

Sources of Polycyclic Aromatic Hydrocarbons in Street Dust from the Chang-Zhu-Tan Region, Hunan, China

Yongzhen Long^{1*}, Guoxiang Chi², Hairuo Qing², Tagen Dai¹, Qianhong Wu¹

¹Educational Key Laboratory of Non-Ferrous Metal Materials Science and Engineering, Central South University, Changsha, China;

²Department of Geology, University of Regina, Regina, Canada.

E-mail: *Jilllongyz@163.com

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ABSTRACT

Street dusts collected from 20 sites as well as three special dust samples collected from chimney of coal-fired plant, smelter and refinery of nonferrous metals and automobile exhaust, respectively, in the Chang-Zhu-Tan (Changsha, Zhuzhou and Xiangtan) urban region, Hunan, China, in May to August 2009, were investigated for sources of polycyclic aromatic hydrocarbons (PAHs). The Σ PAHs₁₆ levels were in the range of 3515 - 24488 ng/g, with a mean of 8760 ng/g. The sources of PAH inputs to street dusts were determined by isomer ratios, principal components analysis and REE geochemical analysis. The isomer ratios suggested a rather uniform mixture of coal combustion and petroleum PAH sources. Factor analysis indicated that the main sources of 16 PAHs were coal combustion/vehicle exhaust and coking/petroleum. Rare earth elements (REE) and Factor score analysis further indicated the possible dust sources were from background soil, coal or coking combustion, nonferrous metal factories, traffic exhaust.

Keywords: Street Dust, Polycyclic Aromatic Hydrocarbons, Rare Earth Element, Sources of Pollution

1. Introduction

The number and diversity of contaminants in our urban environment have significantly increased in recent years [1]. Current evaluations show that increases of urban dust load, alone or in combination with other pollutants, lead to different health effects [2]. Near-surface atmospheric dust was a mixture of particles of the atmosphere and surface dust of the ground which provided important information for pollution management. These substances can be absorbed or taken in by the body through the respiratory tract and skin, and digested, absorbed, and accumulated in the human body. These harmful substances can also be washed out by precipitated water into the soil and rivers leading to direct pollution of the urban environment [3]. The distribution and concentration of polycyclic aromatic hydrocarbons (PAHs) coated to the dust were paid special attention because of their carcinogenicity, mutagenicity and toxicity, and consequently had been put into the list of priority monitoring pollutants by the United States Environment Protection Agency (USEPA) [4,5]. Monitoring and protecting the atmosphere against the adverse effects of persistent organic pollutants (POPs)

were also the main aims of the European Monitoring and Evaluation Programme (EMEP) on long-range transmission of air pollutants [6]. The widespread distributions of PAHs in dust had been intensively investigated [7-9], especially in industrialized countries. PAHs in the environment largely are a product of the incomplete combustion of petroleum, oil, coal, and wood [10]. Sources in the urban environment include industrial emissions and wastes, power plants, wood and coal, home heating with fuel oil, vehicles, mineral/crude oil extraction and petroleum refining processes [11] as well as pavement sealants, also known as sealcoat [12]. The recognition of these anthropogenic sources was very important for improving city management. In this respect, PAH isomer pair ratios had been widely used to elucidate the possible sources. The ratios between low and high molecular weight PAHs [9] and those of specific compounds, such as Flu/(Flu + Pyr), BaA/(BaA + Chry), Flu/Pyr and BaA/Chry have been proposed as valuable source indicators [13]. Factor analysis has also been used to identify the sources of particulate matter in the atmosphere [14]. The rare earth elements (REEs) are well known for their unique, chemically

coherent behavior which makes them ideal geochemical tracers for many geologic processes [15]. Recently, Gabrielli used rare earth elements to tracer the continental dust origin in EPICA Dome C ice during glacial and interglacial periods [16]. Here, we present REE to trace the sources of street dust as well as PAH isomer pair ratios and Factor Analysis to trace the sources of PAHs in dust. The different methods can be integrated in order to better understand the PAH pollution sources in urban areas [9]. The Chang-Zhu-Tan region, one of the pioneers of urban agglomeration in China as well as the hub of communication in the middle and south China, includes the cities of Changsha, Zhuzhou and Xiangtan, where lots of interstate highways cross these metropolitan areas. The Chang-Zhu-Tan region covers an area of approximate 28,088 km², with its inhabitants population swelling from 12.76 millions in 2005 to 13.10 millions in 2008 [17]. Changsha is the capital and the largest city of Hunan Province, as well as the centre of politics, economy, technology, culture and transportation in Hunan province. Zhuzhou is the second largest city and the largest industry city in Hunan province. Xiangtan is the third largest city and an important industry and transportation center in Hunan province. In the mean time, Hunan is well known for its richness of mineral resources and has the name of "the country of nonferrous metals". Hunan is the number one producer of lead and zinc and among the top three producers of ten nonferrous metals in China [18]. Major nonferrous metals industries are distributed in this region. The major sources of combustion-related organic compounds in this region were coal, crude oil and coking, with annual consumption of 11.79 million tons of coal in 2000 [19], 3.83 million tons of crude oil and 1.93 million tons coking in 2007 [17], followed by natural gas, kerosene, gasoline, liquefied petroleum gas and other fuels, with annual consumption of 41.76, 28.66, 19.83 and 15 million tons, respectively [17]. Coal is largely used for thermal power plants in Zhuzhou and Xiangtan, while coking is largely used for Xiangtan iron and steel works, Zhuzhou Smelter and Refinery of nonferrous metals, Zhicheng Chemical plant and other plants. All sorts of plants with their numerous coal or coking ovens were distributed in this region, especially in Zhuzhou and Xiangtan industrial areas. However, in most case, no distinct borderline existed between industrial areas and other function areas, such as residential and office areas. In the recent years, with the accelerating integration process of Chang-Zhu-Tan region, the concomitant increase in traffic circulation (the annual rate of vehicle numbers increase has maintained 15.5% in the recent 10 years [20], industry productions and population density have adversely impacted the air quality in many quarters of this region. Large amount of data on concentration levels for

suspended particulate Matter (SPM), NO_x, SO₂ and CO are available for these urban areas, which have been found to be consistently much higher than the permissible limit. As things stand, air pollution in this region is largely due to industries and vehicles have also been targeted for tacking air pollution. However, not much attention has been paid to measurements of toxic and mutagenic compounds such as PAHs which affect human health. Relatively little information about these compounds in the dust is available. Therefore, measurements of their levels in the urban dust are of great interest.

This paper reports the sources of PAHs in street dust of the Chang-Zhu-Tan area (longitude from 110°53' to 114°15' and latitude from 26°3' to 28°40'). The concentrations of PAHs were analyzed and their spatial variations were evaluated. The possible sources of PAH contamination were studied using the methods of isomer ratios, principal components analysis and REE analyses. The purpose of the study is to evaluate the current situation of PAHs pollution in this area and their potential controlling factors and to provide a reference for regulatory action to improve environmental quality in this region.

2. Materials and Methods

2.1. Sample Collection Method

Sampling sites were selected in the centre of the three cities, based on different anthropogenic activities such as vehicular traffic density and industrial, commercial as well as other local activities. Sets of stainless steel plates (area 60 × 40 cm², height 5 cm, flat bottom) for collecting bulk deposition (dry and wet depositions mixed together) were placed at eight sites in Changsha, six sites in Xiangtan and Zhuzhou respectively. Sampling was conducted from May 15 to August 5, 2009, with sampling sites described in **Table 1**, while the height of all sampling sites to the ground was about 1.5 m. Besides, the special dust samples ZDD, ZYD and CWG were taken from the chimney of Xiangtan coal-fired power plant, the chimney of Zhuzhou Smelter and Refinery of Nonferrous Metals and automobile exhaust, respectively. Dust particles were wiped off from the bottom of plates with a brush, dried in a desiccator for 48 hours, and then ground using a mortar and pestle and sieved (200 mesh). The samples were refrigerated (4°C) during transport to the laboratory, where they were stored at -20°C until analyzed.

2.2. PAHs Analysis

A PAH analysis procedure was developed after modifications of several PAH analysis methods in the literature

Table 1. Sample sites and environmental data for street dust in Chang-Zhu-Tan region.

Number	Sample ID	Sample site	Representative environment
1	C1	Jinfan district	Densely populated with residential house
2	C2	Wuyi Square	The centre of Commercial and residential in Changsha city
3	C3	Changsha Evening Paper	Commercial area, with heavy traffic intersection
4	C4	Dongtun Ferry	Traffic area near Xiangjiang River
5	C5	Yanzi Nest	Residential area
6	C6	Changsha Southern Bus Station	Area of heavy traffic
7	C7	Changsha Municipal Government	Office area with higher percentage of greenery coverage
8	C8	Changsha Western Bus Station	Traffic area, under the Yulu Mountain
9	Z1	Baoting village	Residential area
10	Z2	Zhicheng Chemical plant	Industrial region of chemical plants
11	Z3	Luojiachong	Residential area, between two high ways
12	Z4	Qinyun village	Restaurant near one main road
13	Z5	Zhuzhou Municipal Government	officer area and shopping center , near one main road
14	Z6	Geological Survey of Zhuzhou Institute	Office area
15	X1	Bantangpu	Industry area, near one main road
16	X2	Jianshe Road	Residential area
17	X3	Xiangtan Eastern Bus Station	Area of traffic
18	X4	Yuetang	Industrial area, near one main road.
19	X5	Xiangtan coal-fired power plant	Industrial area
20	X6	Xiangtan Municipal Government	Office area, at the west of Xiangtan coal-fired power plant
21	ZDD	Xiangtan	the chimney of Xiangtan coal-fired power plant
22	ZYD	Zhuzhou	the chimney of Zhuzhou Smelter and Refinery of Nonferrous Metals
23	CWG	Changsha	automobile exhaust

[8]. Analytical procedure, samples extraction, separation, cleanup and concentrating were carried out in the Key Laboratory of Organic in Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Dust sample (5 g dry weight) was weighed into a Soxhelt extractor, while 200 mL dichloromethane, 2 g activated Cu mesh and surrogate standards were added into a 250-mL flask. Activated Cu was added for desulphurization. A mixture of deuterated PAH surrogate standards (NAP-d8, ACE-d10, PHE-d10, CHR-d12) was added into each sample prior to extraction. Then the sample was Soxhlet-extracted continuously for 48 h at a temperature of 46°C. The extract for each sample was concentrated and solvent-exchanged to hexane, and further purified using 1:2 aluminum/silica column chromatography. The first fraction containing aliphatic hydrocarbons was eluted with 15 ml n-hexane. The second fraction containing PAHs and organochlorine pesticides (OCPs) was eluted with 70 ml of a mixture dichloromethane and n-hexane (V:V = 40:60). The third fraction containing PAEs (phthalate esters) was eluted with 40 ml of a mixture acetone and n-hexane (V:V = 20:80), and the mixture was then concentrated with the rotary evaporator and rationed to 1 ml finally. The PAH fraction was analyzed on a Hewlett-

Packard (HP) 6890II GC with a 5973 MSD operated on the scan mode. The separation was carried out on a 30 m × 0.25 mm i.d.HP-5 (film thickness 0.25 μm) fused-silica capillary column from J&W Co. The column temperature was initially set at 70°C for 6 s, raised to 285°C at the speed of 5°C/min, and then held at 285°C for 12 min. The injection port, interface line, and ion source temperature were maintained at 300°C, 300°C, and 230°C, respectively. Helium with high purity was the carrier gas at a flow of 1.2 ml/min and a linear velocity of 25.4 cm/s at 300°C. The operation time lasted for up to 73 min. The instrument was calibrated daily with calibration standards and the relative percent difference between the five-point calibration and daily calibration was less than 20%. The procedure was also checked for recovery efficiencies by analyzing street dusts spiked with PAH standards. Procedural blanks, spiked blanks (standards spiked into solvent) and sample duplicates were analyzed routinely. Surrogate standards were added to all the samples (including QA samples) to monitor procedural performance and matrix effects. The average recoveries were between 85% - 112%.

2.3. REE Analysis

0.1 g of dried sample (mesh 200) was decomposed in a

polytetrafluoroethylene (PTFE) pressure container by means of a combined HF/HClO₄ (10 mL HF and 4 mL HClO₄). After digestion, the samples were evaporated to incipient dryness and redissolved with HNO₃ for 2 times. The final sample dissolution was performed with 2% HNO₃. Before analysis, Ru and Re solutions were added as internal standards to compensate for instrumental drift. Inductively coupled plasma (ICP) mass spectrometry (MS) analysis of the obtained sample solutions was carried out with an externally calibrated Thermo Electron VG PQ EXCELL quadrupole ICP mass spectrometer. Details on the interference corrections applied to correct analytic isotopes for molecular and isobaric interferences are given by Dulski [21]. The analytical procedure was validated by analysis of international reference standards and repeated independent sample preparation. The relative deviations of the standard analyses to the reference values are below $\pm 6\%$.

2.4. Data Analysis Techniques

Isomer ratios of Flu/(Flu + Pyr) vs BaA/(BaA + Chry), and BaA/(BaA + Chry) vs InP/(InP + BgP) were used to identify the possible sources of PAHs. The principal component analysis (PCA) was conducted to quantify the source contributions of PAHs. The significance level and KMO and Bartlett's test of sphericity were performed to test the adaptability of PCA. The number of significant factors was determined during the stepwise multiple linear regression which identified the factors that significantly improved the regression between the factors and the measured total PAH concentrations [8]. PCA with Varimax rotation was performed using PASW statistics 18 for Windows. The REE patterns of the dust samples are chondrite-normalized concentrations.

3. Results and Discussion

3.1. PAHs Concentrations

The concentrations of individual PAHs ranged from 10 to 4316 ng/g, the most serious species were phenanthrene, fluorene, benzo[b]fluoranthene, pyrene and chrysene, the maximal values of which were 13,947 ng g⁻¹ at site of X5, followed by 9910 and 9372 ng/g at site Z2 and C4, respectively. However, acenaphthene, acenaphthylene, anthracene and dibenz[a,h]anthracene had relatively lower concentration in this regions, which was below 200 ng g⁻¹ in most cases, while many of which had less than 3-ring in their structures. The high molecular weight (HMW) PAHs (4 - 6 rings), ranging from 47.51% to 82.11% (mean of 74.79%), were the dominant PAH compounds in almost all of the dust samples. The Σ PAH16 concentrations ranged from 3515 to 14,470 ng/g in Changsha, 4190 to 13,197 ng/g in Zhuzhou and 9530 to 24,488 ng/g in

Xiangtan and the average concentrations of Σ PAH16 were 8760 ng/g in Chang-Zhu-Tan, 6539 ng/g in Changsha, 6953 ng/g in Zhuzhou and 13,527 ng/g in Xiangtan. The highest Σ PAH16 concentrations corresponded to Xiangtan sampling site X5 (24,488 ng/g), then followed by C4 (14,470 ng/g), X1 (13,337 ng/g) and Z2 (13,197 ng/g). The lowest Σ PAH16 concentrations (3515 ng/g) were observed in site C7, then followed by C8 (3935 ng/g) and C1 (4105 ng/g). The PAH concentrations have been compared with results in street dust from other sites reported in literature (**Table 2**). The Σ PAH16 concentrations in this study were higher than those of Shanghai (3180 to 17,090 ng/g, Mean 8480 ng/g [5]), Beijing (660 to 12,100 ng/g [9]), Berlin (2400 to 21,000 ng/g, Mean 6400 ng/g [1]) and USA (Mean 4520 ng/g Max 15,200 ng/g [22]). However, they were lower than those of indoor dust of Macao (2720 to 24,830 ng/g, Mean 10,660 ng/g [23]). The sum of seven carcinogenic PAHs (Benz[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd] pyrene and Dibenz[a,h]anthracene) ranged from 1293 to 11,709 ng/g, with a mean of 3527 ng/g. Benzo[a]pyrene, which is considered to be the most hazardous of all PAHs (Osborne and Crosby 1987; Cerna *et al.* 2000; Benford *et al.* 2010), was detected in all samples analyzed (ranged from 129 to 1827 ng/g, with a mean of 547 ng/g) and was more than two times higher in Xiangtan (971 ng/g) than those in Changsha (309 ng/g) and Zhuzhou (441 ng/g) cities. Compared with the results in street from other sites reported in literature (**Table 2**), the average concentration of Benzo[a]pyrene in this region (547 ng/g) was higher than those in USA (260 ng/g, [22]) and Macao (300 ng g⁻¹, [23]), however, it was lower than the concentration of Shanghai (1280 ng/g [5]).

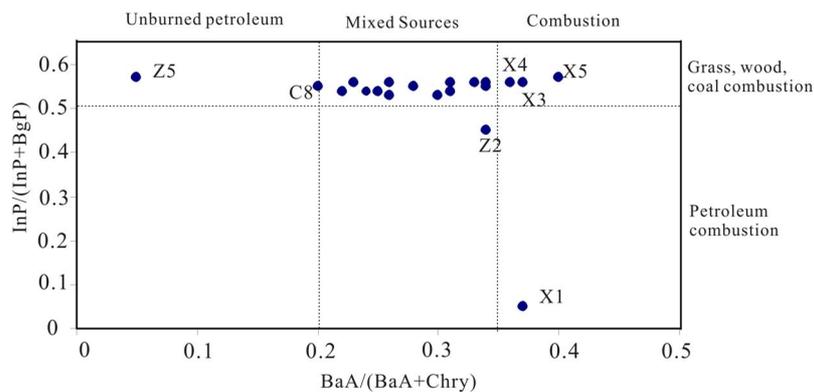
3.2. PAH Isomer Ratios

PAH ratios were widely used as directors to detect PAH sources [5,9,13]. Some PAH pairs ratios, such as Fluo/(Flu + Pyr), BaA/(BaA + Chry) and InP/(InP + BgP), had been used as distinct chemical tracers to infer possible sources of PAHs in environmental samples [8,13]. For Fluo/(Flu + Pyr), ratios < 0.4, 0.4 - 0.5 and >0.5 suggest petroleum origins, petroleum combustion, and combustion origins of coal, grasses and wood, respectively. For InP/(InP + BgP), ratios < 0.2, 0.2 - 0.5, and >0.5 indicated petroleum, petroleum combustion and combustion origins of coal, grasses and wood, respectively [13]. For BaA/(BaA + Chry), ratios < 0.2, 0.2 - 0.35 and 0.35 implied petroleum origins, petroleum or combustion (mixed sources), combustion origins of coal, grasses and wood, respectively. In this study, the corresponding cross plots of the ratios of Fluo/(Flu + Pyr), InP/(InP + BgP) and BaA/(BaA + Chry) are shown in **Figure 1** and **Figure 2**.

Table 2. Comparison of PAHs measurements (ng/g) in street dusts from out door collected in different regions in the world.

	Chang-Zhu-Tan		Changsha		Zhuzhou		Xiangtan		Shanghai		Macao		Berlin		USA	
	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Median	Max	Mean	Max
Nap	459	2212	249	418	375	973	825	2212	530	1310	70	140	200	1900	330	4300
Acy	61	194	51	170	61	194	72	100	Nd	550	50	90	30	100	80	270
Ace	45	190	20	38	49	190	74	112	330	580	20	20	50	260	50	180
Flo	158	720	100	214	194	720	199	311	390	500	6	150	90	240	120	1220
Phe	1380	4316	1066	1917	1468	4316	1711	2260	1640	3580	660	1620	960	2110	440	2150
Ant	125	534	82	183	137	534	171	270	380	370	120	370	70	210	120	750
Flu	1541	3831	1222	2728	1234	2786	2273	3831	520	560	1340	4240	960	3190	520	1890
Pyr	1026	2873	737	1769	845	1826	1593	2873	1460	2980	1960	6150	670	2280	430	1650
BaA	363	1411	228	501	200	340	706	1411	720	1050	450	1200	290	1410	220	690
Chry	790	2146	634	1443	546	650	1243	2146	1060	1840	1920	4000	550	2000	390	2410
BbF	917	2881	866	1578	656	969	1247	2881	970	1440	880	1880	540	1900	#550	#1340
BkF	277	883	217	804	140	220	494	883	830	1080	390	920	370	1910	*250	*610
BaP	547	1827	309	807	441	1292	971	1827	1280	1920	300	700	290	1390	260	750
InP	499	2013	363	973	291	591	887	2013	850	280	640	1510	330	2110	230	630
DbA	135	548	96	227	79	148	242	548	540	930	200	520	50	290	230	700
BgP	438	1543	299	765	239	466	821	1543	760	680	1600	3200	350	1280	100	410
ΣPAH ₁₆	8760	24,488	6539	14,470	6953	13,197	13,527	24,488	8480	17,090	10,660	26,710	☆800	☆22,580	☆4520	☆15,200

Note: #: Sum of Benzo(b)fluoranthene and Benzo(k)fluoranthene; *: the concentration of Coronene; ☆: Sum of ΣPAH₁₆ and Benzo(e)fluoranthene and Coronene.

**Figure 1. PAH cross plots for the ratio InP/(InP + BgP) vs BaA/(BaA + Chry).**

As shown in **Figure 1**, except for the street dusts at the sites of Z5, C8, X3, X4, X1 and X5, the InP/(InP + BgP) Vs BaA/(BaA + Chry) ratios for all the samples within a relatively narrow range of values indicate a major mixed sources of petroleum and combustion, while Z5 and C8, X3 and X4 and X5, X1 indicate a major sources of unburned petroleum, a major combustion of coal, grasses and wood, petroleum combustion, respectively. The results of InP/(InP + BgP) Vs BaA/(BaA + Chry) ratios analysis were confirmed by plotting Flu/(Flu + Pyr) Vs BaA/(BaA + Chry) values except at the site of X1 which indicated a major combustion of coal, grasses and wood

source (**Figure 2**).

3.3. PCA Analysis

Principal component analysis (PCA) was performed to separate PAHs having similar sources and modes of input [8]. PCA of the PAHs for Chang-Zhu-Tan dusts resulted in the first two factors (62.49, 23.28, respectively) accounting for 85.77% of the total variability (**Table 3**). Factor 1 was heavily weighted by pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, and benzo[ghi]perylene. Benz[a]anthra-

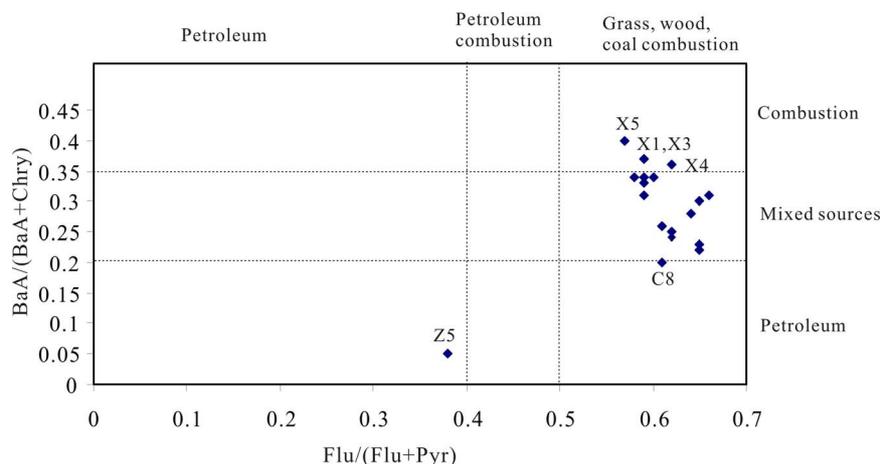


Figure 2. PAH cross plots for the ratio BaA/(BaA + Chry) vs Flu/(Flu + Pyr).

Table 3. Rotated component Matrix of PAHs in street dusts of Chang-Zhu-Tan region.

	Nap	Acy	Ace	Flo	Phe	Ant	Flu	Pyr	BaA	Chry	BbF	BkF	BaP	InP	DbA	BgP	Variance (%)
Factor1	0.46	0.19	0.22	-0.04	0.15	0.16	0.69	0.75	0.90	0.92	0.78	0.91	0.84	0.93	0.95	0.96	62.49
Factor2	0.42	0.85	0.93	0.99	0.97	0.98	0.69	0.65	0.33	0.30	0.06	0.22	0.10	0.05	0.06	0.17	23.28

cene, chrysene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, and benzo[ghi]perylene were consistent with the emission characteristics of PAHs from coal combustion and vehicle emission in China [24], while benzo[b]fluoranthene was consistent with the emission of diesel [7] (Simcik *et al.* 1999).

Factor 2 had a significant positive loading of 2 - 3 ring acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene (Table 3), which could be considered as combined components of petroleum [7] and coking sources [25]. Table 4 showed that at sites of X5, C4, X6 and X2 were characterized by higher score of factor 1 as well as at sites of Z2 and X1 were characterized by higher score of Factor 2.

3.4. REE Distribution

The concentration of REEs and the chondrite-normalized REE patterns in dust samples, background soils [26] and the three special dust samples from Chang-Zhu-Tan region were presented in Table 5 and Figure 3, respectively. The content of total rare earth elements (Σ REE) of dust samples varied from 47.3 to 261.09 $\mu\text{g/g}$ which were

lower than that of the background soil samples except for the sample at the site of Z2 (261.09 $\mu\text{g/g}$) and higher than the values of CWG (8.11 $\mu\text{g/g}$) and ZYD (65.49 $\mu\text{g/g}$) except for the sample at the site of C4 (47.30 $\mu\text{g/g}$). The concentration of the light rare earth elements (LREEs) was higher than that of the heavy rare earth elements (HREEs). The LREE/HREE ratios of the dust samples varied from 3.34 to 10.92, which were similarly to those of ZYD, ZDD and the background soil samples except for the sample at the site C4 which was similar to that of CWG. Almost all the samples showed a negative Ce and Eu anomaly except samples at the sites of X1 and X4, C-soil and ZYD showed positive Ce anomaly and samples at sites of C2, C4, Z6, X1, X3 and X4, CWG and ZYD showed positive Eu anomaly.

3.5. Sources Trace by REE and PCA Analysis

The sample at site of C4 showed a negative Ce and a positive Eu anomaly with a similar chondrite-normalized REE pattern to that of CWG (Figure 3 Changsha) which suggested similar dust sources between the sample at site

Table 4. Factor scores for PAHs in street dusts of Chang-Zhu-Tan region in principal component analysis (PCA).

	Changsha								Zhuzhou						Xiangtan					
	C1	C2	C3	C4	C5	C6	C7	C8	Z1	Z2	Z3	Z4	Z5	Z6	X1	X2	X3	X4	X5	X6
Score of F1	-0.62	-0.38	0.00	1.04	-0.41	-0.56	-0.80	-0.66	-0.54	-1.54	-0.41	-0.58	-0.32	0.01	0.39	0.73	0.44	0.24	3.35	0.62
Score of F2	-0.70	-0.22	-0.05	0.57	-0.58	-0.64	-0.57	-0.62	-0.28	3.73	-0.47	-0.70	-0.74	-0.45	0.93	-0.08	0.23	-0.07	0.50	0.20

Table 5. Rare earth element contents (g/g) in samples and associated geochemical parameters.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣLREE	ΣHREE	ΣREE	L/H	Ce/Ce*	Eu/Eu*
C1	27.29	51.06	5.79	19.31	3.77	0.88	3.44	0.52	2.36	0.59	1.78	0.29	1.93	0.30	108.10	11.20	119.30	9.65	0.85	0.83
C2	20.77	38.05	4.51	15.29	3.06	0.94	3.04	0.44	1.97	0.50	1.45	0.24	1.56	0.24	82.62	9.43	92.05	8.76	0.82	1.05
C3	25.73	48.56	5.42	18.08	3.51	0.81	2.98	0.47	2.21	0.54	1.59	0.27	1.73	0.27	102.11	10.06	112.17	10.15	0.86	0.86
C4	10.50	15.00	2.44	5.55	2.03	0.87	2.51	0.60	2.37	0.63	1.92	0.33	2.22	0.32	36.39	10.90	47.30	3.34	0.62	1.31
C5	29.71	59.34	6.09	21.91	3.88	0.89	3.21	0.49	2.55	0.59	1.78	0.29	1.95	0.30	121.82	11.16	132.98	10.92	0.92	0.86
C6	22.43	43.07	4.76	17.25	3.10	0.66	2.55	0.40	2.09	0.46	1.40	0.23	1.51	0.24	91.27	8.87	100.14	10.29	0.87	0.80
C7	34.26	66.86	7.61	24.30	4.85	1.04	3.74	0.64	3.00	0.76	2.20	0.38	2.48	0.39	138.92	13.60	152.52	10.22	0.86	0.83
C8	25.34	49.22	5.75	18.98	3.85	0.85	3.32	0.52	2.44	0.61	1.83	0.31	2.06	0.32	104.00	11.40	115.40	9.12	0.85	0.81
Z1	30.67	55.37	6.79	21.76	4.45	0.90	3.63	0.63	3.04	0.76	2.22	0.38	2.43	0.37	119.94	13.43	133.37	8.93	0.80	0.77
Z2	57.37	105.40	13.55	44.80	9.43	1.73	7.05	1.36	7.05	1.76	4.88	0.81	5.14	0.76	232.28	28.81	261.09	8.06	0.79	0.72
Z3	26.35	49.25	5.92	19.49	3.96	0.86	3.50	0.56	2.75	0.68	2.06	0.34	2.29	0.35	105.82	12.52	118.34	8.46	0.82	0.79
Z4	30.45	58.14	6.81	15.35	4.88	0.93	4.11	0.72	3.17	0.85	2.55	0.44	2.81	0.42	116.56	15.06	131.62	7.74	0.83	0.72
Z5	26.07	49.14	5.89	20.17	4.13	0.82	3.70	0.56	2.55	0.65	1.90	0.31	2.09	0.32	106.23	12.07	118.30	8.80	0.83	0.72
Z6	29.37	49.87	6.32	19.20	4.04	1.25	3.37	0.56	2.72	0.68	2.01	0.34	2.19	0.34	110.05	12.21	122.26	9.01	0.76	1.16
X1	13.30	49.31	3.33	12.38	3.87	1.23	3.49	0.56	2.42	0.67	2.03	0.34	2.28	0.35	83.41	12.14	95.55	6.87	1.54	1.14
X2	24.46	47.65	5.59	18.76	3.87	0.99	3.51	0.55	2.51	0.64	1.91	0.32	2.10	0.33	101.31	11.88	113.19	8.53	0.85	0.91
X3	26.67	52.81	5.92	13.44	4.21	1.24	3.21	0.55	2.46	0.69	2.08	0.36	2.40	0.38	104.29	12.13	116.42	8.60	0.88	1.15
X4	10.35	45.00	2.88	9.46	3.02	1.12	2.59	0.42	1.86	0.53	1.58	0.27	1.69	0.27	71.83	9.21	81.04	7.80	1.72	1.36
X5	27.42	49.33	5.76	18.81	4.05	0.96	3.16	0.55	2.53	0.64	1.88	0.32	2.10	0.33	106.33	11.52	117.84	9.23	0.82	0.91
X6	24.00	46.19	5.03	19.00	3.60	0.98	3.83	0.57	2.64	0.62	1.88	0.30	1.97	0.31	98.81	12.12	110.93	8.15	0.88	0.90
C-soil	37.86	103.50	8.66	31.17	5.29	1.12	5.52	0.99	5.82	1.16	3.54	0.59	3.39	0.52	187.60	21.53	209.13	8.71	1.19	0.71
Z-soil	50.93	112.10	12.45	47.16	8.92	1.96	7.86	1.34	6.95	1.15	3.31	0.57	3.70	0.58	233.51	25.46	258.97	9.17	0.93	0.80
X-soil	45.56	97.71	10.74	37.99	6.87	1.53	6.34	1.02	5.65	1.29	3.36	0.55	3.57	0.58	200.40	22.35	222.75	8.97	0.92	0.79
CWG	2.33	1.53	0.54	0.98	0.44	0.24	0.51	0.14	0.51	0.12	0.34	0.07	0.31	0.05	6.06	2.05	8.11	2.96	0.28	1.76
ZYD	9.47	40.61	1.86	5.89	1.34	0.56	1.64	0.24	1.12	0.45	1.11	0.16	0.90	0.15	59.73	5.76	65.49	10.37	2.02	1.29
ZDD	27.81	53.58	6.36	21.66	4.84	0.98	4.36	0.70	3.48	0.86	2.25	0.43	2.56	0.40	115.24	15.04	130.28	7.66	0.84	0.73

L/H = LREE(La-Eu)/HREE(Gd-Lu); Ce/Ce* = Cen/(Lan × Pm) 0.5; Eu/Eu* = Eun/(Smn × Gdn) 0.5; subscripts n stands for chondrite-normalized value; C-soil, Z-soil and X-soil (Changsha, Zhuzhou and Xiangtan background soil in 2006, respectively): Dai *et al.* 2008.

of C4 and CWG (automobile exhaust). However, the REE concentrations at site C4 were higher than those of CWG which may be attributed to a small proportion of background soil in the dust sample. As shown in **Table 1**, C4 located in a busy ferry of Xiangjiang River, Changsha, where ships and trucks used diesel as well as cars used petroleum. The PCA analysis also indicated that C4 has high score of factor 1 which was consistent with the emission characteristics of PAHs from coal combustion and vehicle emission. It could be inferred that the PAHs pollution at the site of C4 mainly come from traffic emission. The sample from C7 showed high LREEs enrichment and negative Ce and Eu anomaly with a similar chondrite-normalized REE pattern to that of C-soil sample (**Figure 3** Changsha). As mentioned before, C7 bearing the lowest total PAH concentrations in this region

was located in an Office area and far away from any factories. It could be inferred that the dust as well as the PAHs pollution at C7 mainly come from the background soil. The sample from C2 showed relatively low LREEs enrichment and positive Eu and negative Ce anomalies with chondrite-normalized REE pattern between that of ZDD and CWG samples (**Figure 3** Changsha), which implied a mixed dust pollution sources. The other samples of Changsha city (from sites of C1, C3, C5, C6 and C8) showed negative Ce and Eu anomalies with similar chondrite-normalized REE patterns to that of ZDD sample (**Figure 3** Changsha), which suggested that those dusts may have been derived from a similar sources of ZDD as well as the PAHs pollution mainly from coal or coking combustion.

The sample from Z2 showed significant high LREEs

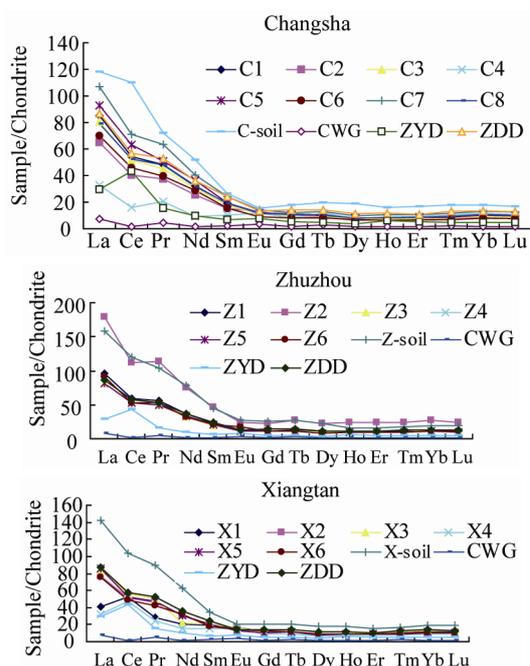


Figure 3. Chondrite-normalized patterns for Chang-Zhu-Tan dust and background soil samples. Note: C-soil, REE Values of Changsha background soil in 2006 (Dai *et al.*, 2009); Z-soil REE Values of Zhuzhou background soil in 2006 (Dai *et al.*, 2009); X-soil, REE Values of Xiangtan background soil in 2006 (Dai *et al.*, 2009).

enrichment and characteristic negative Ce and Eu anomalies (Figure 3 Zhuzhou), however, its chondrite-normalized REE pattern was different from that of the Z-soil (whose L/H was lower than that of Z-soil) and approximately parallel to that of ZDD sample (Figure 3 Zhuzhou), as mentioned before, Z2 located in Zhicheng Chemical plant (Table 1) and characterized by high score of Factor 2 (Table 5) which was attributed to petroleum and coking sources. It could be inferred that the chemical production and coking combustion used in the chemical production should be its major PAH sources. The other samples in Zhuzhou city showed similar chondrite normalized REE patterns to that of ZDD sample (Figure 3 Zhuzhou). Thereby, a good connection between the dust samples at sites of Z1, Z3, Z4, Z5, Z6 and the sample ZDD must be assumed. It would be inferred that the sources of PAHs pollution mainly come from coal or coking combustion.

The samples from X1 and X4 showed positive Ce and Eu anomalies with similar chondrite-normalized REE patterns to that of the ZYD sample (Figure 3 Xiangtan), which suggested the samples from X1 and X4 have been derived from a similar source of ZYD. Table 1 showed that X1 and X4 were located in Bantang industrial area and Yuetang industrial area, respectively, and near main

highways. PAC analysis also showed high score of factor 2 at site of X1 and moderate scores of factor 1 at sites of X1 and X4. It could be inferred that the sources of PAHs pollution at X1 and X4 mainly come from industrial production (Smelter and Refinery of Nonferrous Metals production), then from the petroleum emission of vehicles. At the sites of X2, X5 and X6, the samples showed negative Ce and Eu anomalies with similar REE patterns to that of the ZDD sample. As Table 1 showed, X5 located in Xiangtan coal-fired power plant and X6 located in an office area but near the Xiangtan coal-fired power plant, while X2 located in a residential area where coal was the main fuel for the residents. The PCA analysis also indicated that at sites of X2, X5 and X6 had high scores of factor 1. It should be inferred that the dust as well as the PAHs pollution mainly come from coal combustion. The sample from X3 showed negative Ce and positive Eu anomalies with chondrite-normalized REE patterns between ZDD and ZYD (Figure 3 Xiangtan). As mentioned before, X3 was located in Xiangtan Eastern Bus Station, a traffic area and shopping centre, characterized by moderate high scores of factor 1 and factor 2 (Table 4), which suggested a mixed PAHs pollution sources.

The present study also indicates that the heavy PAHs pollution sites corresponded to the areas where factories, heavy traffic were interweaved, while the light PAHs pollution sites corresponded to the areas where far away from any factories. However, the boundaries among the industry areas, resident area, office areas and traffic areas were not distinct. They always weaved together and almost all of the PAHs in this region had mixing sources, which corresponds to the results of the PAH isomer ratios, PCA and REE analysis as well as the energy structure of this region.

4. Conclusions

The PAH levels in dust of Chang-Zhu-Tan urban region were relatively high worldwide. The spatial variation of the PAH concentrations was significantly connected to the distribution of factories which was associated with coal or coking combustion and traffic circulation. Isomer ratios and factor analysis indicated that the main sources of PAHs were the mixing of coal combustion/traffic emissions and coking/petroleum combustion, REE analysis and Factor scores concretely showed the possible dust sources of each sample sites. The major PAHs pollution was coal or coking combustion from all sorts of factories and families, then, followed by traffic exhaust.

The PAHs pollution in dust of Chang-Zhu-Tan urban region should be reduced by means of reducing coal and coking combustion, controlling the number of cars as well as planning residential areas away from the Indus-

trial and traffic zones.

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