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Polycyclic aromatic hydrocarbons (PAHs) and their derivatives (alkyl-PAHs, oxygenated-PAHs, nitrated-PAHs and azaarenes) in urban road dusts from Xi'an, Central China

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HIGHLIGHTS

- PAHs, AZAs, OPAHs and NPAHs were measured in road dusts and surface soils.
- Higher loadings of PACs in road dusts particularly for PACs with MW > 192 g mol^{-1}.
- Dust:soil EFs of individual PACs are significantly correlated with log K_{OA} and log K_{OW}.
- PAHs, OPAHs and AZAs are mostly emitted from combustion activities while NPAHs not.
- ILCR model suggests a non-negligible cancer risk of road dusts to residents.

ARTICLE INFO

ABSTRACT

Urban road dusts are carriers of polycyclic aromatic compounds (PACs) and are therefore considered to be a major source of contamination of other environmental compartments and a source of exposure to PACs for urban populations. We determined the occurrence, composition pattern and sources of several PACs (29 alkyl- and parent-PAHs, 15 oxygenated-PAHs (OPAHs), 4 azaarenes (AZAs), and 11 nitrated-PAHs (NPAHs)) in twenty urban road dusts and six suburban surface soils (0–5 cm) from Xi'an, central China. The average concentrations of $\sum$29PAHs, $\sum$4AZAs, $\sum$15OPAHs, and $\sum$11NPAHs were 15 767, 673, 4754, and 885 ng g^{-1} in road dusts and 2067, 784, 854, and 118 ng g^{-1} in surface soils, respectively. The concentrations of most individual PACs were higher in street dusts than suburban soils, particularly for PACs with molecular weight >192 g mol^{-1}. The enrichment factors of individual PACs were significantly positively correlated with log K_{OA} and log K_{OW}, indicating an increasing deposition and co-sorption of the PACs in urban dusts with decreasing volatility and increasing hydrophobicity. Significant correlations between the concentrations of individual and sum of PACs, carbon fractions (soot and char), and source-characteristic PACs (combustion-derived PAHs and retene, etc.), indicated that PAHs, OPAHs and AZAs were mostly directly emitted from combustion activities and had similar post-emission fates, but NPAHs were possibly more intensely photolyzed after deposition as well as being emitted from vehicle exhaust sources. The incremental lifetime cancer risk (ILCR) resulting from exposure to urban dust bound-PACs was higher than 10^{-6}, indicating a non-negligible cancer risk to residents of Xi'an.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic contaminants containing two or more fused benzene rings that occur ubiquitously in environmental matrices worldwide, alongside elemental carbon (EC) (Han et al., 2015). Oxygenated-PAHs (OPAHs) and nitrated-PAHs (NPAHs) are derivatives of PAHs with hydrogen on the aromatic ring substituted by carbonyl- and nitro-functional groups, respectively (Atkinson and Arey, 1994; Lundstedt et al., 2007), whereas azaarenes (AZAs) are a group of heterocyclic PAHs containing one nitrogen atom in place of a carbon atom in the aromatic ring (Bleeker et al., 1999). Some OPAHs, NPAHs, and AZAs have been recognized as similarly or more toxic than their parent-PAHs (Atkinson and Arey, 1994; Bleeker et al., 1999; Lundstedt et al., 2007).

All PACs (PAHs, OPAHs, NPAHs, and AZAs) and EC are mainly formed and released into the environment from the incomplete combustion of carbon-based materials (Bleeker et al., 1999; Lundstedt et al., 2007; Han et al., 2015). Because OPAHs, AZAs, alkyl-PAHs and their parent-PAHs are constituents of liquid fuels/petroleum products (diesel, gasoline, tar products, etc.), spillage of these products during their processing, transport, and usage is an additional source of these PACs (Lundstedt et al., 2007; Bandowe et al., 2014a). There are also natural sources of AZAs (e.g., microbial mycotoxins and plant-produced alkaloids) (Bleeker et al., 1999) and PAHs (e.g., naphthalene and perylene) (Wilcke et al., 1999) in the environment. Furthermore, OPAHs and NPAHs are also formed from post-emission transformation of PAHs by photo-chemical oxidation (reactions with O_3, OH, and NO_x) and biodegradation (Arey et al., 1986; Atkinson and Arey, 1994; Lundstedt et al., 2007; Tsapakis and Stephanou, 2007).

Urban road dusts on paved roads in cities is a mixture containing significant quantities of organic pollutants (e.g., PAHs, NPAHs), toxic heavy metals, EC, and its subdivided char and soot fractions (Rogge et al., 1993; Ho et al., 2003; Han et al., 2009). Char is carbonaceous materials obtained directly from the pyrolysis of organic substances or combustion residues, while soot consists of submicron particles formed at high temperatures (>600 °C) via gas-to-particle conversion of molecular precursors (Schmidt and Noack, 2000; Han et al., 2015). There are many diverse sources of paved road dusts, such as automobile exhaust, lubricating oil residues, weathered street surface particles, particles from the wear of tires and brake linings, soils, and biogenic material (e.g., leaf detritus from trees growing near streets) (Rogge et al., 1993). Atmospheric transport and deposition also introduces pollutants from other anthropogenic or natural sources from outside the specific paved road area (Rogge et al., 1993). Road dusts can easily be re-suspended to become airborne particles through wind scavenging and vehicle-induced turbulences (Rogge et al., 1993; Lorenzi et al., 2011). Furthermore, urban dusts act as carriers of toxic substances into other environmental compartments (water bodies, plants, air etc.) via street and urban runoff, re-suspension and re-deposition, and through the municipal sewage system which pose a threat to the ecosystem and human health (Mostafa et al., 2009). For urban residents, ingestion, dermal contact, and inhalation of the re-suspended dusts are the main routes of exposure to road dusts and the toxic organic pollutants they contain, which can induce adverse effects on human health (U.S.EPA, 2001; Shi et al., 2011; Wang et al., 2011).

Some studies have measured OPAHs and NPAHs in road dust standard reference materials (SRM 1649 and 2975) (Durant et al., 1998; Albinet et al., 2006; Mirivel et al., 2010; Nocun and Schantz, 2013), but little is known about their concentrations, patterns of composition, spatial distribution, and cancer risk in real environmental matrices such as road dusts (Rogge et al., 1993; Oda et al., 2001; Prycek et al., 2007) and soils (Bandowe et al., 2014a; Wilcke et al., 2014), and their relationship with parent-PAHs and carbon fractions (Liu et al., 2007; Wilcke et al., 2014). The objectives of this study were: (1) to determine the concentrations and patterns of composition of PAHs, AZAs, OPAHs, and NPAHs in road dusts and suburban soils from Xi'an; (2) to assess the relationship of the concentrations of PAH derivatives with those of their parent-PAHs and of all PACs concentrations, and with those of various carbon fractions in road dusts; and (3) to assess the probable carcinogenic risk via ingestion, dermal contact, and the inhalation of urban dust with a particular focus on the PAH derivatives.

2. Materials and methods

Twenty road dust samples were collected from paved road surface in Xi'an as previously described by Han et al. (2009), and six surface soil samples (0–5 cm) were simultaneously collected from suburban area in southern Xi'an (Fig. S1). All samples were freeze-dried, sieved (75 μm), and preserved in a refrigerator at −4 °C before analysis. Concentrations of 29 parent- and alkyl-PAHs ($\sum$29PAHs), 4 AZAs ($\sum$4AZAs), 15 OPAHs ($\sum$15OPAHs) and 11 NPAHs ($\sum$11NPAHs) (Tables 1, S1) were determined following techniques used in previous studies (Bandowe et al., 2014b; Lundstedt et al., 2014; Wei et al., 2015). Total organic carbon (TOC) and total nitrogen were measured using a CHN Elemental Analyzer (Vario EL III, Elementar Analysensysteme, Hanau, Germany) following Han et al. (2015). EC, char and soot were determined using a Thermal/Optical Carbon Analyzer (DRI Model 2001, Atmoslytic Inc. Calabasas, CA, USA) using the IMPROVE protocol following Han et al. (2009). Details of the sampling, analytical procedures, quality assurance/control, and calculations of enrichment factor (EF) of PACs and incremental lifetime cancer risk (ILCR) of road dusts are further explained in the Supplementary materials.

3. Results and discussion

3.1. PACs concentrations in surface soils

The concentration of $\sum$29PAHs in suburban surface soils averaged 2067 ± 1097 ng g^{-1} (Table 1). The concentrations of 16 U.S. EPA PAHs ($\sum$16PAHs) in suburban soils were about one order of magnitude higher than those of the surface soils from the surrounding Guangzhong Plain (GZP) (Han et al., 2015), and at the lower end of concentrations reported in soils from other major Chinese cities (Table S2) such as Beijing (Tang et al., 2005) and Shanghai (Jiang et al., 2009), but higher than in soils from Hong Kong (Zhang et al., 2006), which was possibly because of better emission control and environmental protection measures in Hong Kong than in mainland China. Concentrations of $\sum$16PAHs and $\sum$29PAHs were also higher than those measured in soils from background locations in Argentina (Wilcke et al., 2014) and Bangkok, Thailand (Wilcke et al., 1999), within the range measured in New Delhi (Agarwal et al., 2009), several European and North American cities (Wilcke, 2007; Bandowe et al., 2011), but lower than in soils of industrial and waste deposit areas of Uzbekistan, Slovakia, Germany, and Sweden (Lundstedt et al., 2007; Bandowe et al., 2010, 2011) (Table S2). The composition of the PAH mixtures in surface soils were on average dominated by phenanthrene > fluorene > anthracene (Fig. 1). Large contributions of phenanthrene to the total PAHs were also found in the surrounding GZP soils and Wei River sediments (Han et al., 2015). The average $\sum$low molecular weight (LMW)-PAHs/$\sum$high molecular weight (HMW)-PAHs in soils was 4.68 ± 1.04, probably because LMW-PAHs, which

Table 1
Concentrations of PACs and carbon fractions in surface soils and road dusts from Xi'an.

Analytes	TEF[b]	Surface soil (n = 6)				Road dust (n = 20)			
		Min[b]	Max[b]	Mean	SD[b]	Min[b]	Max[b]	Mean	SD[b]
PAHs (ng g⁻¹)									
1,2,3,4-Tetrahydronaphthalene		n.d.[b]	1.3	0.6	0.5	0.3	28.3	7.0	6.8
Naphthalene	0.001[c]	25.2	122.5	55.1	34.6	229.8	761.0	432.4	157.0
2-Methylnaphthalene	0.001[c]	21.6	122.1	59.8	35.0	123.5	622.8	258.9	132.1
1-Methylnaphthalene	0.0025[d]	29.2	105.6	63.3	28.5	135.1	534.1	287.3	95.1
Biphenyl		39.5	163.5	78.2	44.8	116.5	442.5	244.3	85.0
1,3-Dimethylnaphthalene		48.7	141.8	81.4	35.9	194.2	512.5	340.2	92.0
Acenaphthylene	0.001[c]	5.1	31.2	13.5	9.1	26.0	107.2	45.8	19.4
Acenaphthene	0.001[c]	19.6	90.3	54.7	26.7	65.1	264.8	126.9	54.9
Fluorene	0.0005[e]	61.6	239.7	136.0	64.8	181.8	549.8	290.4	92.2
Phenanthrene	0.0005[e]	546.9	1998.7	928.0	539.2	2682.1	5004.5	3514.9	632.9
Anthracene	0.0005[e]	84.9	226.7	114.5	55.4	188.3	679.9	365.7	124.4
2-Methylphenanthrene		53.0	205.8	93.1	57.1	464.4	1186.8	735.3	178.2
3,6-Dimethylphenanthrene		9.7	48.6	22.0	16.6	155.4	617.5	302.9	110.8
Fluoranthene	0.05[e]	23.6	79.0	44.2	27.0	338.5	1521.8	824.2	247.7
Pyrene	0.001[e]	20.1	79.1	44.0	26.7	289.6	1778.7	868.1	349.2
Retene		36.9	195.2	83.8	66.6	609.6	4887.1	2040.9	1060.6
Benzo[a]anthracene	0.005[e]	12.7	41.5	22.3	12.0	242.3	2505.3	1219.4	572.6
Chrysene + Triphenylene	0.03[e]	6.4	20.9	13.4	5.0	164.1	964.2	445.6	173.2
Benzo[b + j + k]fluoranthenes[a]	0.1[f]	37.5	112.2	69.8	29.8	334.7	3386.0	1224.7	641.5
Benzo[e]pyrene	0.002[e]	14.5	50.3	28.5	13.4	187.1	1480.3	637.4	310.1
Benzo[a]pyrene	1[e]	6.6	19.6	11.8	5.2	72.8	861.2	271.0	170.1
Perylene	0.001[g]	2.2	6.8	4.0	1.6	22.5	242.1	73.9	46.5
Indeno[1,2,3-cd]pyrene	0.1[e]	8.9	28.5	16.3	7.5	116.3	1378.3	481.4	266.0
Dibenzo[a,h]anthracene	1.1[e]	3.7	10.5	5.9	2.7	58.6	508.7	181.0	94.1
Benzo[g,h,i]perylene	0.02[e]	7.6	29.3	14.6	8.0	90.0	820.8	328.3	158.9
Coronene	0.01[e]	5.5	12.9	8.6	2.9	63.0	439.1	219.3	93.4
∑LMW-PAHs[a]		745	2693	1302	707	3571	6437	4776	842
∑HMW-PAHs[a]		164	488	283	137	1979	15887	6774	3002
∑Comb-PAHs[a]		161	481	280	135	1957	15645	6700	2958
∑6alk-PAHs[a]		232	819	404	229	2483	7886	3965	1444
∑21PAHs[a]		909	3181	1585	828	7745	20636	11550	3372
∑16PAHs		883	3111	1544	811	7259	18475	10620	2946
∑29PAHs		1181	4164	2067	1097	10422	26259	15767	4375
Azaarenes (ng g⁻¹)									
Quinoline		363.0	1261.4	761.3	320.2	136.8	726.1	301.6	153.5
Benzo[h]quinoline		8.5	26.8	13.9	6.6	61.6	181.3	98.7	34.8
Acridine		0.4	1.8	1.0	0.6	17.1	77.8	38.0	17.8
Carbazole		4.0	14.2	7.5	3.8	67.9	535.7	235.0	103.1
∑4 AZAs		376	1304	784	330	440	1171	673	199
OPAHs (ng g⁻¹)									
1-Indanone		32.4	59.7	45.8	11.1	58.9	177.6	98.7	27.9
1,4-Naphthoquinone		2.2	10.7	6.9	3.7	31.1	234.7	76.1	45.6
1-Naphthaldehyde		7.9	35.0	17.6	9.4	48.1	119.2	78.4	20.8
2-Biphenylcarboxaldehyde		10.9	22.8	15.3	4.9	11.0	38.3	20.6	6.7
9-Fluorenone		371.0	1243.8	603.8	338.0	680.1	1968.6	1055.6	337.4
1,2-Acenaphthenequinone		2.4	6.7	3.7	1.6	31.2	292.1	103.3	64.9
9,10-Anthraquinone		36.7	92.9	56.8	19.5	139.3	1024.3	492.7	211.5
1,8-Naphtalic anhydride		0.2	9.7	3.1	3.9	30.6	2286.0	253.9	485.0
4H-Cyclopenta[d,e,f]phenanthrenone	0.005[d]	12.2	48.0	20.7	13.8	133.8	360.4	243.7	72.4
2-Meth-9,10-anthraquinone		7.9	27.7	14.6	7.9	129.0	571.4	326.6	108.0
Benzo[a]florenone		7.1	37.0	16.3	12.0	165.4	1084.1	643.7	217.6
7H-Benzo[d,e]anthracen-7-one	0.0039[d]	3.5	19.2	11.2	5.4	68.8	597.7	242.1	124.4
Benzo[a]anthracene-7,12-dione		12.1	58.1	22.0	17.9	92.8	1200.8	497.0	322.3
5,12-Naphthacenequinone		2.9	28.6	9.6	10.4	140.1	1162.4	508.0	301.6
6H-Benzo[c,d]pyren-6-one	0.32[d]	2.0	10.7	6.4	4.4	27.6	209.4	113.7	58.6
∑15OPAHs		523	1692	854	447	2799	7824	4754	1467
NPAHs (ng g⁻¹)									
1-Nitronaphthalene		0.4	1.8	0.9	0.5	0.4	23.9	11.6	7.1
2-Nitrobiphenyl		0.0	0.4	0.2	0.1	0.5	11.8	4.8	3.3
5-Nitroacenaphthene	0.01[f]	0.5	3.5	1.3	1.1	1.2	544.6	185.1	148.1
2-Nitrofluorene	0.01[f]	0.2	0.8	0.4	0.2	3.6	80.5	37.6	21.8
9-Nitrophenanthrene		0.4	1.9	1.2	0.6	10.7	103.6	55.1	25.3
9-Nitroanthracene	0.0032[d]	0.1	0.7	0.4	0.2	3.2	39.0	22.2	8.8
(2 + 3)-Nitrofluoranthenes[a]	0.0026[d]	5.2	16.3	11.2	4.3	22.1	207.8	82.5	44.0
1-Nitropyrene	0.1[f]	2.3	6.0	4.0	1.3	6.4	67.5	25.1	18.8
2,7-Dinitrofluorene		13.0	39.0	25.0	9.8	53.5	725.3	194.9	138.7
6-Nitrochrysene	10[f]	5.7	11.4	8.0	3.0	17.7	137.9	63.9	32.8
6-Nitrobenzo[a]pyrene		49.9	86.1	65.0	18.8	51.2	662.2	202.2	177.4
∑11NPAHs		29	158	118	52	404	2258	885	464

Table 1 (continued)

Analytes	TEF[b]	Surface soil (n = 6)				Road dust (n = 20)			
		Min[b]	Max[b]	Mean	SD[b]	Min[b]	Max[b]	Mean	SD[b]
Carbon fractions (mg g⁻¹)									
TOC		5.04	10.87	7.92	1.88	17.47	73.08	36.90	14.00
TN		0.81	1.46	1.10	0.24	0.76	4.67	2.27	1.13
OC		2.64	9.82	5.80	2.70	10.59	63.70	31.01	12.89
EC		1.05	4.08	2.11	1.20	2.68	9.38	5.52	1.82
Char		0.67	1.65	0.93	0.37	1.41	4.83	2.75	0.85
Soot		0.22	0.73	0.39	0.18	1.27	5.88	2.77	1.14

[a] Benzo[b + j + k]fluoranthenes is sum of benzo[b]fluoranthene + benzo[j]fluoranthene + benzo[k]fluoranthene; ∑LMW-PAHs is sum of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene; ∑HMW-PAHs is sum of fluoranthene, pyrene, benzo[a]anthracene, chrysene + triphenylene, benzo[b + j + k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene, and coronene; Combustion-derived PAHs (∑Comb-PAHs) is calculated as ∑HMW-PAHs minus perylene. ∑6alk-PAHs is sum of 2-methylnaphthalene, 1-methylnaphthalene, 1,3-dimethylnaphthalene, 2-methylphenanthrene and 3,6-dimethylphenanthrene; ∑21PAHs is sum of ∑LMW-PAHs and ∑HMW-PAHs mentioned above; (2 + 3)-Nitrofluoranthenes is sum of 2-nitrofluoranthene + 3-nitrofluoranthene.

[b] TEF is toxicity equivalency factor of individual PAC relative to benzo[a]pyrene; min, max and SD are minimum, maximum and standard deviation of the data, respectively; n.d. refers to not detected.

[c] From Nisbet and LaGoy (1992).

[d] From Durant et al. (1996).

[e] From Hester and Harrison (1998).

[f] From OEHHA (1994).

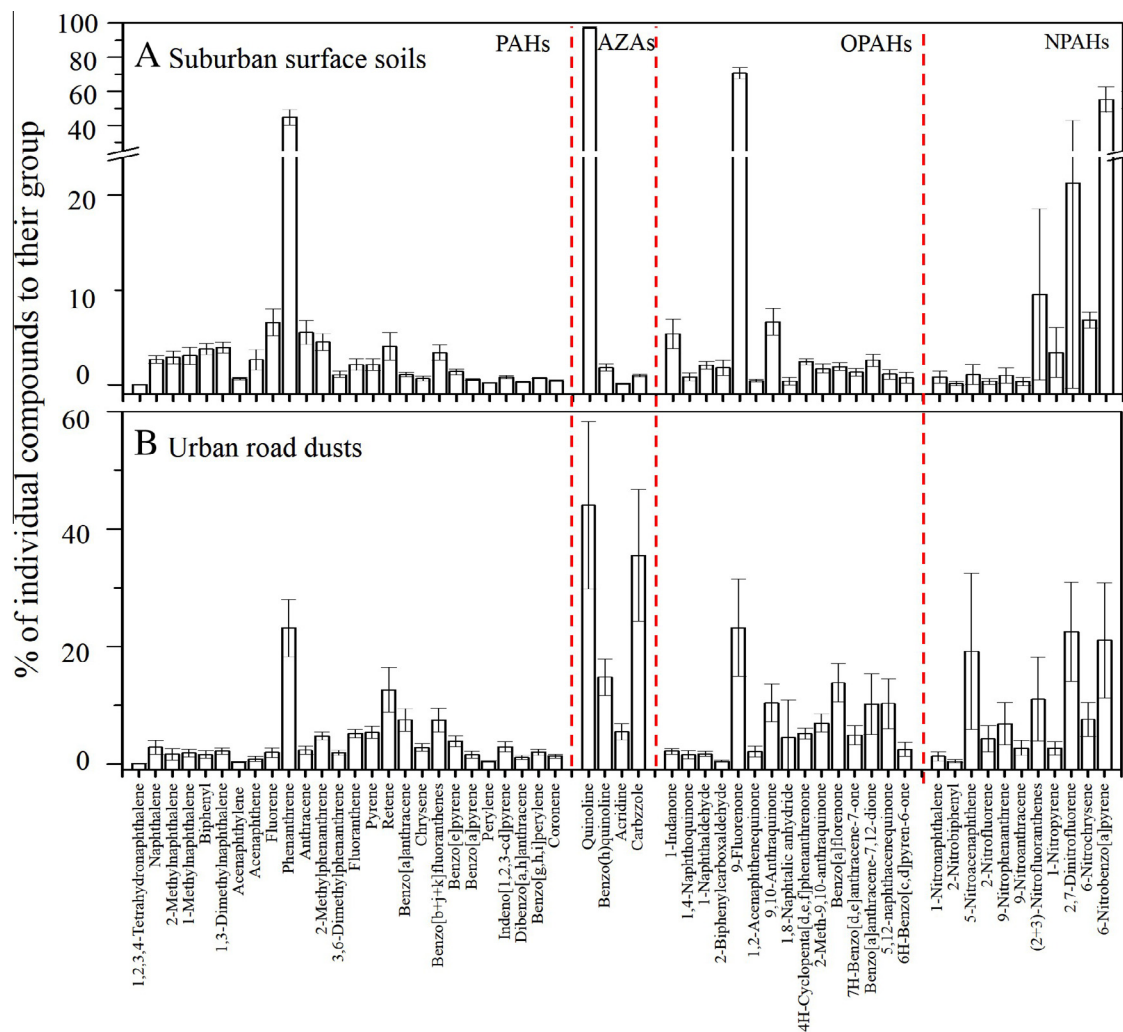[g] From Malcolm et al. (1994).

Fig. 1. Mean composition of the mixtures of 29 PAHs, 4 AZAs, 15 OPAHs and 11 NPAHs in suburban surface soil (A, n = 6) and urban road dust (B, n = 20). Error bars represent standard deviations.

predominantly occur in the gaseous phase, are easily transported from urban sources and accumulate in soils (Glaser et al., 2005; Albinet et al., 2007; Bandowe et al., 2011).

The concentrations of $\sum$4AZAs and $\sum$15OPAHs averaged 784 ± 330 ng g^{-1} and 854 ± 447 ng g^{-1} in surface soils (Table 1), respectively. These values are one to two orders of magnitude higher than those reported in background/remote sites (Bandowe and Wilcke, 2010; Brorström-Lundén et al., 2010; Wilcke et al., 2014), similar or a little higher than several urban areas of Europe and Asia (Niederer, 1998; Oda et al., 2001; Bandowe and Wilcke, 2010; Bandowe et al., 2014a), but lower than those measured at industrial sites, such as gasworks, coking, and power plants (Lundstedt et al., 2007; Bandowe and Wilcke, 2010) (Tables S3 and S4). The concentrations of $\sum$11NPAHs averaged 118 ± 52 ng g^{-1} in soils (Table 1), which were higher than the levels in surface soils from Basel, Switzerland (Niederer, 1998) and Gothenburg, Sweden (Brorström-Lundén et al., 2010) (Table S5).

The composition of the AZAs mixtures in surface soils dominated in the order of quinoline > benzo[h]quinoline > carbazole. The composition pattern of AZAs was similar to that in Argentinian soils where quinoline was the predominant AZA (Wilcke et al., 2014), but it differed from Bangkok soils where carbazole was the most abundant AZA (Bandowe et al., 2014a). The concentration of OPAHs in soils decreased in the order of 9-fluorenone > 9,10-anthroquinone > 1-indanone, which has frequently been the case in atmospheric samples and urban soils in studies elsewhere (Albinet et al., 2007; Lundstedt et al., 2007; Bandowe et al., 2011). The composition of the NPAH mixtures was dominated by 6-nitrobenzo[a]pyrene >2,7-dinitrofluorene>(2 + 3)-nitrofluoranthene (Fig. 1A).

The concentrations of $\sum$Comb-PAHs (sum of combustion-derived PAHs, Table 1) and retene (a tracer for biomass burning (Ramdahl, 1983)) were significantly correlated with the concentrations of $\sum$15OPAHs ($r = 0.93$, $p = 0.007$ and $r = 0.95$, $p = 0.003$, respectively) and $\sum$4AZAs ($r = 0.93$, $p = 0.006$ and $r = 0.88$, $p = 0.021$, respectively), but not with $\sum$11NPAHs ($r = 0.79$, $p = 0.060$ and $r = 0.77$, $p = 0.069$, respectively). This suggests that the main sources (fossil fuel and biomass combustion) and fate of OPAHs and AZAs in these suburban soils are similar, while NPAHs are likely having additional sources (e.g., photochemical formation during atmospheric transport or photolysis after deposition to soil surfaces in addition to some vehicular emissions) and different post-emission fate than their parent-PAHs (Arey et al., 1986; Atkinson and Arey, 1994; Tsapakis and Stephanou, 2007).

3.2. PACs concentrations in road dusts

The concentrations of $\sum$29PAHs, $\sum$15OPAHs, and $\sum$11NPAHs averaged 15 767 ± 4375, 4754 ± 1467, 885 ± 464 ng g^{-1} in road dust samples, respectively, which was about one order of magnitude higher than in suburban surface soils (Table 1), mainly because paved roads received more PACs from vehicle emissions, tire debris, and brake pad wear, etc. (Rogge et al., 1993; Aatmeeyata and Sharma, 2010). The $\sum$4AZAs concentration averaged 673 ± 199 ng g^{-1} in road dusts, which was lower than in suburban surface soils mainly because of the low quinoline concentrations in dusts (Table 1). This suggests that traffic emissions were not a major source of AZAs, or the measured 2–3 ring AZAs emitted from vehicle exhausts mainly existed in the gaseous phase and were distributed over long distances.

The composition pattern of PAHs mixtures in urban dusts were on average dominated by phenanthrene > retene > benzo[a]anthracene, and AZAs by quinoline > carbazole > benzo[h]quinoline. OPAHs mixtures were dominated by 9-fluorenone > benzo[a]fluorenone > 9,10-anthroquinone, and NPAHs by

2,7-dinitrofluorene > 6-nitrobenzo[a]pyrene > 5-nitroacenaphthene (Fig. 1B). Although phenanthrene was the most abundant PAH in both soils and dusts, the dusts contained a higher proportion of HMW-PAHs, which are mainly derived from combustion sources (Fig. 1). The average $\sum$LMW-PAHs/$\sum$HMW-PAHs ratio in dust was (0.72 ± 0.17) < 1, while that in soil (4.68 ± 1.04) was > 1. This is further evidence of higher contribution of vehicular exhausts (with higher proportion of HMW-PAHs) to the total PAH concentrations in dusts than in soils. Two of the most abundant OPAHs (i.e., 9-Fluorenone and 9,10-anthraquinone) in urban dusts from Xi'an (Fig. 1) were also reported to be the most abundant from other locations, while benzo[a]fluorenone was not included in previous studies (Rogge et al., 1993; Oda et al., 2001). The concentrations of $\sum$15OPAHs were significantly correlated with those of $\sum$Comb-PAHs ($r = 0.60$, $p = 0.005$) but not with those of retene ($r = 0.40$, $p = 0.078$) illustrating that OPAHs in dusts mainly originate from traffic-related emissions (e.g., vehicle exhausts and non-exhaust sources like tire wear), but not from biomass burning. This can also explain the difference in the pattern of OPAHs between road dusts and soils (Fig. 1). The concentrations of $\sum$Comb-PAHs and retene were significantly correlated with those of $\sum$AZAs ($r = 0.54$, $p = 0.015$ and $r = 0.45$, $p = 0.048$, respectively) but not with $\sum$11NPAHs ($r = 0.35$, $p = 0.136$ and $r = 0.18$, $p = 0.455$, respectively) suggesting that AZAs might also originate from traffic-related activities, but NPAHs were partially formed from photochemical reactions of oxidants with parent-PAHs, or were rapidly degraded by photolysis after deposition in addition to originating from exhaust emissions (Garcia et al., 2014).

The average concentration of the sum of the four PACs groups ($\sum$29PAHs + $\sum$4AZAs + $\sum$15OPAHs + $\sum$11NPAHs), was markedly higher in urban road dusts (22 079 ± 5775 ng g^{-1}) than in the suburban surface soils (3782 ± 1894 ng g^{-1}). Both, the concentration of PAHs (e.g. $\sum$16PAHs) in road dusts, as well as PAHs in surface soils indicated a moderate contamination compared to other locations in the world (Table S2). However, there was little available data regarding the concentration of AZAs, OPAHs, and NPAHs in road dusts from other locations (Tables S3–S5). The ratios of individual PACs concentration in road dust to average concentration of the same PAC in soils (EFs) were calculated to explore the probable reasons for higher PACs loads of urban dusts relative to suburban surface soils (Fig. 2). All PACs were enriched in road dusts (EF > 1), except quinoline. Furthermore, compounds with a molecular weight (MW) higher than 192 g mol^{-1} (2-methylphenanthrene) were markedly enriched (EF > 5) by human activities (e.g., vehicle exhaust), while other PACs with MW < 192 g mol^{-1} only showed a moderate enrichment (Fig. 2A, Table S1). In addition to being influenced by traffic-related emissions, the EF pattern can be partly explained by a local distillation effect (Glaser et al., 2005), which was confirmed by the significant correlations between EFs and physicochemical properties (i.e. octanol–water-partition coefficient (K_{OW}), octanol–air-partition coefficient (K_{OA}) and sub-cooled vapor pressure (P_L^0), (Fig. 2B–D)). These physicochemical properties can be used to describe the gas/particle partition and hence deposition of these compounds (Delgado-Saborit et al., 2013; Wei et al., 2015). Generally, PACs with MW > 192 g mol^{-1} are deposited close to their emission sources because they are predominantly associated with particles, while PACs with MW < 192 g mol^{-1} will predominantly occur in the gaseous phase, and can thus be transported or deposited to locations further away such as suburban soils (Albinet et al., 2007; Bandowe et al., 2011).

Concentration ratios of $\sum$15OPAHs/$\sum$29PAHs and individual OPAHs to their parent-PAHs, as well as $\sum$11NPAHs/$\sum$29PAHs and individual NPAHs to their parent-PAHs were calculated (Table S6) to trace the potential formation of the derivatives
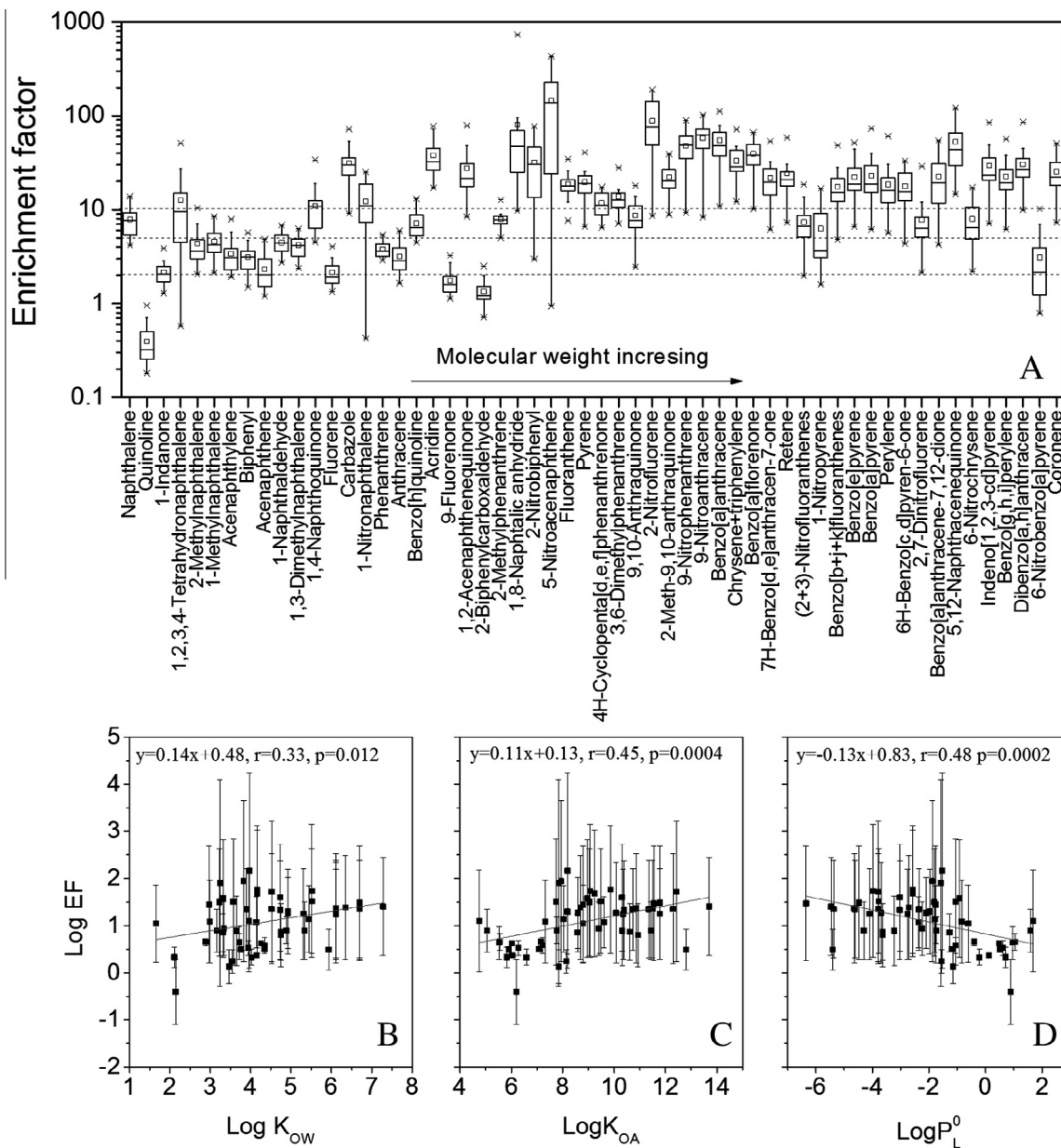
Fig. 2. Enrichment factors (EFs) of PACs in road dusts relative to surface soils (A), and relationship between EFs and their octanol–water-partition coefficient (K_{OW}) (B), octanol–air-partition coefficient (K_{OA}) (C), and sub-cooled vapor pressure (P_L^0) (D). The boxplot (A) divides the normalized EFs into quartiles. The dark line inside the box represents the median; the boxes mark the 25th and 75th percentiles; the horizontal line outside the box marks the values that extend 1.5 times the width of the box; the asterisks are the extreme values of the data set. Error bars in B, C and D represent standard deviations.

(OPAHs, NPAHs) from their parent-PAHs (Alam et al., 2013; Wei et al., 2015). The concentration ratios of $\sum15OPAHs/\sum29PAHs$ in road dusts were significantly lower than those in soils. Some OPAHs and NPAHs can be formed via photochemical activities, which could contribute to the PACs concentrations in urban dusts, albeit probably with a much lesser contribution than the partitioning from the gaseous phase to the dusts (Albinet et al., 2008), especially for LMW PAHs (Table S6). However, for HMW PACs (both PAHs and their derivatives), which predominantly occur in the particulate phase, the ratios of individual OPAH/parent-PAH and NPAH/parent-PAH would increase in soils (Table S6) probably because of the increasing formation of OPAHs and NPAHs via the photochemical reactions of parent-PAHs during transport (Glaser et al., 2005).

3.3. The relationship between carbon fractions and PACs concentrations in road dusts

TOC, EC, char and soot concentrations (Table 1) were significantly correlated with those of various individual PACs and $\sum29PAHs$, $\sum$Comb-PAHs, and $\sum11NPAHs$ (Fig. S2A, Table S7). This is mainly because PACs and EC (and its sub-fractions: char and soot) are emitted together from traffic-related sources (both exhaust and non-exhaust), and are also co-sorbed, co-transported, and co-deposited. For example, $\sum$LMW-PAHs were significantly correlated with char (Fig. S2B), as well as EC ($r = 0.53$, $p = 0.015$) (Table S7). $\sum$LMW-PAHs account for 45% of the total PAHs concentrations in carbon black (manufactured at 1950 °C) (Tsai et al., 2001), which is used as a filling and reinforcing agent in tires

Table 2
The incremental lifetime cancer risk (ILCR, unitless) of PACs in urban road dusts to child and adult through ingestion, dermal contact and inhalation.

	CS^a ($\mu g\,g^{-1}$)	Children				Adults			
		Ingestion	Dermal contact	Inhalation	Cancer risk	Ingestion	Dermal contact	Inhalation	Cancer risk
PACs									
Min[b]	8.60E-01	2.12E-06	2.64E-06	4.10E-11	4.75E-06	1.65E-06	2.94E-06	1.28E-10	4.59E-06
Max[b]	4.33E + 00	1.07E-05	1.33E-05	2.07E-10	2.40E-05	8.33E-06	1.48E-05	6.46E-10	2.31E-05
Mean	1.83E + 00	4.50E-06	5.61E-06	8.73E-11	1.01E-05	3.51E-06	6.24E-06	2.73E-10	9.76E-06
SD[b]	7.68E-01	1.89E-06	2.36E-06	3.67E-11	4.25E-06	1.48E-06	2.62E-06	1.14E-10	4.10E-06
PAHs									
Min[b]	3.82E-01	9.41E-07	1.17E-06	1.82E-11	2.11E-06	7.35E-07	1.31E-06	5.70E-11	2.04E-06
Max[b]	2.88E+00	7.08E-06	8.83E-06	1.37E-10	1.59E-05	5.53E-06	9.82E-06	4.29E-10	1.54E-05
Mean	1.15E+00	2.82E-06	3.52E-06	5.47E-11	6.34E-06	2.20E-06	3.91E-06	1.71E-10	6.12E-06
SD[b]	5.16E-01	1.27E-06	1.58E-06	2.46E-11	2.86E-06	9.92E-07	1.76E-06	7.70E-11	2.76E-06
OPAHs									
Min[b]	1.08E-02	2.65E-08	3.31E-08	5.14E-13	5.96E-08	2.07E-08	3.68E-08	1.61E-12	5.75E-08
Max[b]	7.01E-02	1.73E-07	2.15E-07	3.35E-12	3.88E-07	1.35E-07	2.39E-07	1.04E-11	3.74E-07
Mean	3.85E-02	9.49E-08	1.18E-07	1.84E-12	2.13E-07	7.41E-08	1.32E-07	5.75E-12	2.06E-07
Std[b]	1.91E-02	4.71E-08	5.87E-08	9.13E-13	1.06E-07	3.67E-08	6.53E-08	2.85E-12	1.02E-07
NPAHs									
Min[b]	1.79E-01	4.40E-07	5.48E-07	8.53E-12	9.88E-07	3.43E-07	6.10E-07	2.66E-11	9.53E-07
Max[b]	1.39E+00	3.42E-06	4.27E-06	6.64E-11	7.69E-06	2.67E-06	4.75E-06	2.07E-10	7.42E-06
Mean	6.44E-01	1.58E-06	1.98E-06	3.07E-11	3.56E-06	1.24E-06	2.20E-06	9.60E-11	3.44E-06
SD[b]	3.30E-01	8.14E-07	1.01E-06	1.58E-11	1.83E-06	6.35E-07	1.13E-06	4.93E-11	1.76E-06

[a] CS: the sum of converted values of PACs based on toxic equivalents of BaP using Toxic Equivalency Factors (Table 1).
[b] Min, max and SD refer to minimum, maximum and standard deviation of the data, respectively.

and constitutes ∼20–30% of the tire formula (Rogge et al., 1993). Thus tire wear could introduce large amounts of char or EC fractions and LMW-PAHs into paved road dusts (Schauer et al., 1996; Aatmeeyata and Sharma, 2010). Furthermore, PACs and EC are both co-produced and released into the urban environment from the incomplete combustion of carbon-containing materials which occurs during many urban activities (Larsen and Baker, 2003; Masiello, 2004).

3.4. Cancer risk assessment of PACs in road dust

Humans are exposed to PACs in road dusts via ingestion, dermal contact, and inhalation of contaminated road dust (Table 2). The total ILCR can be used as an indicator of the cancer risk (due to exposure to PACs in urban dusts) to humans living in the study area (Chen and Liao, 2006; Peng et al., 2011; Wang et al., 2011). The total cancer risk attributable to PACs (with known toxicity equivalency factor (TEF) values, Table 1) in urban dust ranged from 10^{-6} to 10^{-5} for both children and adults. Under most regulatory programs, an ILCR value of $\leqslant 10^{-6}$ indicates a negligible risk, a value between 10^{-6} and 10^{-4} suggests a potential risk, while a value $>10^{-4}$ is considered to be a high risk (Chen and Liao, 2006). In this study, the total ILCR ranged from 4.75×10^{-6} to 2.40×10^{-5} for children and 4.59×10^{-6} to 2.31×10^{-5} for adults, suggesting potential cancer risks for both children and adults, with children suffering a higher cancer risk than adults (Table 2). It must be further emphasized that other sources of exposure to PACs, in addition to those bound to urban dust, could increase the exposure and raise the ILCR values. Furthermore, although the average $\sum 29$PAHs concentrations were nearly 20 times higher than those of $\sum 11$NPAHs (Table 1), the ILCR of PAHs and NPAHs were of the same magnitude, and were one order of magnitude higher than OPAHs (Table 2), because of the higher TEF values assigned to NPAHs compared to PAHs and OPAHs (Table 1).

The ILCR model suggests that ingestion and dermal contact are equally important routes of human exposure (and carcinogenic risks), while inhalation is the least important pathway of exposure. Similar conclusions about the relative importance of these intake pathways of human exposure to urban dust bound trace metals (Shi et al., 2011) and PAHs (Wang et al., 2011) have been reported previously. Dermal contact was the predominant exposure route

for both children and adults, followed by ingestion and inhalation. Cancer risks via ingestion are higher for children than adults, while risks via dermal contact and inhalation are higher for adults than children (Table 2). Contaminated dust can be readily ingested by children because of their hand-to-mouth activity (Meza-Figueroa et al., 2007), and the PACs intake rate of children is believed to be greater than that of adults because of their lower body weight (Wang et al., 2011). The higher cancer risk for adults through dermal contact can be explained by their higher dermal exposure area and duration of exposure (Table S8). The higher cancer risks via inhalation for adults are also due to their higher duration exposure and inhalation rate (Table S8).

4. Conclusions

The PACs concentrations in the suburban surface soils of Xi'an were higher than those in remote background soils outside of urban areas, and similar to those in urban soils in European and North American cities, but lower than in soils from contaminated industrial sites. The concentrations of $\sum 29$PAHs, $\sum 15$OPAHs and $\sum 11$NPAHs in road dusts were about one order of magnitude higher than those in suburban surface soils, while the concentrations of $\sum 4$AZAs were lower in dusts. The EFs suggested that all PACs, especially PACs with MW > 192 g mol^{-1}, were significantly enriched by traffic related activities. Carbon fractions, PAHs, AZAs, and OPAHs in road dusts were probably derived from vehicular emissions (e.g., the combustion of fossil fuel in engines), tire wear, brake wear, and particles from road asphalt and tar. However, a significant portion of the NPAHs were probably derived from secondary transformation of parent-PAHs by photochemical reactions, in addition to some emissions from vehicle exhaust. The total ILCR due to PACs in road dusts was > 10^{-6}, indicating that the exposure of the population of Xi'an to urban dusts represents a potential cancer risk.

Appendix A. Supplementary material

The supplementary information provides detailed descriptions of the materials and methods (such as study area, sampling protocol, analysis of PACs and carbon fractions, quality assurance/control, and cancer risk assessment), carbon fractions in soils and dusts, and spatial distribution in road dusts. The monitored ions, qualifier ions, limits of detection, and blanks used for target PACs are summarized in Table S1. Tables S2–S5 compare PAHs, AZAs, OPAHs, and NPAHs concentrations in soils and dusts with those from other studies around the world. Table S6 compares the ratios of the sum and individual concentrations of OPAHs and NPAHs to PAHs in road dusts and soils. Table S7 gives the correlation coefficients between PACs and carbon fractions. Table S8 summarizes the variables used in the incremental lifetime cancer risk assessment. Table S9 compares the concentrations of carbon fractions in road dusts and soils with other studies. Fig. S1 shows the sampling sites of dusts and soils in Xi'an. Figs. S2 and S3 show the relationship between the concentrations of TOC and other carbon fractions, and the spatial distribution of PACs in road dusts in Xi'an.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2014.11.052.

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