1178
B3	140	512	553	693	F2	488	1622	1729	2217
B4	398	1725	1903	2302	F3	34	45	87	121
C1	144	853	966	1110	F4	66	214	214	280
C2	75	191	218	293	F5	139	622	688	827
C3	65	348	402	467	F6	489	1814	2170	2659
C4	97	459	484	582	F7	92	178	224	316
C5	88	385	450	538	F8	68	325	364	433
C6	346	1137	1296	1642	F9	78	250	250	329
C7	41	103	141	182	F10	163	897	967	1130
C8	535	2423	2795	3330	F11	127	561	629	755
C9	117	459	541	659	F12	713	2896	3476	4189
D1	783	3417	3781	4564	F13	53	348	348	402
D2	125	362	445	570	G1	78	414	441	519
D3	82	282	282	364	G2	94	547	579	673
D4	59	165	218	277	G3	306	1222	1388	1694
D5	76	211	251	327	G4	366	1367	1436	1802
E1	89	287	320	409	G5	231	1056	1188	1419
E2	108	274	333	441	G6	3123	12,672	15,315	18,438
Mean	316	1245	1443	1759					
Suntuan mining area (b)									
STT-1	1044	3554	4418	5462	STT-11	1211	4673	5538	6749
STT-2	860	3413	4203	5063	STT-12	862	4024	4668	5530
STT-3	1267	5345	6240	7507	STT-13	1038	4691	5660	6698
STT-4	1094	5058	5860	6953	STT-14	504	2672	3142	3645
STT-5	535	2502	2959	3494	STT-15	270	1226	1574	1843
STT-6	2027	7494	8998	11,025	STT-16	372	951	1326	1698
STT-7	1769	7666	8932	10,701	STT-17	841	3307	3814	4655
STT-8	1629	7006	8226	9855	STT-18	3371	9523	11,287	14,658
STT-9	1067	5593	6375	7442	STT-19	2765	11,899	13,904	16,669
STT-10	1014	4722	5483	6497	Mean	1239	5017	5927	7166
Liuqiao mining area (c)									
LQT-1	1109	662	1249	2359	LQT-8	1641	1671	2411	4052
LQT-2	1349	751	1247	2596	LQT-9	683	631	970	1653
LQT-3	3603	6085	7704	11,306	LQT-10	5771	3917	5968	11,738
LQT-4	1584	1520	2343	3928	LQT-11	401	660	868	1269
LQT-5	3154	2935	4193	7347	LQT-12	2145	2133	3470	5615
LQT-6	834	910	1417	2251	LQT-13	1190	2030	3108	4299
LQT-7	793	1098	1648	2441	Mean	1866	1923	2815	4681

ANAPs + APHEs: Sum of C1-C4 NAP and C1-C4 PHE

PACs: Sum of 16PAHs and APAHs

Mean: Mean concentration of each mine

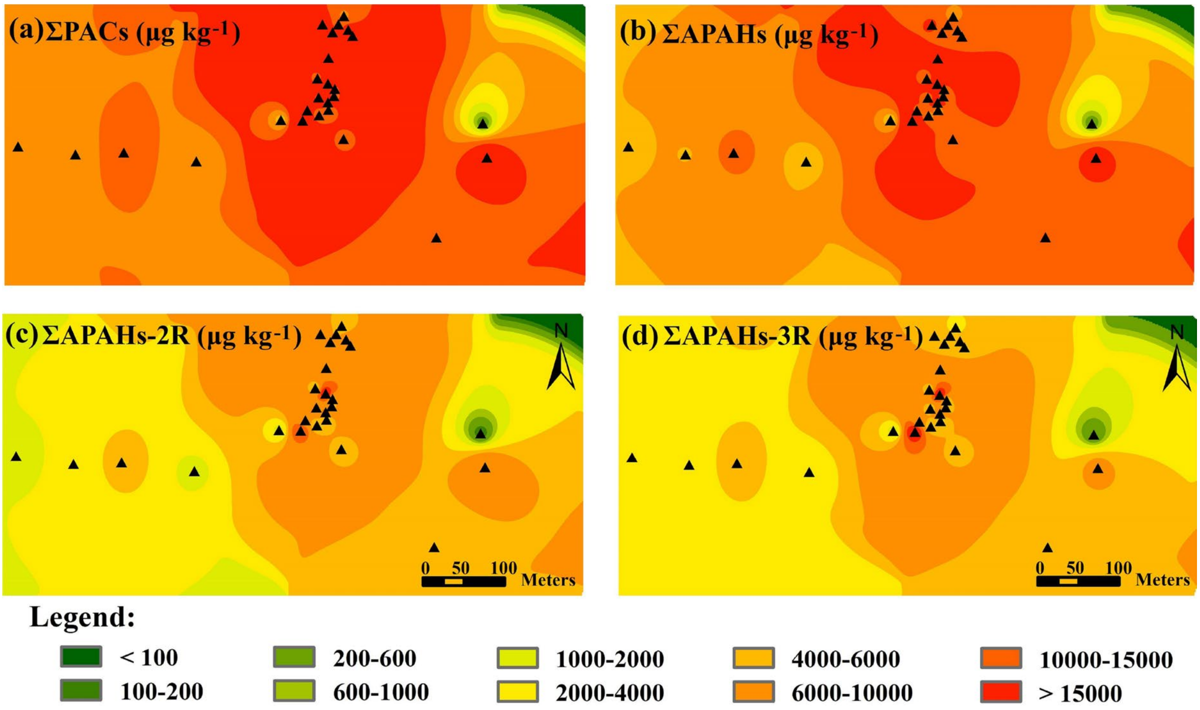

Fig. 2 Spatial distribution of PACs (**a**), APAHs-2R (**b**), APAHs-3R (**c**), and APAHs-4R (**d**) in dust samples from mining area (**a**)

pollution (600 μg kg$^{-1} \leq$ 16 PAHs $<$ 1000 μg kg^{-1}), and heavy pollution (16 PAHs $>$ 1000 μg kg^{-1}). Studies data have revealed that APAHs may be more toxic than the conventional 16 PAHs. In the spatial distribution map of dust, the APAH concentration in BC-4 (355 μg kg^{-1}) was mild, whereas the rest of the 25 dust samples contained more than 1000 μg kg^{-1} (Table 1), indicating heavy pollution. If $\sum$APAHs $>$ 1000 μg kg^{-1} as the evaluation standard of heavy pollution, then 98% of the areas were heavily polluted (Fig. 2b). Combined with the sampling diagram, the heavily polluted area is located around the gangue heap, which was likely related to the escape of PACs in the gangue. Considering the APAHs in topsoil samples in the spatial distribution map, heavy pollution, moderate pollution, light pollution, and no pollution accounted for 41%, 18%, 27%, and 14%, respectively (Fig. 3b), which is substantially lower than the dust pollution. The points of unpolluted and slightly polluted areas were in the farmland outside the mining area (Fig. 3).

The spatial distribution pattern of PACs in dust and topsoil were consistent with that of APAH, APAHS-2R, and APAHS-3R, indicating that the source of PACs in dust and topsoil is probably the same, which is related to coal gangue. Additionally, coal burning in mining areas produces PAC pollution, which increases PAC concentrations in dust and topsoil. Currently, local environmental testing in China is limited and is only applicable for the assessment of conventional 16 PAHs. Therefore, APAHs should be included in the assessment of environmental organic pollutants.

Source identification of PACs in dust and topsoil

Most studies have traced the origin of APAHs using the conventional molecular ratio method of 16 PAHs (Liang et al., 2019; Tobiszewski & Namiesnik, 2012; Zhang et al., 2020); however, this method lacks detection and source analysis of APAHs. In this study, the APAH concentrations in dust and topsoil of the coal mining areas were higher than those of the 16 PAHs, and there was a significant positive correlation between concentrations of APAHs and 16 PAHs in the dust of mining areas (a), (b), and (c), with correlation coefficients of 0.97, 0.70, and 0.47, respectively (Fig. S4-a). Such a strong positive correlation was

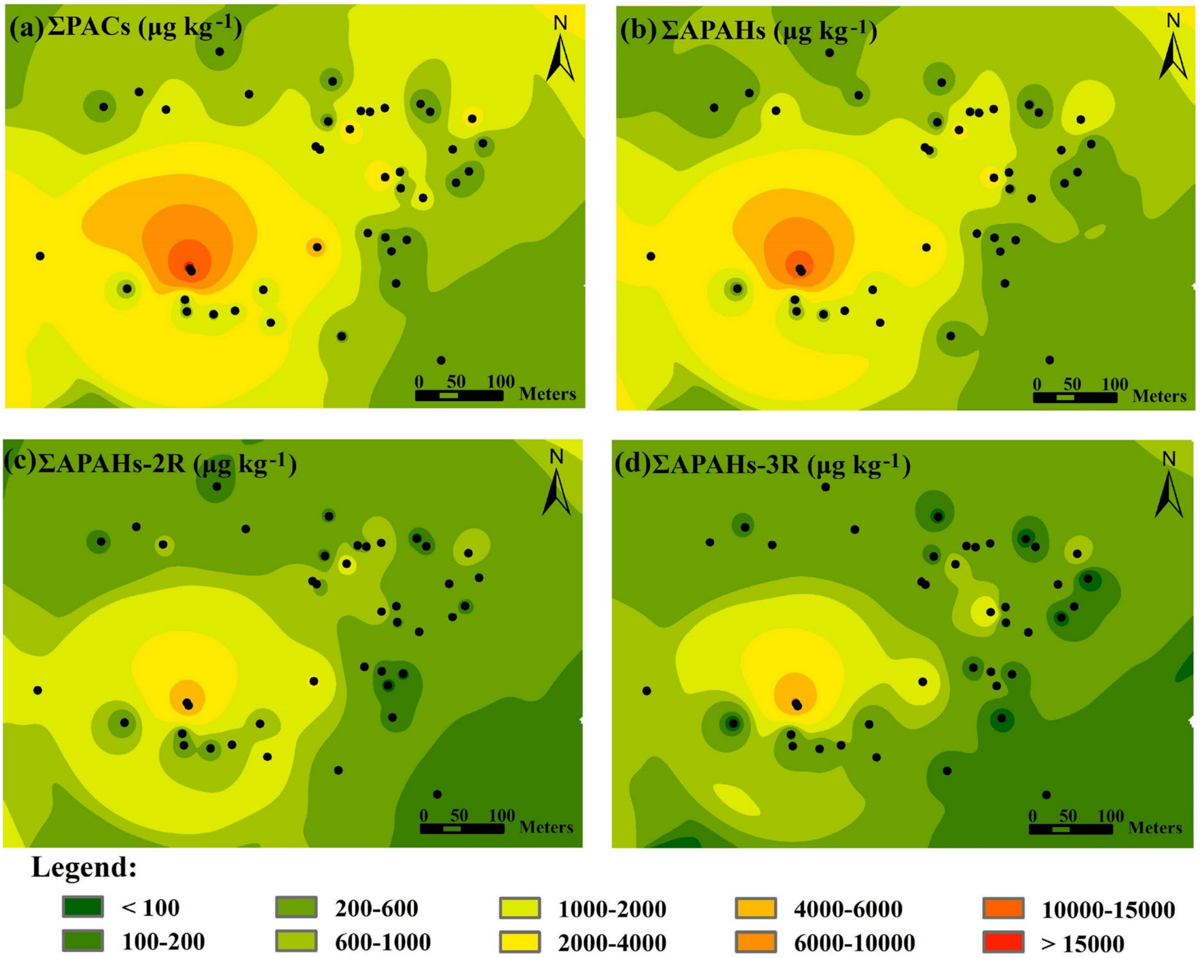

Fig. 3 Spatial distribution of PACs (**a**), APAHs-2R (**b**), APAHs-3R (**c**), and APAHs-4R (**d**) in topsoil samples from mining area (**a**)

also noted in the topsoil, with correlation coefficients of 0.99, 0.90, and 0.75, respectively (Fig. S4-b). This suggests that they were released from similar source. Therefore, PACs tracing methods can be reasonably used to analyze the sources of dust and topsoil pollution in three mining areas.

To date, PCA is the most commonly used multivariate analysis tool in soil research (Fang et al., 2004; Navarro et al., 2006; Wang et al., 2006). In this paper, it was performed on data of 136 PAC samples from three mining areas, and eigenvalues greater than 1 were extracted into 4 factors, with the sum of variance contribution rate of 82.8% (Fig. 4). The variance contribution rate of factor 1 was 61.2%, and FLU, PHE, C1-PHE, C3-PHE, C4-NAP, C1-FLA, and C1-PYR had higher loadings, among which the correlation between NAP, PHE, and C1-PHE was greater than 0.90 (Table S3). This indicated good correlation. In addition to C4-PHE, the loadings of methyl substituents of naphthalene and phenanthrene were generally high, and their correlation coefficients ranged from 0.71 to 0.99 (Table S3). This suggests that they

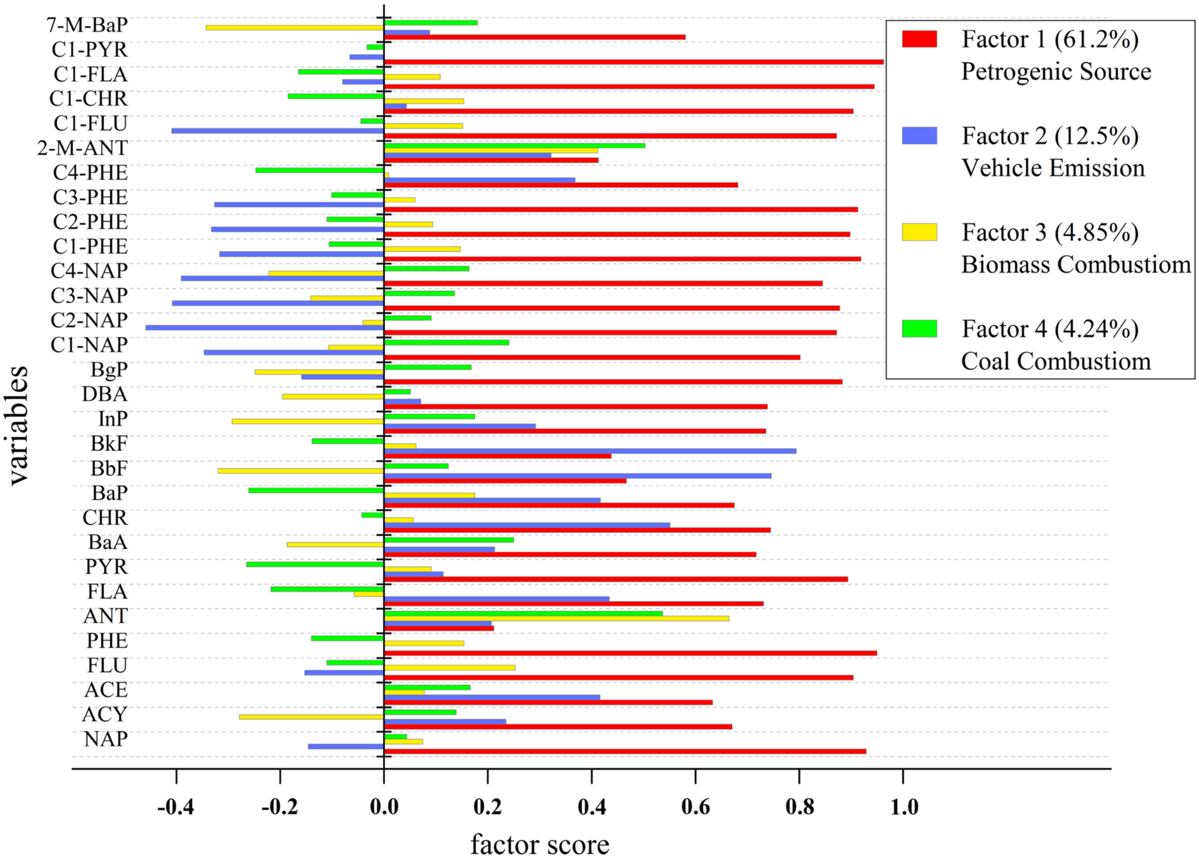

Fig. 4 Factor score of principal component analysis

may be derived from a common source. The petrogenic source PACs were mainly characterized by the dominant 2-ring and 3-ring PAHs (Wang et al., 2013; Zhang et al., 2019), which are also the main components of factor 1. Therefore, factor 1 was identified as a petrogenic source. The variance contribution rate of factor 2 was 12.5%, among which the load of BbF, BkF, and CHR was higher, and their correlation coefficients were 0.83, 0.75, and 0.78, respectively (Table S3). Studies have identified BbF, BkF, and CHR as markers of traffic pollution (Ho et al., 2009; Wang et al., 2013, 2022). Therefore, factor 2 was identified as vehicle emissions. The variance contribution rates of factors 3 was 4.85%, with ACY, FLU, ANT, BbF, InP, BgP and 2-M-ANT being the largest components. Biomass combustion mainly contained ACY, PHE, FLU, ANT, BbF, InP and BgP. ACY, FLU, PHE and ANT are emitted through wood combustion processes (Taghvaee et al., 2018; Wang et al., 2015). Therefore, Factor 3 represented a biomass combustion source. Factor 4 accounted for 4.24%, with ANT, PYR, BaA and 2-M-ANT being the largest contributors. Wang et al. (2013) reported ANT as markers of coal burning, and 2-M-ANT is the methylated derivative of ANT, which is generally generated in the presence of an oxidizing agent. Sulfur and metal elements are oxidized during coal combustion, which is conducive to ANT methylation (Shen, 1999).

PYR can be used as tracers of coal combustion, and BaA can be used as tracers of residential coal combustion (Callen et al., 2014; Chao et al., 2019; Zhang et al., 2019). Therefore, factors 4 were mainly derived from coal combustion.

At the same time, the method of PMF was used to analyze the source of PACs in dust and topsoil from three mining areas for cross-validation (Fig. S5). Four sources derived from PMF model were consistent with PCA, which made the results of source analysis more reliable.

PACs fingerprinting information comparison

The composition characteristics of PACs in coal gangue are similar to dust and topsoil in this work, and APAHs are dominant, accounting for 82% of total PACs (Table S4). No matter fresh or weathered coal gangue, PAC concentrations in Tongting mining area is obviously higher than that in Suntuan and Liuqiao mining area. This is consistent with the high PAC concentrations of dust in Tongting mining area. Additionally, the concentration of PACs in fresh coal gangue was generally higher than that in weathered coal gangue, which indicating that weathering would promote the escape of PACs in coal gangue to the surrounding environment.

As shown in Fig. 5, to verify the source of PACs in dust and topsoil samples, the fingerprinting information of PACs in fresh coal gangue, weathered coal gangue, dust and topsoil were analyzed. It can be seen that the fingerprinting information of coal gangue, dust and soil has a high matching degree, and it is speculated that PACs in dust and topsoil in mining areas were likely to come from coal gangue. Additionally, the relative abundance of C1-C4 NAP and C1-C4 PHE shows a “bell-shaped” distribution, indicating the source of petrogenic. Most current studies regard the petrogenic PACs as petroleum-derived. A typical characteristic of a petroleum source is the “bell-shaped” distribution pattern of APAHs (Hindersmann et al., 2018; Stout, 2007; Youngblood & Blumer, 1975). The overall trend of the samples in the mining area displays a bell-shaped distribution, which is typical of materials originating from coal and other rocks, and coal gangue in the Huaibei coalfield are also petrogenic sources.

Coal mining and processing activities in the Huaibei coalfield have been conducted over a prolonged time and an excess of coal gangue is generated during the production process. Coal gangue simultaneously accumulates in varying degrees in coal mines, coal preparation plants, and nearby power plants. After long-term weathering of coal gangue, PACs gradually migrate to the surrounding soil, resulting in different degrees of pollution in the soil surrounding the mining area. Therefore, PAC pollutants in dust and topsoil in the research area are likely to have originated from spontaneous weathering and escape of coal gangue.

Conclusions

APAHs were the main contributors to PACs in the Huaibei coalfield. The mean concentrations of dust and topsoil were 9197 μg kg^{-1} and 2835 μg kg^{-1}, respectively. This accounted for 80% and 77% of the total amount of PACs. The dust and topsoil of the Huaibei coalfield were dominated by low molecular weight APAHs, which accounted for more than 72% of the total APAHs. Existing contamination assessments do not include APAHs, and the actual risk could be underestimated. Additionally, the spatial distribution patterns of PACs, APAHs, APAHS-2R, and APAHS-3R in dust and topsoil were mostly consistent, indicating that they may have the same pollution source. According to source identification, the PAC pollution in Huaibei coalfield originated from petrogenic source, vehicle emissions, biomass and coal combustion. The PACs fingerprinting information of dust, topsoil, and coal gangue were consistent, indicating that PACs in dust and topsoil may come from coal gangue, a neglected petrogenic source.

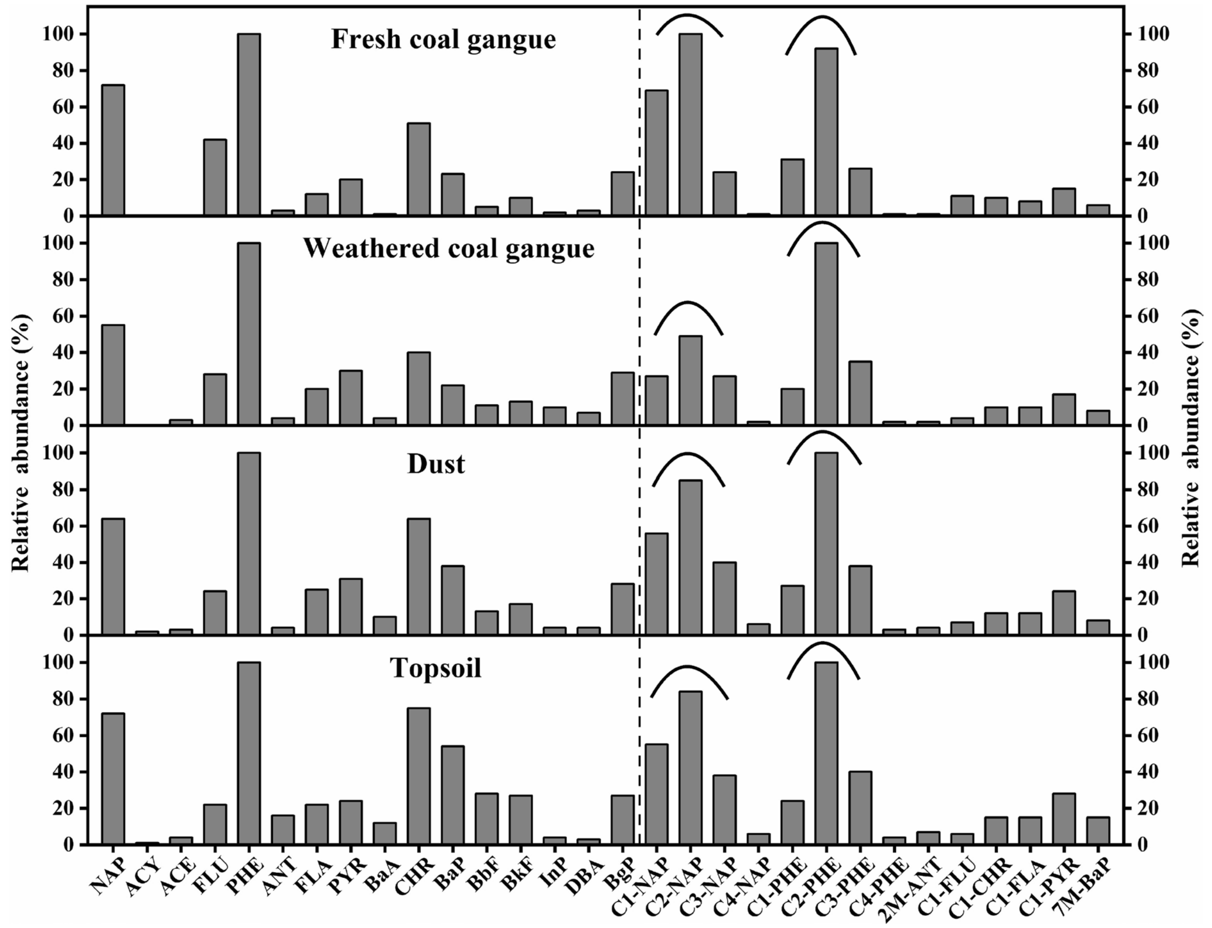

Fig. 5 PACs fingerprint information in different types of samples

Author contribution YQ: Conceptualization, Sample analyses, Data interpretation and presentation, Writing original draft; KY: Image rendering, Data analysis; XH: Sample collection; ZX: Experiments; HL: Supervision, Validation, Review.

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Data availability The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest The authors declared no conflict of interest.

Consent to participate and consent to publish Consent for publication was obtained from all participants.

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